

**Study of conductive composite materials by using
phase inversion method**

(相転換法を用いた導電性複合材料に関する研究)

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Chapter 1

General Introduction

1.1 Research Background of Conductive Polymers

Science and technology in recent years has been rapid progress. In particular, the polymeric material is advanced to study a wide range of fields. Have been required to have a characteristic that the new polymer. Conductive polymer was developed in 1977 by Shirakawa and coworkers (1). It is one of the applications of advanced materials for a wide range of fields, and researches have been done until now. The conductive polymers with conjugated double bonds has been attracted much attention as advanced materials. The conductive polymers could be distinguished between three types: electron conducting polymers (2, 3), proton conducting polymers (4, 5) and ion conducting polymers (6,7). Each polymer type has already found widespread use in many, mainly optical and electronic applications such as batteries (8, 9), displays (10, 11), and optical signal processing (12, 13), solar energy conversion (14, 15). The conductive polymer material has many advantages compared to the metals, such as highly corrosion resistance (16, 17), low density (18), high elasticity (19, 20) and cheap. Therefore, the conductive

polymer has been applied as an alternative material for metallic materials in wide fields.

There are categorized in the chemical structure of conductive polymers, there have been roughly classified as aliphatic, aromatic, heterocyclic and heteroatom containing type as shown in the chemical structure inserted in Table 1. For example, the typical types of aliphatic, aromatic, heterocyclic and heteroatomic polymers are seen for polyacetylene, poly (*p*-phenylene), polypyrrole (PPy) and polythiophene (PTh), and polyaniline (PANI), respectively. These polymers in double bonds have π -electrons derived from the conjugated chemical structure and the electron can move along polymer backbone freely. Hence, such conductive polymer shows specific properties relative to typical insulating polymer having only single bonds. Generally, their electrical and physical properties are influenced by their molecular structure, polymerization procedure and condition, chemical doping and so on. From these benefits and practicality of conductive polymer, many studies have been reported. Table 2 shows the number of publications of conductive polymer with the Scifinder (30). Number of reports of PPy and PANI are more than 20000, and many papers has been reported across the board also other conductive polymers. In addition, number of patent applications for conductive polymer technology is also increasing

Table 1 Classification of conductive polymers.

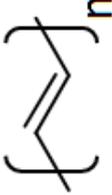
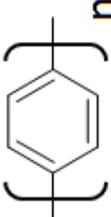
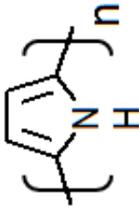
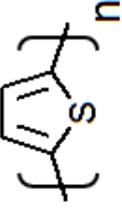
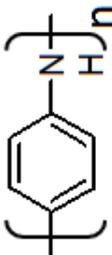
Polymer	Chemical structure	Characteristic	Reference
Polyacetylene		High conductivity, High stability,	21,22
Poly (<i>p</i> -phenylene)		High stability, Resistant to heat.	23,24
Polypyrrole (PPy)		High stability, Easy synthesis,	25,26
Polythiophene (PTh)		Optical properties, High stability	27
Polyaniline (PANI)		High stability. Easy addition and elimination of a proton by doping	28,29

Table 2 number of publications of conductive polymer with the Scifinder

Subject	Number of publications
Polypyrrole	20560
Polyaniline	26786
Polythiophene	12158
Polyacetylene	14233
Conductive polymers	53054

(Figure1). Tend to increasingly trend of patent applications in the world according to the Patent Office published the report "Technology Trends survey patent application". (31)

1.1.1 Conductive expression of the conductive polymer

The conductivity of a polymer can be increased severalfold by doping it with oxidative/reductive substituent or by donor/acceptor radicals (Table 3). Shirakawa and Ikeda discovered that doping of polyacetylene (PA) with metallic regimes increases its conductivity by 9 to 13 orders of magnitude. The doping is usually quantitative and the carrier concentration is directly proportional to the dopant concentration (32). Doping of conductive polymers involves random dispersion or aggregation of dopant in molar concentrations in the disordered structure of entangled chain and fibrils. Polymer doping

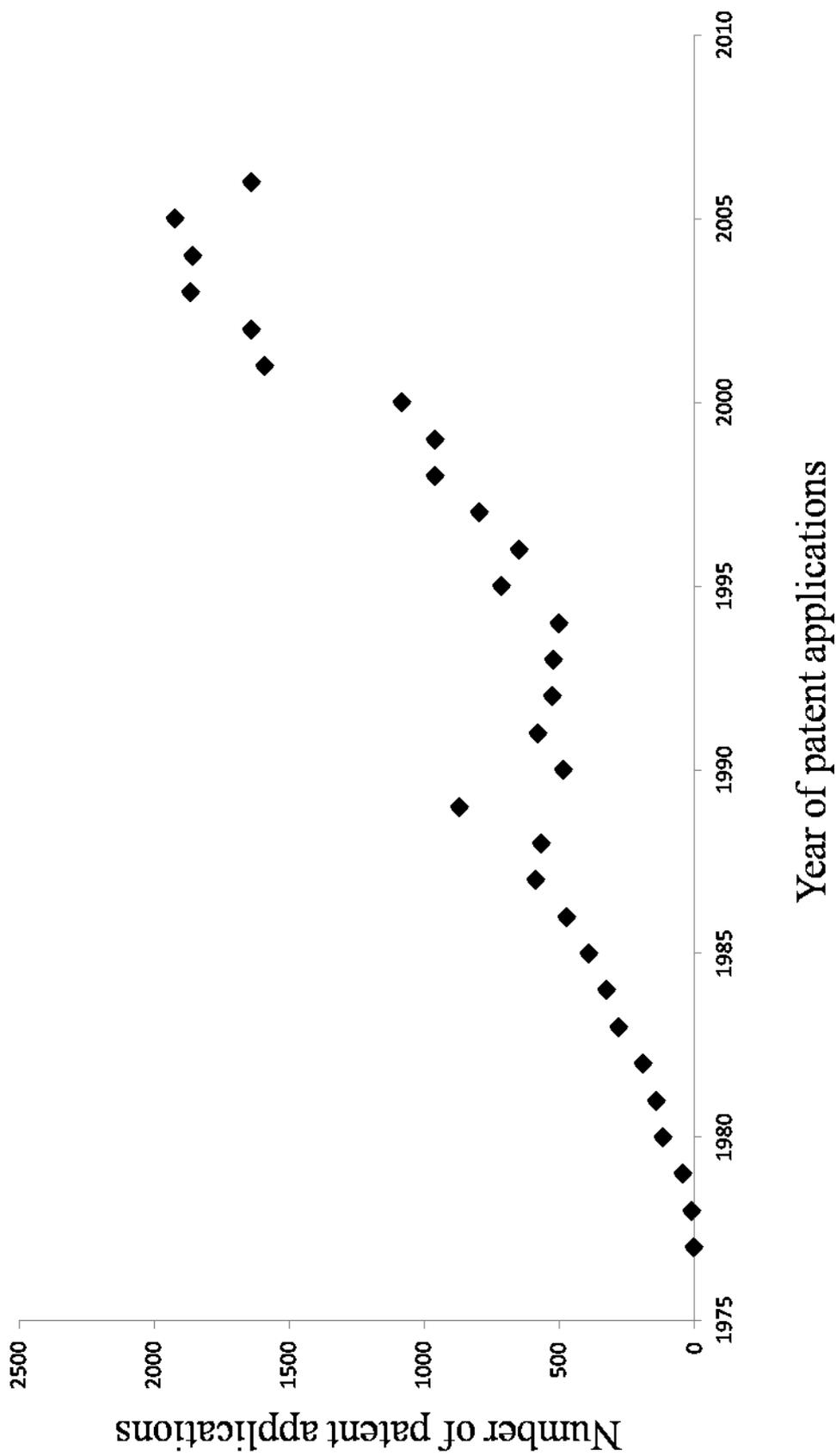


Figure 1 Number of patent applications for conductive polymer technology for the period 1977-2006

Table 3 The dopant used in doping of the conductive polymer

	Acceptor
Halogen	Cl ₂ , Br ₂ , I ₂ , ICl, ICl ₃ , IBr, IF
Lewis acid	PF ₅ , AsF ₅ , SbF ₅ , BF ₃ , BCl ₃ , BBr ₃ , SO ₃
Protic acid	HF, HCl, HNO ₃ , H ₂ SO ₄ , HClO ₄ , FSO ₃ H, ClSO ₃ H, CF ₃ SO ₃ H, Organic acid, amino acid
Transition metal compound	FeCl ₃ , FeOCl, TiCl ₄ , ZrCl ₄ , HfCl ₄ , NbF ₅ , NbCl ₅ , TaCl ₅ , MoF ₅ , MoCl ₅ , WF ₆ , WCl ₆ , UF ₆ , LnCl ₃ (Ln=lanthanoid)
Electrolyte anion	Cl ⁻ , Br ⁻ , I ⁻ , Cl ₄ ⁻ , PF ₆ ⁻ , AsF ₆ ⁻ , SbF ₆ ⁻ , BF ₄ ⁻ , Sulfonate anion
Other	O ₂ , XeOF ₄ , (NO ₂ ⁺)(SbF ₆ ⁻), (NO ₂ ⁺)(SbCl ₆ ⁻), (NO ₂ ⁺)(BF ₄ ⁻), FSO ₂ OOSO ₂ F, AgClO ₄ , H ₂ IrCl ₆ , La(NO ₃) ₃ · 6H ₂ O
	Donor
Alkali metal	Li, Na, K, Rb, Cs
Alkali earth metal	Ca, Sr, Ba
Lanthanoid	Eu
Other	R ₄ N ⁺ , R ₄ P ⁺ , R ₄ As ⁺ , R ₃ S ⁺ , Acetylcholine

leads to the formation of conjugational defects, viz. solitons, polarons or bipolaron in the polymer chain (Figure 2). An x-ray diffraction study on iodine-doped polyacetylene shows that the C-C bond length of the polyacetylene chain increases with donor doping but decreases on acceptor doping (33). The presence of localized electronic states of energies less than the band gap arising from changes in local bond order, including the formation of solitons, polarons and bipolaron have led to the possibility of new types of charge conduction present in these polymer systems. Doping is generally performed in the chemical doping that is reacted with the conductive polymer in the gas/liquid phase dopant (34,35) and electrochemical doping that performed electrochemically reacted by electrode as conductive polymer(36).

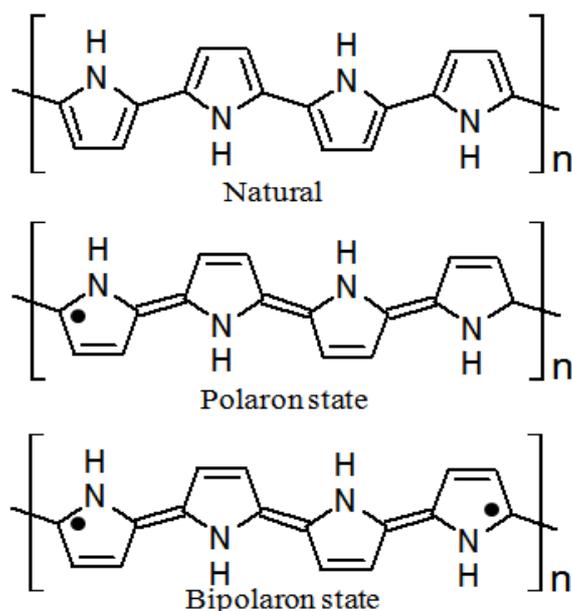


Figure 2 Electronic structure of PPy-doped acceptor.

1.1.2 Preparation methods of conductive polymers

There is no singular method for synthesizing polymers that can be transformed into conductive polymers, the incorporation of extended *p*-electron conjugation is of foremost importance. Conductive polymers except ionomeric polymers may be synthesized using standard methods of polymerization including conventional as well as specific routes which include Witting, Horner and Grignard reactions, polycondensation processes and metal catalyzed polymerization techniques. Oxidative coupling with oxidizing Lewis acid catalysts generally leads to polymers with aromatic or heterocyclic building blocks. Conductive polymers may be synthesized by any one of the following techniques: Chemical polymerization (37-40), Electrochemical polymerization (41,42), Photochemical polymerization (43), Metathesis polymerization (44,45), Concentrated emulsion polymerization (46), Inclusion polymerization(47), Solid-state polymerization(48), Plasma polymerization (49), Pyrolysis (50) and Soluble precursor polymer preparation (51).

Among all the above categories, chemical polymerization is the most useful method for preparing large amounts of conductive polymers, since it is performed without electrodes. Chemical polymerization (oxidative coupling) is followed by the oxidation of

monomers to a cation radical and their coupling to form dication and the repetition of this process generates a polymer. All the classes of conjugated polymers may be synthesized by this technique.

1.2 Polypyrrole

Polypyrrole (PPy) is a chemical compound formed from a number of connected pyrrole ring structures. PPys are conducting polymers of the rigid rod polymer host family, all basically derivatives of polyacetylene. Polypyrrole was the first polyacetylene derivative to show high conductivity. PPys are also called pyrrole blacks or polypyrrole blacks. PPys also exist naturally, especially as part of a mixed copolymer with polyacetylene and polyaniline in some melanin. Recently, studies of polypyrrole have been made to various fields because of its molecular characteristics as well as conductive property. Application of new properties polypyrrole has been studied such as drug delivery system (51,52), heavy metal adsorbent (53,54) and so on. Generally, PPy is prepared by chemical polymerization and electrochemical polymerization (Figure 3). When the PPy prepared by electrochemical polymerization, yield is low and frangible films are created. There is also a disadvantage in the electrochemical polymerization is that special equipment is required further. In other hands, Chemical polymerization method can be

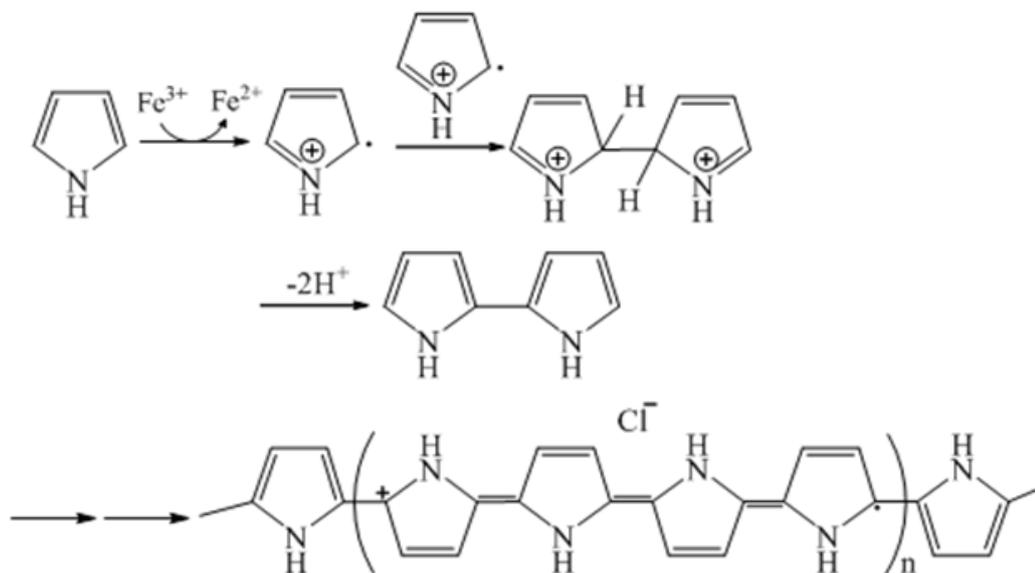


Figure 3 Polymerization mechanism of Py.

easily synthesized polypyrrole (55,56). However the prepared PPy by chemical polymerization are in powder form. It is also important to the establishment of a new polymerization process to compensate for these disadvantages. PPy has many advantages as described above, research and development had been actively carried out in various fields. In particular, it is composited with other materials, polypyrrole is an effective means to broaden the range of applications. There were reports in recent year for SnO_2 -polypyrrole composite material was synthesized using a chemical polymerization method by L. Yuan and coworkers, for using lithium-ion battery (58). J. Wang and coworkers reported that the electrochemical capacitance properties of composite films prepared from electrically

conducting polypyrrole and single wall carbon nanotubes have been investigated for super capacitor application (59). In the present work, oxidation polymerization of Py was observed to proceed simultaneously with the coagulation of CA for formation of PPy-CA composite films. In the wet-coagulated films, porous CA was found with PPy layer on the scaffold, when the CA solution in Py was used in the oxidation of Py polymerization. Such idea suggests an attractive method for preparing conductive composite films. When the Py polymerization occurred in the composite films, effects of FeCl_3 concentration and coagulation conditions were examined.

1.3 Polyaniline

Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family. Although the compound itself was discovered over 150 years ago, only since the early 1980s has polyaniline captured the intense attention of the scientific community. This interest is due to the rediscovery of high electrical conductivity. Amongst the family of conducting polymers and organic semiconductors, polyaniline has many attractive processing properties. Because of its rich chemistry, polyaniline is one of the most studied conducting polymers of the past 50 years.

The characteristics of the PANI are a change in the structure by

the oxidation state (60,61). The PANI can take two structures. These are the amine which is the nitrogen atoms has been reduced and the imines which is oxidized. There is also protonation of the nitrogen atoms. Therefore, the molecular structure of polyaniline is quite complex. It is known that PANI takes the structure of fully reduced form of leucoemeraldine (LB), partially reduced form of emeraldine (EB), and fully oxidized form of pernigraniline (PB) (Figure 4). And it is showing high conductivity by the doping with some dopant. Some polyaniline based materials are solution and melt processable. They offer clear benefits over traditional plastics made conductive by the addition of fillers (carbon blacks, metal particles and flakes, metal fibers, carbon fibers, and others). They provide precisely controlled electrical conductivity over a wide range, improve phase compatibility and thus blend ability with bulk polymers, provide easier means of processing and forming conductive products and provide low cost solutions for the production of transparent and colored thin films and coatings.

1.4 Cellulose acetate.

Cellulose acetate (CA) is one of the most important esters of cellulose. Depending on the way it has been processed cellulose acetate can be used for great varies of applications (e.g. for films,

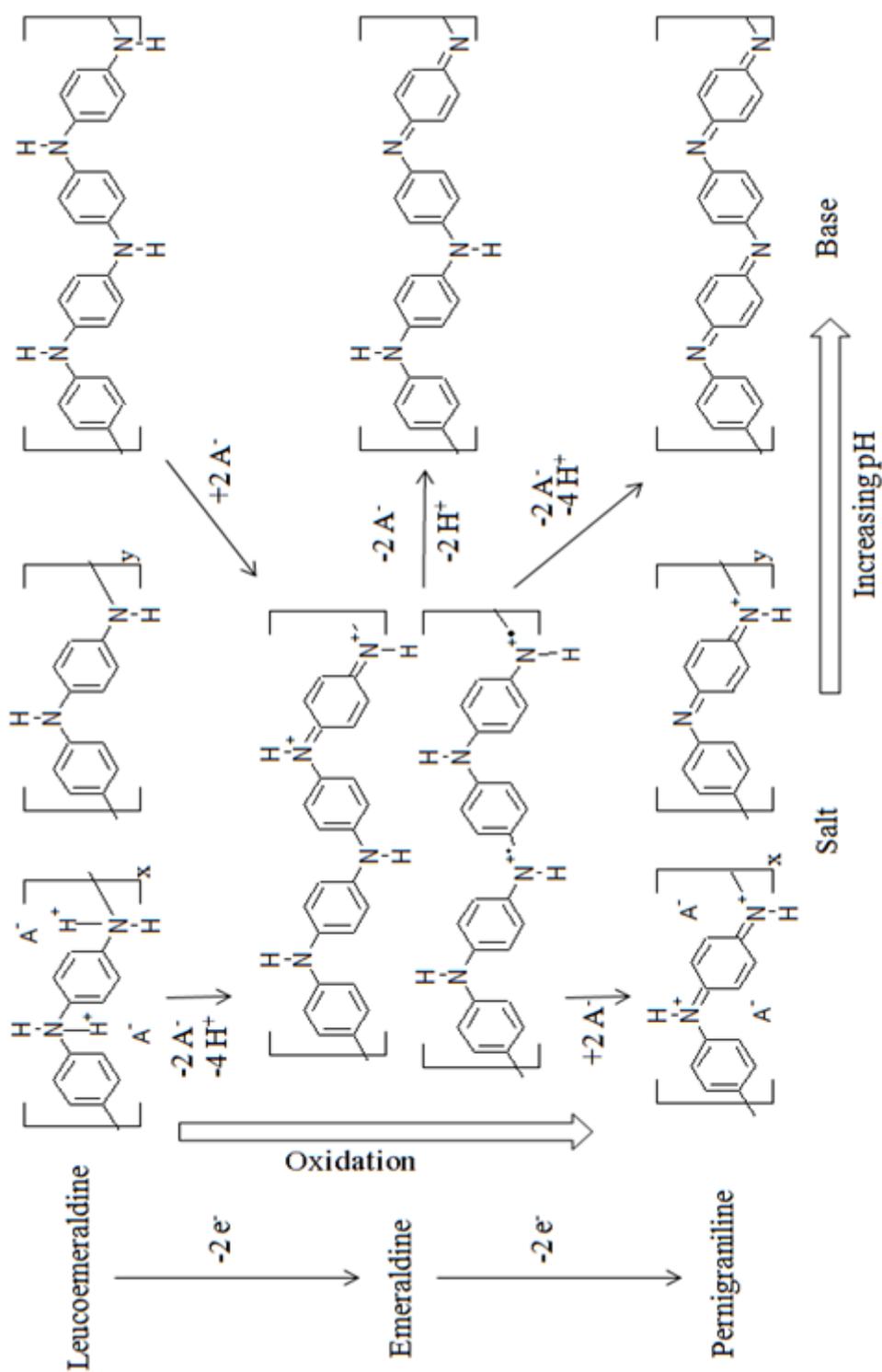
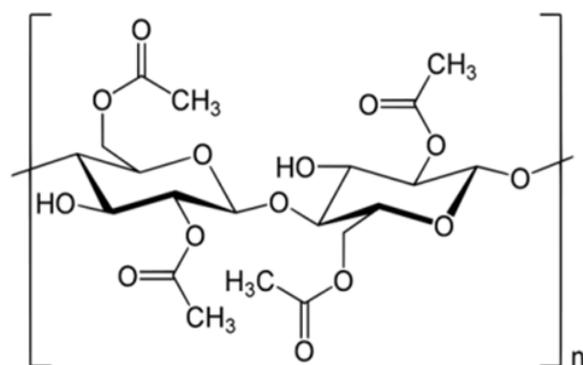


Figure 4 Electrochemical oxidation state of PANI



Cellulose acetate (CA)

membranes or fibers).

The properties of the applied cellulose acetates are very important for these applications. A special field for using cellulose acetate is the synthesis of porous, spherical particles. CA shows good abilities like excellent chemical resistance, heat resistance and flammability. It can be used in wide fields that CA was applied cigarette filters, photographic film and separation membranes. In addition, CA has also well known to dissolve in various solvents easily. From these properties, it has been studied as a composite material with various substances. Many cellulose has used as a membrane prepared by phase inversion method that has many advantages such as easy to prepare membranes, the resulting membranes are porous, thickness and hole size were can be control and so on. As will be described later, it is one of the most important aspects of this study. CA is readily soluble in the pyrrole monomer and aniline monomer, and insoluble monomers.

1.5 Phase inversion method

Phase inversion method is a typical process in which the polymer dissolved homogeneously in the solvent can be precipitated from the coagulation bath which is miscible with the polymeric solvent. It bears merits such as easy, fast, and versatile that it is commonly used to prepare symmetric and asymmetric polymeric membranes for a wide range of applications in water treatment, biomedical technology, as well as electrical industry.

The main route of the phase inversion process involves two different types of phase transition (62), which can be illustrated in a ternary phase diagram (Figure 5). These are: (1) liquid-liquid phase separation, in which the completely miscible solution crosses the bimodal boundary to enter the two phase region (from I to II), and (2) solidification (from I to III or from II to III); since the viscosity of the polymer solution increases to a certain assumed value, the motion of polymer chains will be limited and the system can be regarded as a solid to fix the membrane structure. Liquid-liquid phase separation in homogeneous polymer solution can be caused by variation in temperature and/or composition of the mixture. When a homogeneous solution becomes thermodynamically unstable, the solution can decrease its free energy from mixing by dividing into two liquid phases of different composition that is a

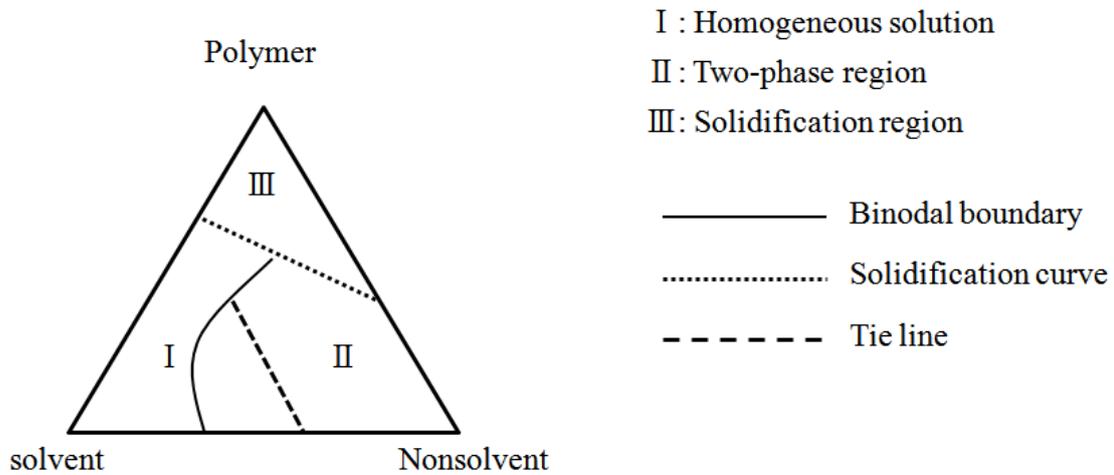


Figure 5 Ternary phase diagram

nucleus of the polymer-poor phase that forms the nascent pore and a polymer-rich phase that surrounds the pore. Hence, a nascent pore comprises the polymer-poor phase surrounded by the polymer-rich phase. The two liquid phases are in thermodynamic equilibrium and can be connected by the tie line in the phase diagram (63).

1.6 Composite materials and New wet cast technique

In recent years, a number of innovative new materials had been developed in chemistry field. These materials had been applied in various ways in order to add additional properties and industrial values. In various application techniques, the hybrid technique into multiple materials due to expansion of the values and properties of the materials are widely used. Table 4 shows an application and its characteristics of the composite materials and techniques. The

Table 4 Application of composite materials

Composite materials	Methods	Product	Purpose, application	References
PPy	In-suit chemical oxidation polymerization of pyrrole in the host of inorganic matrix.	Core shell nanostructure composite	Catalysis, electro-magnetic shields, batteries	64
PPy	PVA film was prepared containing FeCl ₃ , then polymerized by addition of Py.	Membrane	Preparation and characterization of film	65
PPy	The radical polymerization on the surface of the cellulose.	Film	Electrode	66
PANI	Emulsion polymerization: Aniline, PMMA, initiator and solvent are dissolved.	Powder	Optical analysis	67
PANI	Dissolved in a solvent and PANI, then, added Cd compounds.	Powder	Catalyst of Hydrogen evolution from water	68
PANI	Phase inversion method: PANI, PES and solvent are dissolved, and coagulated in water.	Membrane	Gas separation, pervaporation	69
PTh	Electro oxidation of polythiophene onto a natural or synthetic rubber coated platinum electrode.	Film	Electrolytic film	70
PA	ScCO ₂ polymerization	Nanotube	To create new nanotubes based materials	71

composite materials had been prepared using various methods and techniques depending on the purpose. In this thesis would described composite materials of conductive material and film (Membrane) materials, established technique of prepared composite materials is a unique way ever and has high future potential.

New phase inversion method was established has been developed by applying the existing phase inversion methods. Figure 7 shows a schematic diagram. Features of this method, the monomers of conductive polymer could be used as a solvent for dissolving the membrane substrate, and oxidation polymerization of conductive polymer was observed to proceed simultaneously with the coagulation of scaffold material for formation of composite material by contained polymerization initiator into the coagulation water in advance. Thus, it is possible to prepare the composite material easily and simply. In addition, it could be control the shapes of composite materials. In the case of spread of the homogeneous solution of scaffold material was dissolved by monomer of conductive polymer on the flat material such as glass plate and immersion in the coagulation solution contained polymerization initiator, the resultant material form to film shape. Furthermore, properties of resultant material could be controlled by changing the coagulation condition. The homogeneous solution was injected to

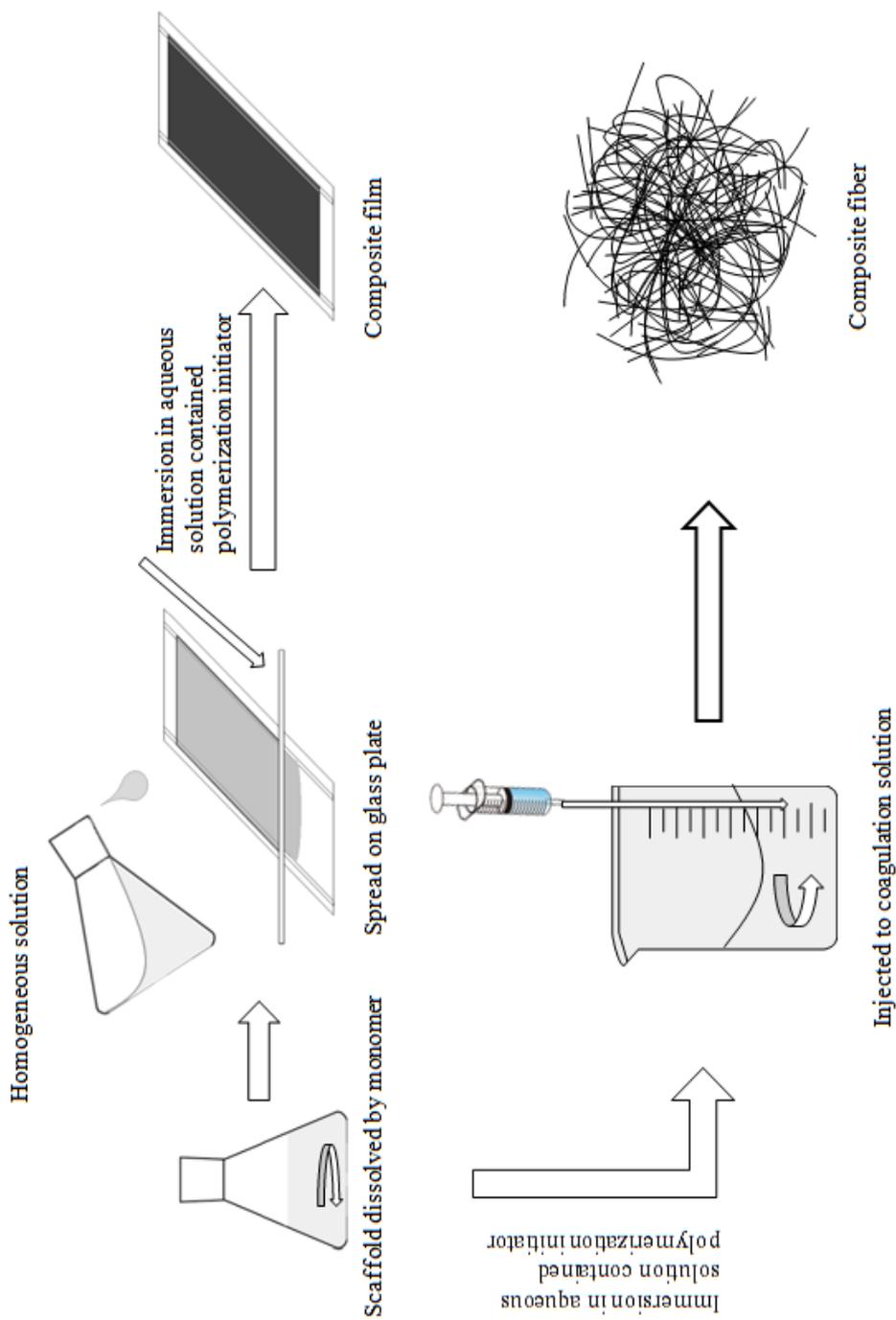


Figure 7 Schematic diagram of the new wet cast technique

coagulation solution using syringe, the resultant materials formed fiber shape. Surprisingly, under certain conditions, the resultant fiber formed dual layer hollow fiber shape. It is possible to produce a composite material with a simple step, the method can be controlled in accordance with the intended shape. The resulting composite material is not only as the conductive material. In the future and can also be applied as a membrane material. From the viewpoint of shape control, as well as the field of research, it is applicable as a method available industrially produced in the future.

1.7 Outline of this thesis

This thesis is described from view points of preparation of conductive composite materials with new simple wet cast technique. Thus, this consists five chapters as following. Chapter 1 is general introduction for conductive polymers and new simple wet cast technique. Chapter 2 describes conductive PPy composite films prepared using wet cast technique with a Py-CA solution. In this chapter, using new simple wet cast technique was applied for preparation of PPy-CA composite film. Py was used as a solvent for CA which was dissolved. Then, in order to prepare PPy-CA composite film, the Py viscous solution of CA was cast on glass plate and immersed in FeCl_3 aqueous solution. It was also studied that

the effects of the properties of the PPy-CA films by the coagulation conditions. Chapter 3 shows application of new wet cast technique. This chapter focuses to dual layer hollow fiber of polyaniline-cellulose acetate prepared with simple wet technique of chemical polymerization of aniline. Then, the characteristics of the PANI-CA hollow fiber are described. Chapter 4 is the summary of this dissertation.

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Chapter 2

Conductive Polypyrrole Composite Films Prepared Using Wet Cast Technique with a Pyrrole-Cellulose Acetate Solution

Abstract

Conductive polypyrrole-cellulose acetate films were prepared from cellulose acetate (CA) solution of pyrrole (Py) using wet cast method. In the composite films, Py was used as a solvent for CA which was dissolved with different concentration. Then, in order to prepare PPy-CA composite film, the Py viscous solution of CA was cast on glass plate and immersed in FeCl₃ aqueous solution. When the CA film was formed in the aqueous solution, the polymerized PPy particles having about 1 μm diameter were formed in composite film. The resultant composite films were characterized, showing good film fabrication and electrical conductivity of around 6.9×10^{-4} to 3.6×10^1 S/cm.

2.1 Introduction

Polypyrrole (PPy) is known as an important conducting polymer and has been widely used in recent years for electrical and electronic applications such as sensors and solar cells [1-7]. Conductive polymers are known to have extensive π electron conjugated systems in the chemical structure of the

main chain. This is the reasons for its electrical conductivity expressed by delocalizing a main chain using a dopant such as halogen and alkali metal in conjugated polymer [8-11]. Most of PPy films can be produced by electrochemical polymerization, but film fabrication presents some important shortcomings: the resultant film is fragile, and dedicated equipment must be used. Relative to the electrochemical method, chemical reactions were also used to prepare PPy [12]. Among them, oxidative polymerization of Py formed PPy in the presence of FeCl_3 [13]. But, the obtained PPy in chemical polymerization are generally limited to powders, and they are difficult in several applications for film formation. To solve these problems, synthesis of PPy can be performed by dissolution in the solvent [14] which disperses PPy particles in the film. Although PPy has been studied in various fields, PPy presents difficulties in mechanical strength and shape control of the films. Nevertheless, appropriate composite films can be expected to provide various new applications for PPy. For example, conductive films made of PPy have been applied and used particularly as antistatic agents [15], transistors [16, 17], and actuators [18, 19]. In report for composite conductive polymer films, a method of forming PPy was developed using a nitrate-cellulose acetate composite film by a two-compartment cellulose-polypyrrole. Dongtao Ge and coworkers reported that the composite material could be applied to drug delivery system [20]. But, still little is known about such composite conductive films, although

they have advantages in shaping films with better mechanical strength and flexibility.

The present paper describes a unique technique of preparation of conductive PPy composite films. In our preliminary study, it is revealed that Py can dissolve many polymers such as polyethylene glycol, polysulfone, polystyrene and cellulose acetate. With emphasis on cellulose acetate (CA), preparation of PPy composite film is attempted using a straightforward wet cast technique. Here, CA is well known as a derivative of cellulose obtained by its acetylation. CA film shows good capabilities such as excellent chemical resistance, heat resistance, and flame resistance. In diverse applications, CA has been used for cigarette filters, photographic film and separation membranes [21–25]. Among these applications, CA film was reported to be formed using the phase inversion method [26, 27]. This wet cast method was known to be useful for transforming polymer liquid solution to a solid state in wet cast technique. The polymer solidification was performed via polymer coagulation in poor solvent by immersion for coagulation [28-29]. When the coagulation occurred, forming a porous CA film was proceeded in coagulation water. In the present work, oxidation polymerization of Py was observed to proceed simultaneously with the coagulation of CA for formation of PPy-CA composite films. In the wet-coagulated films, porous CA was found with PPy layer on the scaffold, when the CA solution in Py was used in the oxidation of Py polymerization. Such idea suggests an attractive method for preparing

conductive composite films. When the Py polymerization occurred in the composite films, effects of FeCl_3 concentration and coagulation conditions were examined.

2.2 Experimental

2.2.1 Materials

Pyrrole (Py) was used as the solvent and monomer (Tokyo Kasei Kogyo Co. Ltd., Japan). The cellulose acetate (CA) used contained 39.7 wt% acetyl content (Aldrich, USA) with average molecular weight of ca. 50,000. Iron (III) chloride (anhydrous FeCl_3 ; Nacalai Tesque Japan) was used as the polymerization initiator and dopant.

2.2.2 Preparation of PPy-CA composite films

In a typical procedure, CA was soluble in pyrrole with 14 wt% of CA in the Py solvent. The Py-CA viscous solution was stirred overnight at room temperature until a homogeneous solution was obtained. The CA film was then prepared using wet cast technique as follows. The resultant Py-CA viscous solution was spread on a glass plate (75mm \times 25mm) with about 100 μm thickness of the spread solution. The thickness of the film was controlled by using lumirror film (Toray, Japan) used as a spacer to be about 100 μm . Then, the plate with the spread Py-CA solution layer was immersed immediately in aqueous solution containing different concentrations of FeCl_3

at 25 °C. The CA coagulation was conducted in water (100ml) containing different concentration of FeCl₃, since the oxidation polymerization of Py was occurred [30]. The PPy formed in the CA film matrix on the glass plate became black after a certain time. The resultant black film was washed using distilled water to remove excess Py and PPy from the composite film. Then, the films were dried in vacuum at room temperature overnight.

2.2.3 Characterization of polymer solutions and films

The sample solution viscosities were measured using a B type viscosity meter (Tokyo Keiki Inc., Japan). Fourier transform infrared (FT-IR) spectra of the film samples were measured using a IRprestige-21 spectrometer (Shimadzu Corp., Japan) with transmittance mode. Spectra were recorded at the 400–4600 cm⁻¹ region. To evaluate PPy amounts in the CA films, FT-IR spectra were measured. When the loading content of PPy in the CA film was changed in different contents in mixing together with KBr powder, FT-IR spectra was applied for their mixtures as calibration. In the spectral data characteristic IR bands for PPy and CA were chosen for estimation of PPy loading in the composite films. Reflection FT-IR spectra of thick film samples were measured using an infrared microscope (AIM8800; Shimadzu Corp., Japan) connected to an existing infrared spectrometer at 670–4600 cm⁻¹. UV-vis spectra in transmittance and reflection models for the samples were obtained using a UV-vis spectrometer (V-570; Jasco Corp., Japan). Electrical

conductivity of the PPy-CA films was determined using a resistivity meter (Loresta-GP MCP; Mitsubishi Chemical Corp., Japan) with a four-probe method. Sample film morphology was observed using scanning electron microscopy (SEM)(JSM-5400; JEOL, Japan). The sample films were sputtered with gold under vacuum using a coater (Quick Cool Coater SC-701MC; Sanyu Denshi K.K., Japan). In addition, for the measurement of another evaluation of PPy-CA films, the strength of the film was determined (LTS-500N-S20; Minebea Co. Ltd., Japan). The elasticity data were recorded with pulling speeds of 10 mm/min.

2.3 Result and Discussion

2.3.1 Preparation of PPy-CA composite films

Table 1 shows PPy amounts in CA film. When the FeCl_3 concentration was changed in the range of 10 mM to 100 mM, PPy loading in the composite films was changed from 3.6×10^{-6} g/g_{CA} to 8.0×10^{-3} g/g_{CA}. Here, the PPy-CA films were prepared in FeCl_3 aqueous medium by coagulation of CA for 24h. The PPy loading amount in the CA scaffold increased gradually to be 2.1×10^{-3} % to 4.7 %, when the concentration of the FeCl_3 solution was increased from 10 mM to 100 mM, respectively. Table 1 also lists tensile strength of the resultant films. The values of tensile strength were decreased from 38.1 to 6.8 N/mm², as the FeCl_3 concentration was changed from 0 to

TABLE.1 Calculated results of PPy amount, yield, and tensile strength of PPy-CA films prepared in several concentrations of FeCl₃ in aqueous solution.

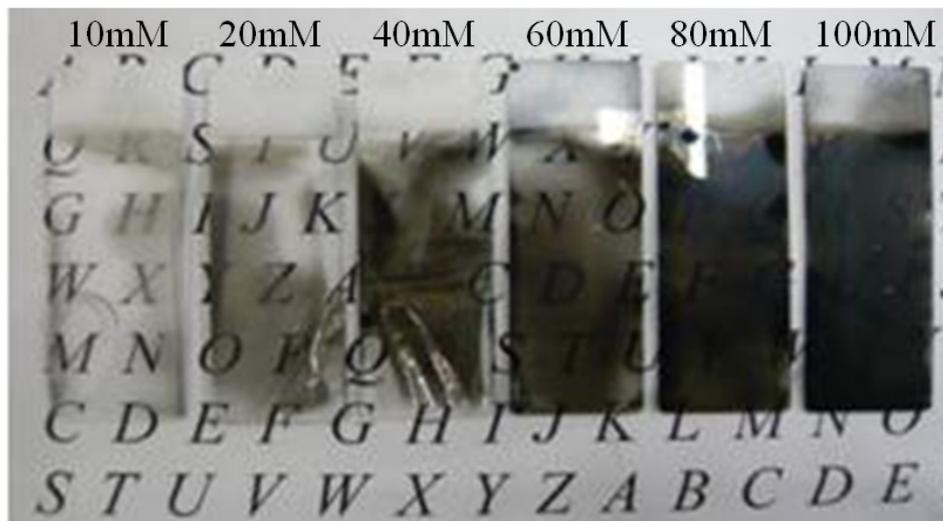
FeCl ₃ solution (mM)	PPy amount in CA ¹⁾ (g/g _{CA})	Yield of PPy (%)	Tensile strength (N/mm ²)
0	0	-	38.1
10	3.6×10^{-6}	2.1×10^{-3}	33.8
20	8.1×10^{-4}	4.7×10^{-1}	26.5
40	1.4×10^{-3}	7.9×10^{-1}	14.4
60	3.0×10^{-3}	1.7	9.4
80	7.1×10^{-3}	4.1	8.2
100	8.0×10^{-3}	4.7	6.8

1) The values were estimated from FT-IR spectra of sample by using those of mixture films of PPy and CA.

100mM.

Figure 1 depicts pictures of the PPy–CA film formed on the glass plate at different FeCl₃ concentrations. As changed from 10 mM to 100 mM of FeCl₃, it was apparent that the resultant film color became black with increasing FeCl₃ concentration. This indicated that Py in the water layer was polymerized in the presence of FeCl₃ on the CA scaffold. In addition, these data meant that efficient formation of PPy occurred on the surface of the CA scaffold film, when FeCl₃ became high concentration.

In figure 2, the following SEM images of the resultant PPy–CA composites are shown for films prepared in 100 mM FeCl₃ aqueous solution at room temperature. For the film obtained in the presence of FeCl₃, panels (a) and (b) show the typical surface morphology of the PPy–CA film on the solution



side and on the side of the glass plate. The glass side of the PPy-CA film had a smooth surface in the shape, but the solution side of the PPy-CA film indicated that there were many PPy particles with diameter of about 1 μm . Furthermore, the cross-section image of the PPy-CA film shown in panel (c) presented that the thickness of the film was about 25 μm . Then, in panel (d), the surface layer attached consisted of the PPy particles with about a few μm thickness of the PPy. Furthermore, in Figure 2 (e), SEM image was focused on the PPy particles on the composite film having thickness of 0.2mm. It could be observed that the PPy particles showing about 1 μm diameter were attached on CA layer. These results indicate that the PPy layers were distributed on the CA scaffold.

Figure 3 shows FT-IR spectra of the PPy-CA films. The characteristic peaks of CA for the carboxylate group (C=O) were observed at 1745 cm^{-1} and the

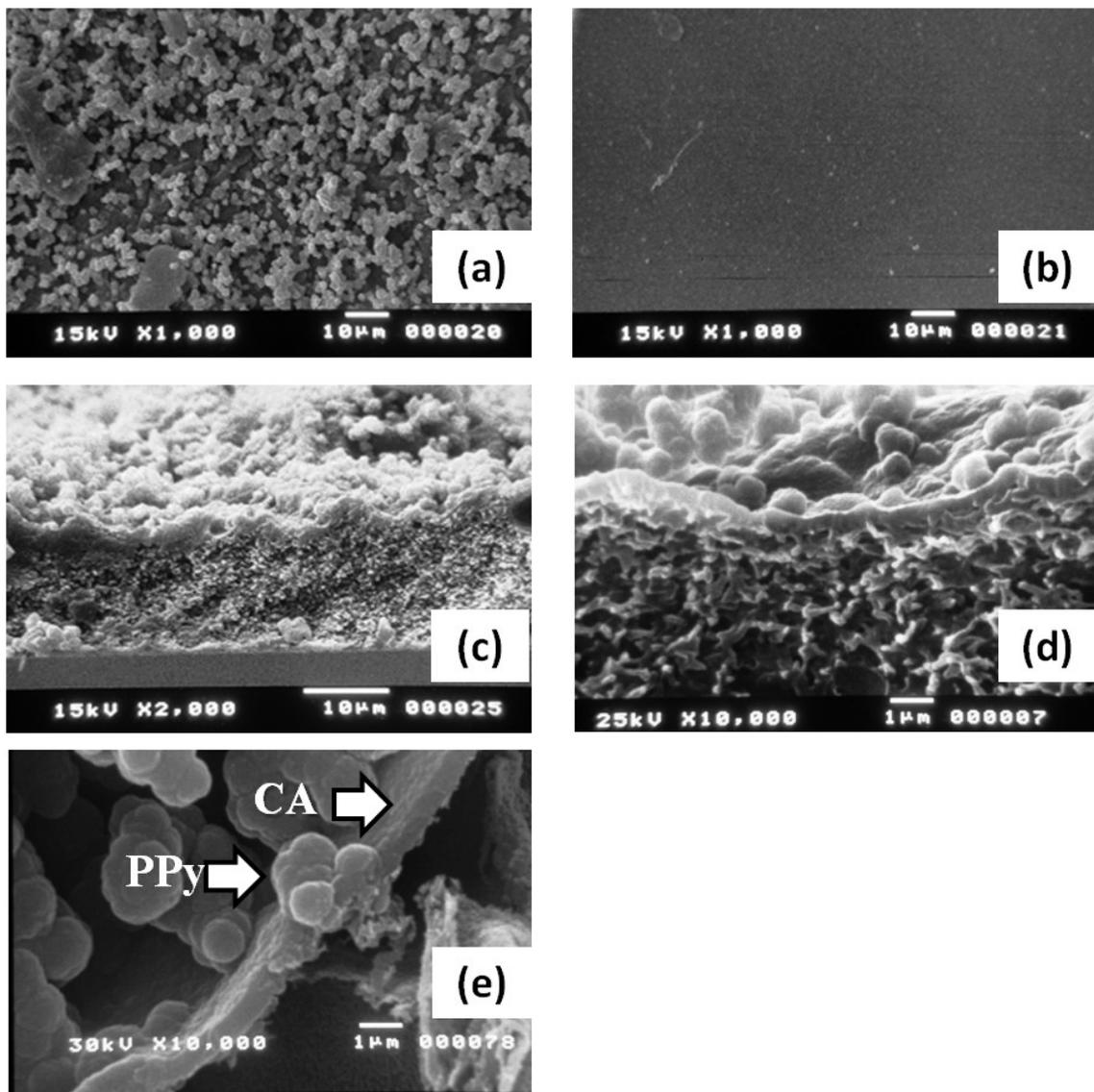


FIG. 2. SEM images of PPy-CA film of (a) solution side, (b) glass side, (c) cross section PPy particles on the high magnification for (d) cross-section , and (e)

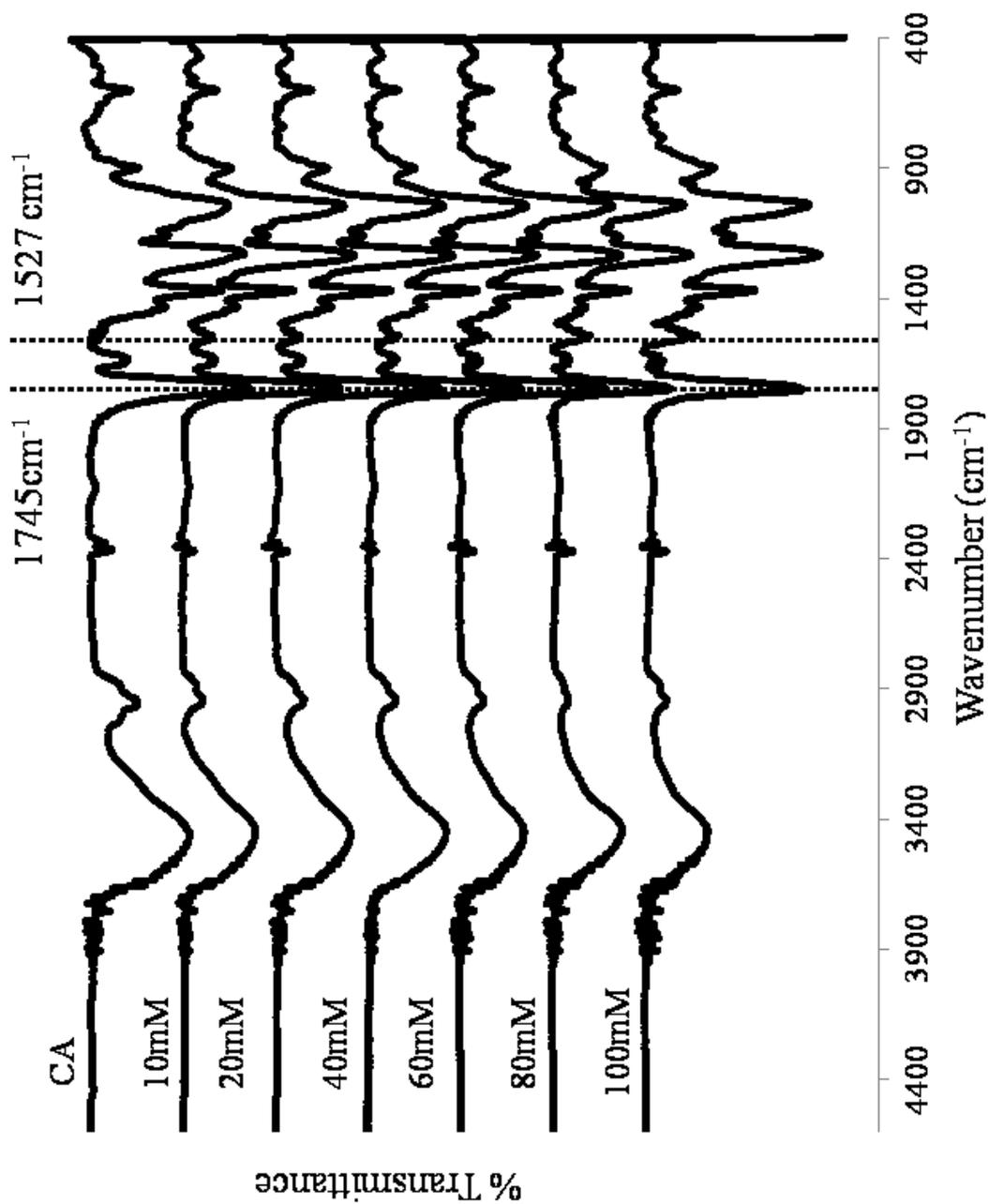


FIG. 3. FT-IR spectra of the PPY-CA films prepared at a concentration from 10 mM to 100 mM of FeCl_3 aqueous solution.

C-O group at 1219 cm^{-1} . The strong band at 1029 cm^{-1} was assigned to the C-O-C band. Reportedly, the broad band centered at 3441 cm^{-1} was assigned to O-H stretching of CA [31]. In addition with their CA bands, the related PPy bonds were assigned in the fundamental vibration centered at 1527 cm^{-1} , the =C-H inplane vibration at 1290 and 1122 cm^{-1} , and the N-H stretching vibration at 3400 cm^{-1} for the pyrrole ring. With the increase of FeCl_3 concentration in the aqueous solution, the 1527 cm^{-1} band became intense, indicating that the PPy formation was enhanced in the CA film.

The FT-IR spectra data show that the amounts of PPy in the PPy-CA film were calculated from the peak intensity ratio of 1745 cm^{-1} of the CA with 1527 cm^{-1} derived from the PPy. Results clarified that the value of the peak intensity of the 1527 cm^{-1} band was increased relative to that of 1745 cm^{-1} band, when the FeCl_3 concentration increased. This supports that the formed amounts of PPy in the CA scaffold film increased with increasing FeCl_3 concentration. To compare the presence of measure PPys in the glass side and the solution side on the scaffold film, reflection FT-IR spectra of the PPy-CA film were measured (Figure 4). The comparison of these spectra was made that the solution side had high PPy band at 1527 cm^{-1} relative to that of the glass side. Observations revealed that the 1745 cm^{-1} band of the CA was weaker in the spectrum (a), apparently because the PPy component was formed gradually to be decreased from the surface of the film to the inside.

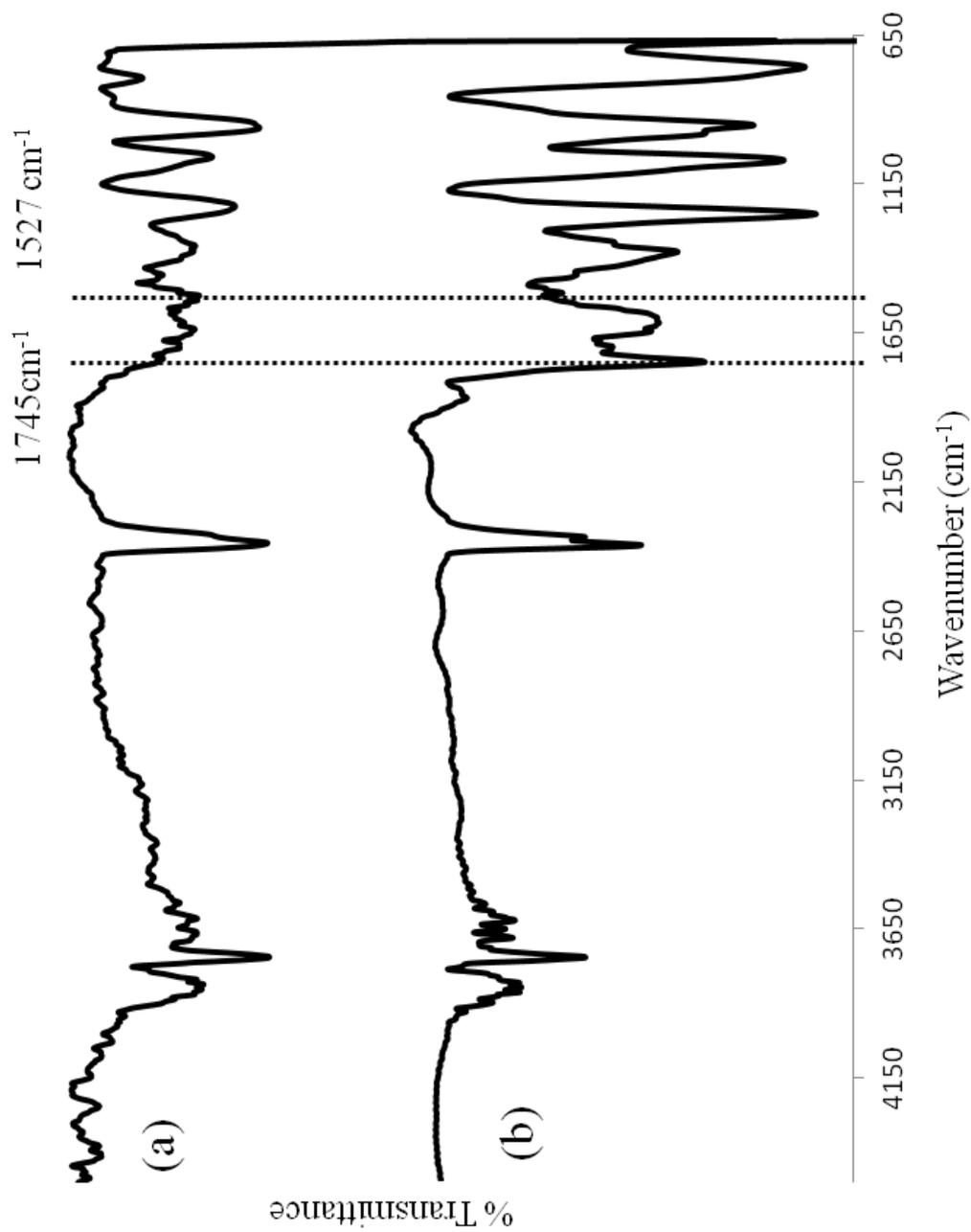


FIG. 4. FT-IR spectra of the PPY-CA film of (a) solution side and (b) glass side for the film prepared with 100 mM FeCl₃.

2.3.2 Electrical conductivity of PPy-CA film

Figure 5 presents the influence of immersion time on electrical conductivity of the resultant films at different concentration of FeCl_3 . Results for the solution side of the film show a tendency with an increase of the electrical conductivity of the PPy-CA film, when the immersion time was changed from 1 h to 6 h. However, immersion beyond 8 h changed the value of the electrical conductivity only slightly, because the formation of polymerized PPy layer was almost stopped at these times. Moreover, a progressive increase was observed in the electrical conductivity of the PPy-CA film, as higher concentrations of FeCl_3 were used in the aqueous solution. These data show that a high concentration of FeCl_3 can influence formation of the numbers of PPy particles on the CA scaffold film. On the other hand, the electrical conductivity on the glass side of the film shows lower values than that of the solution side of the film, showing that the PPy formation was began from the solution side to inside of the film.

Figure 6 presents the influence of FeCl_3 concentration on the film electrical conductivity prepared for 2, 6 and 24 hours in the coagulation time. When the immersion time was increased, the difference in electrical conductivity of the resultant films in solution side and glass side became to be almost same. However a comparison of the results for 2 hour immersion showed large difference in the electrical conductivity. From these results, these FeCl_3 concentrations and the immersion time were influenced in the film electrical

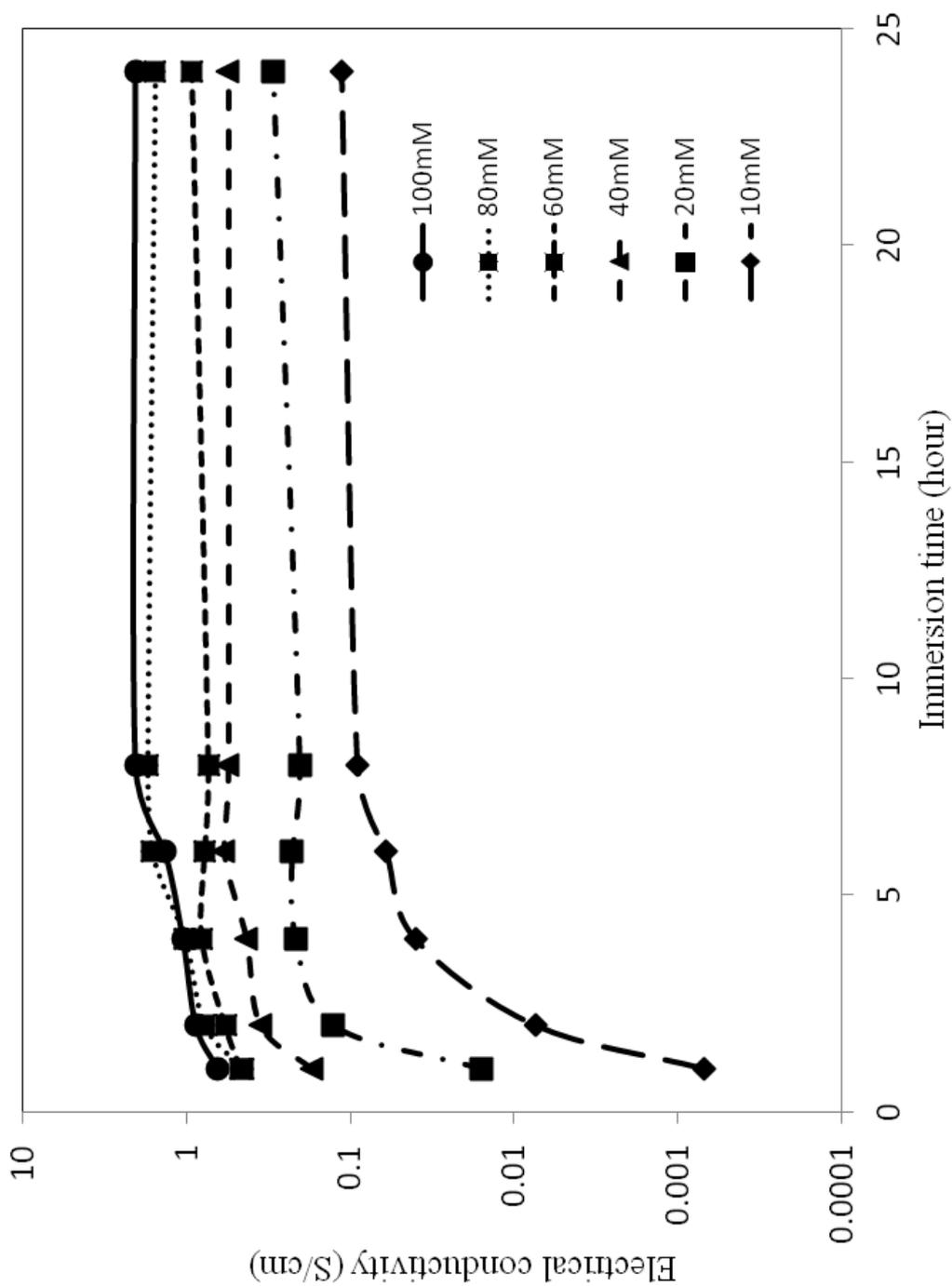


FIG. 5. Electrical conductivity of PPY-CA film prepared in various concentration FeCl_3 aqueous solution at various immersion times.

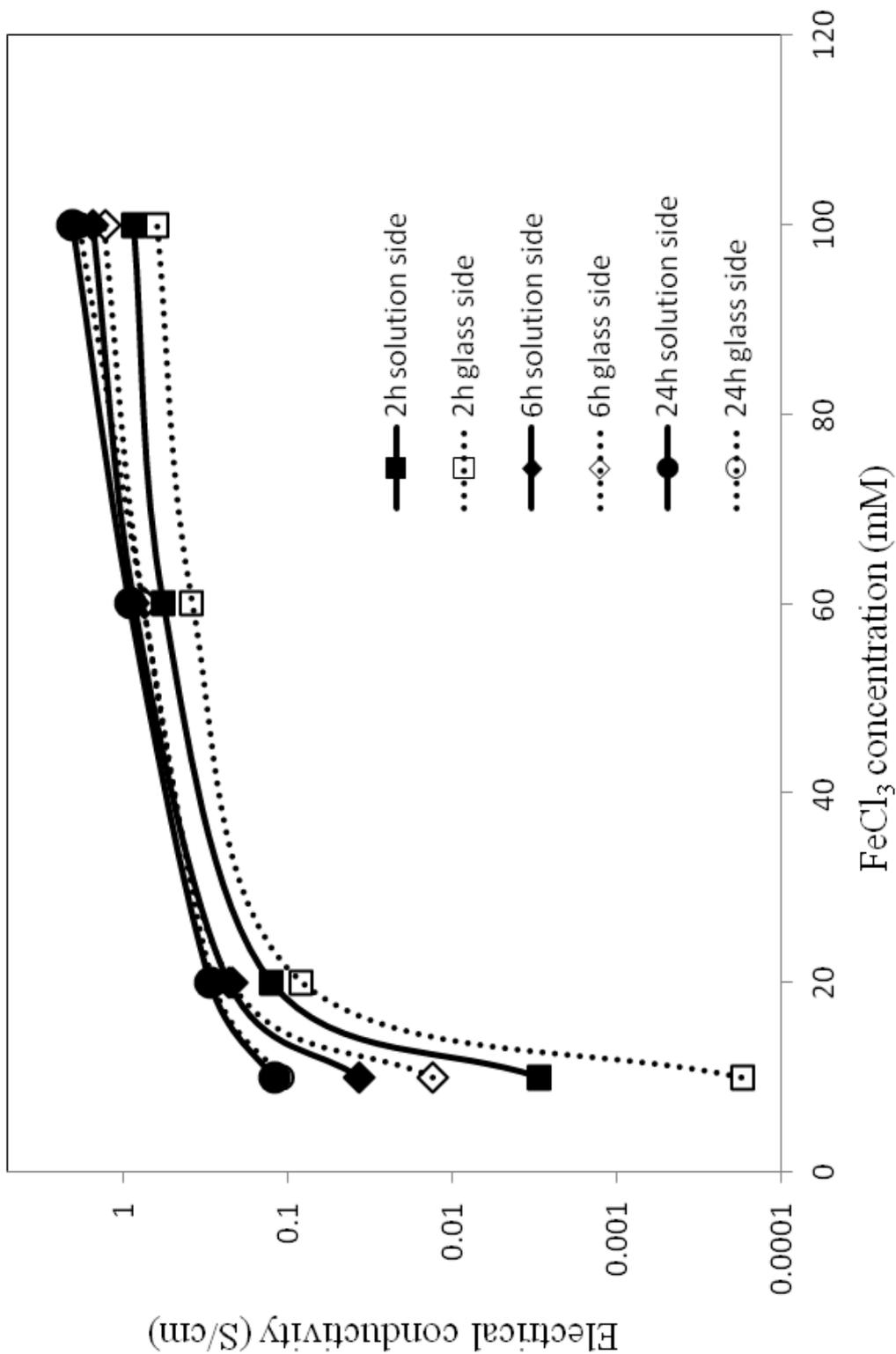


FIG. 6. Electrical conductivity of the solution side and the glass side of the PPy-CA film prepared in various concentration FeCl₃ aqueous solution at various immersion times.

conductivity and the electrical conductivity was searched to be distributed in the CA film inside, at 24 hours.

Figure 7 shows reflection UV-Vis spectra of the PPy–CA film prepared in the FeCl_3 aqueous solution. Here, these were measured on the glass side and the water solution side. The solution side shows that the absorption band around 400 nm was caused by $\pi \rightarrow \pi^*$ electronic transition of the PPy component. It was noted that the broaden band was observed around 500–700 nm in the spectra indicating that the PPy had bipolaron transition band on the CA scaffold film. This result suggests that the PPy interacted with dopant of Cl^- [32]. The peak intensity of the $\pi \rightarrow \pi^*$ band of the PPy showed almost identical intensity on the surface, but the bipolaron band intensity increased gradually on the solution side, when the concentration of the FeCl_3 solution was increased.

Figure 8 (a) shows relationship of both electrical conductivity of the resultant PPy–CA film and PPy contents in the CA scaffold for the films prepared with different immersion temperature. Here, the FeCl_3 concentration was fixed at 100 mM in the coagulation water. Decreasing change in the temperature of the coagulation bath apparently caused higher electrical conductivity of the PPy–CA film. Furthermore, the PPy contents in the CA scaffold was decreased, when the temperature was increased from 5 °C to 50 °C. To ascertain the temperature effects, the change in the viscosity of the Py–CA cast solution was also measured at different temperatures. As shown in

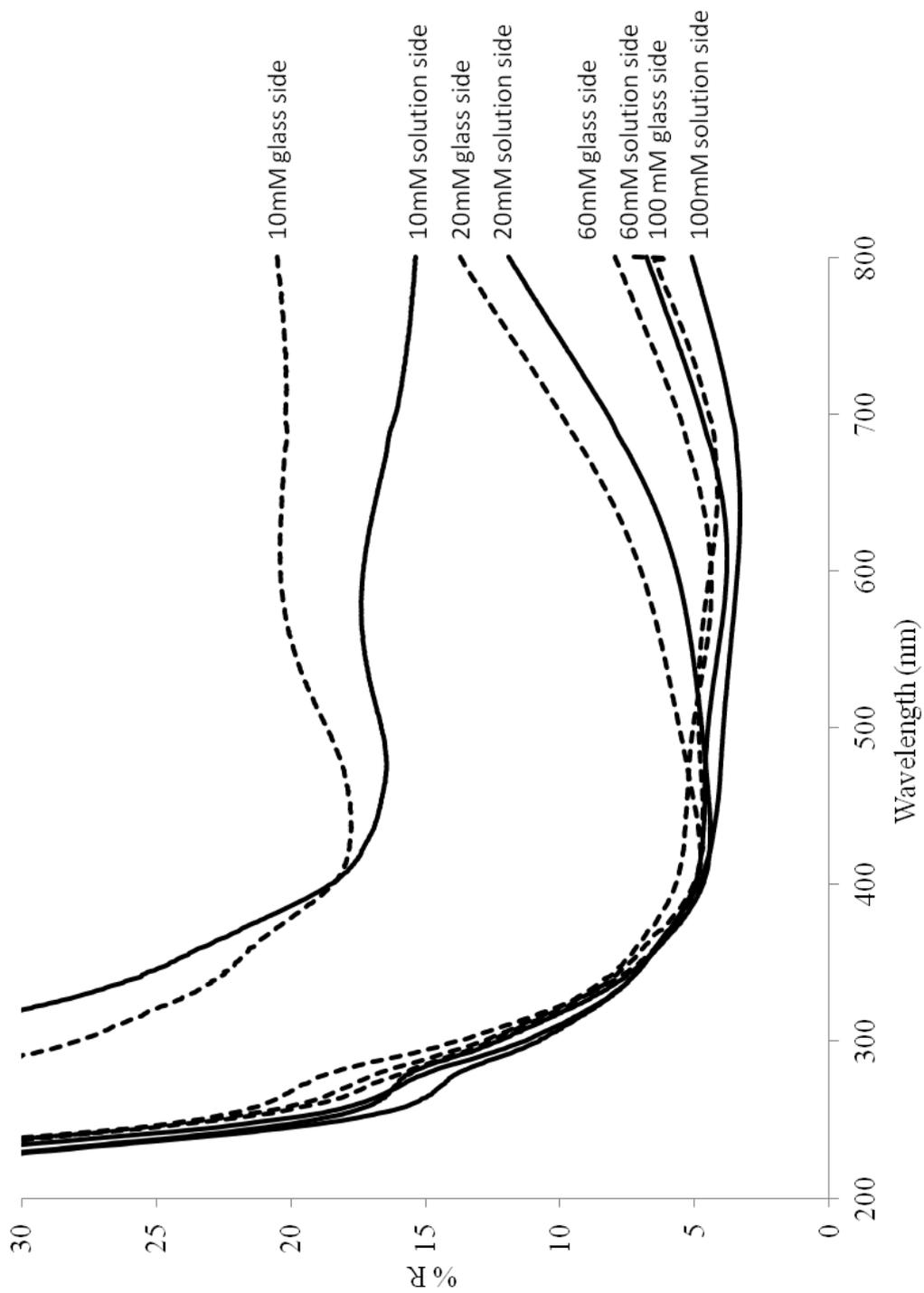
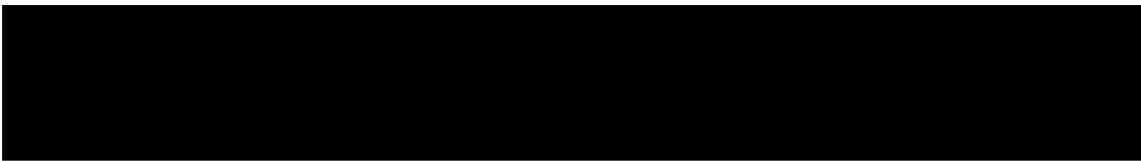
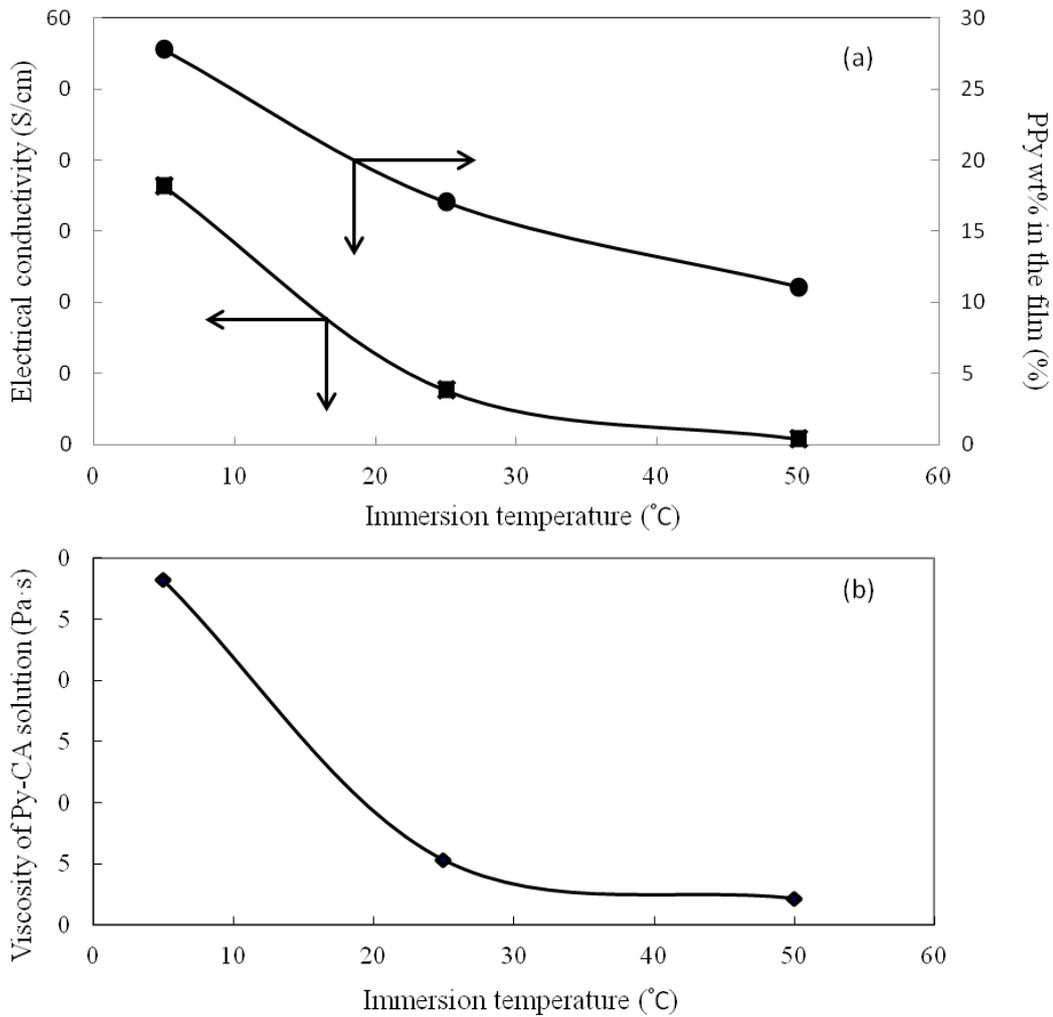


FIG. 7. Reflection UV-vis spectrum of PPy-CA film prepared from 10 mM to 100 mM of FeCl₃ aqueous solution.

Figure 8 (b), the viscosity of the Py–CA solution increased more at 5 °C than at 25 °C. The comparison indicates 10 times higher viscosity achieved at 5 °C for 28.2 Pa·s than at 50 °C for 2.2 Pa·s, meaning that the low temperature became highly viscous solution. These data suggested that the formation of PPy particles in the PPy CA films strongly depended upon the coagulation temperature. The electrical conductivity data on (a) showed that in the low viscosity at 5 °C, Py polymerization was highly occurred. This might be due to that the Py monomers were moved to water layer at high temperature during the film was formed. Therefore, in order to ensure Py concentration in water solution used for CA coagulation during the film formation, absorption spectra of Py in the coagulation water were measured at different temperature. Figure 9 shows the Py amount coagulated in water measuring by UV absorption at 210 nm, at different immersion times for different temperatures. These data showed that the Py concentration in the water solution was increased at higher temperatures. This was because that the solvent exchange of Py with H₂O occurred more rapidly at higher temperatures. The UV absorption intensity at 210 nm for the Py band was increased with an increase of the immersion time, and then became constant. It was noted that the dissolution amount of the Py became markedly higher at 50 °C, meaning that the Py monomer in the coagulated CA layer became low and decrease the number of PPy particles. As results, the electrical conductivity became lower at higher temperature.



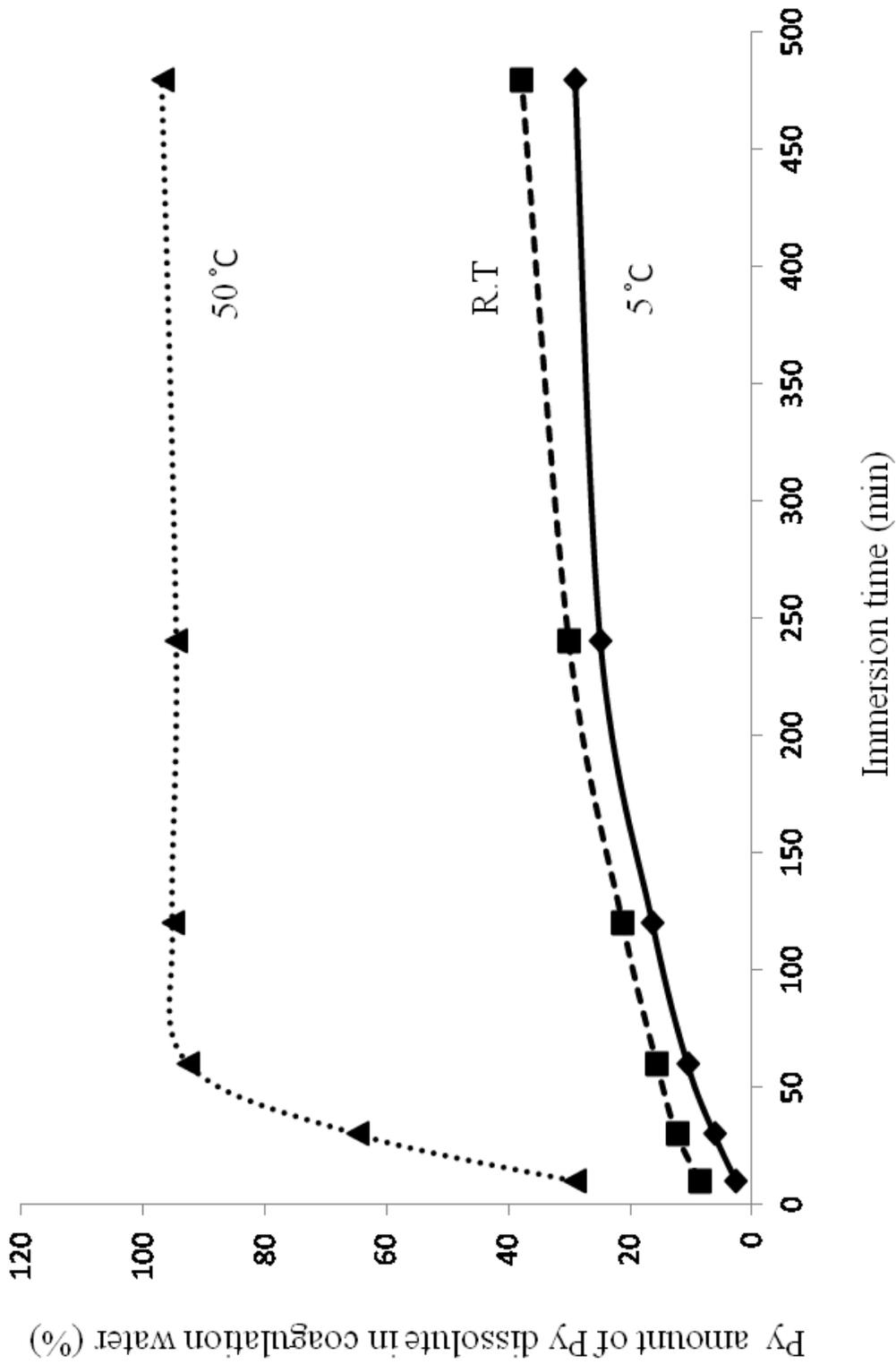


FIG. 9. Calculated dissolution rate of Py from Py-CA viscous solution in the water.

2.4 Conclusions

As a unique technique, PPy–CA composite films were prepared using wet cast method, when Py–CA solution was used. In the method proposed, the resultant composite CA included PPy particles having about 1 μm diameters. The amounts of PPy changed from $3.6 \times 10^{-6} \text{ g/g}_{\text{CA}}$ to $8.0 \times 10^{-3} \text{ g/g}_{\text{CA}}$, when FeCl_3 concentration was from 10 mM to 100 mM, respectively. At 100 mM FeCl_3 , resultant film expressed $3.6 \times 10^1 \text{ S/cm}$ electrical conductivity on the solution side of the film. Also, electrical conductivity was observed depending on the preparation conditions like immersion time, and immersion temperature in addition with FeCl_3 concentration.

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Chapter 3

Dual layer hollow fiber of polyaniline-cellulose acetate prepared with simple wet technique of chemical polymerization of aniline

Abstract

Polyaniline-cellulose acetate hollow fibers prepared from cellulose acetate (CA) solution of aniline (ANI) were founded to show dual layers structure, when wet technique was applied for using syringe injection of the solution to acidic water for ANI polymerization. In this technique, the polymerization of ANI occurred simultaneously by the monomer injection in coagulated CA fibers. Then, the PANI-CA composite fibers were obtained. The formation of the PANI-CA composite fiber was dependent upon HCl concentration and initiator of ammonium persulfate. Especially, when the coagulation time was 1 min, the obtained PANI-CA fibers showed hollowed dual layer structure having outer layer of PANI and inner layer of CA. Evidence was presented that the dual structure fiber had 40 μm outer layer and 60 μm inner porous layer in their thicknesses. Cyclic voltammograms of the PANI-CA fiber were indicated that the outer layer was composed of PANI layer showing electrochemical properties with electrical capacity of about 0.003 C.

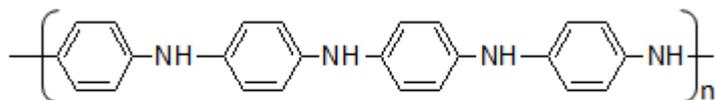
Key words: polyaniline, cellulose acetate, hollow fiber, composite material

3.1 Introduction

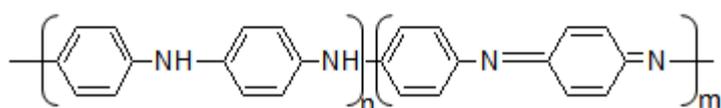
Polyaniline (PANI) is a conjugated polymer obtained by polymerization of aniline (ANI) monomer and very useful for conductive materials. Since PANI is one of the most important conducting polymers, such polymer has been widely used in recent years as electrochemical and electronic materials for electromagnetic shield, antistatic agent, secondary batteries, and electrochromic display [1]. It is known that PANI takes chemical structure in fully reduced form of leucoemeraldine (LB), partially reduced emeraldine (EB), and fully oxidized one of pernigraniline (PB) (Scheme 1), depending on the preparation method [2, 3]. Physical properties of such PANI applied for conductive and optical materials are seriously influenced by chemical structures in their polymers. There were reports in recent year for PANIs on the application for fabrication of the polymers [4]. PANI rectangular tubes were synthesized by hydrogen adsorption using for carbon nanosphere template [5]. Nina Jiang et al. reported that adsorption of the heavy metals of Cu^{2+} and Pb^{2+} by the

PANI nanofibers was found by assembled alginate microsphere. Many of these papers have focused in shape control of PANI. However, PANIs have very poor mechanical properties and still problems are shown in their materials for, limiting their uses in the self-standing form. To compensate this problem, a method of PANI complexed with other polymers has widely investigated. Among them, in particular, cellulose acetate (CA) is quite

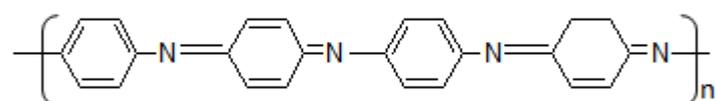
Leucoemeraldine (LB)



Emeraldine (EB)



Pernigraniline (PB)



Shame 1. Oxidation states of PANI

often used as scaffold matrices for PANI. So, their derivatives have an important industrial advantage for transparent film [6]. Representative CA is obtained by acetylation in cellulose derivative, showing good abilities like excellent chemical resistance, heat resistance and flammability. It can be used in wide industrial fields that CA is applied in cigarette filters, photographic film and separation membranes [7-10]. In our research group, it was studied that conductive polymer composite films with CA were prepared by wet phase inversion process [11]. In their progresses, it was found that the ANI monomer could dissolve CA, which was used as film substrate. When the CA-ANI solution prepared was poured to acidic aqueous solution, the obtained polymer composites were shown inadvertently to be film shape. In the present work, the PANI-CA composites were modified to form fiber shape. It was inadvertently found that the PANI-CA composite

fibers showed quite interesting nature in morphological observation like hollow fiber structure.

On the other hand, in current trends for hollow fibers, uses of separation membranes have been paid more attention [12-16], because of some important advantages in high membrane packing and self-supporting ability. The hollow fiber allows a compact packing in module. In general, such fiber is prepared with extrusion method and water treatment hollow fiber becomes very popular now [17, 18]. However, there are very few reports on fiber conductive polymers. Therefore, the present work provides a quite simple process including with wet coagulation for preparation of hollow fibers having dual layers of PANI and CA. Thus, the originality in the present work is to use scaffold CA for PANI composite fiber prepared by wet coagulation CA and chemical polymerization of ANI. Such idea can propose an attractive method for preparing composite hollow fibers. During the CA was coagulated in water solution, the ANI polymerization appeared in the coagulated CA fibers. Effects of oxidation catalyst of the ANI polymerization and HCl concentration were examined in different conditions for the resultant composite fibers.

3.2 Experimental

3.2.1 Materials

Aniline (ANI) used as solvent of cellulose acetate (CA) and monomer for PANI was purchased from Tokyo Kasei (Japan). CA contained 39.7 wt% in acetyl content (Aldrich, USA) with average molecule weight of ca. 50,000 was used. Ammonium persulfate (APS) for the polymerization initiator of ANI was product of Nakalai Tesque (Japan) and used without purification.

3.2.2 Preparation of PANI-CA composite fibers

The PANI-CA fiber was prepared by wet phase inversion process by using syringe injection to acidic water. In a typical procedure, CA was soluble in ANI with 14 wt% was concentration by using in ANI solvent. The ANI-CA viscous solution was stirred overnight at room temperature until a homogeneous solution was obtained. Then, the resultant ANI-CA solution was poured from Needle (TERUMO., Japan) having inner diameter of 0.6 mm into the aqueous solution, which contained different concentration of HCl and APS. After injection of the ANI-CA solution into the medium the CA coagulation was conducted and simultaneously oxidation polymerization of ANI was occurred [18]. The coagulation of CA was carried out in water for more than the minute in the aqueous solution. Then, Since the PANI was formed with the CA fiber matrix, the composite fiber became black after a certain time. The resultant black fiber was washed using distilled water to

remove excess ANI and HCl from the composite fibers. Then, the fiber was dried in vacuum at room temperature overnight.

3.2.3 Measurements

The CA fibers containing PANI were prepared by wet phase inversion process of CA-ANI solution by using syringe injection into acidic water. In a typical procedure, CA was dissolved in ANI solvent with 14 wt% concentration. The CA-ANI viscous solution was stirred overnight at room temperature until a homogeneous solution was obtained. Then, the resultant CA-ANI solution was packed in syringe (15 mm diameter) (TERUMO, Japan) having inner needle (0.6 mm diameter) and then injected into the acidic aqueous solution, which contained different concentration of HCl and APS. After the injection of the CA-ANI solution into the aqueous solution, CA coagulation was conducted and simultaneously oxidation polymerization of ANI was occurred [18]. The coagulation of CA was carried out in the water solution for 1, 3, 5 and 10 min. During the coagulation of CA, the PANI was formed in the CA fiber matrix. It was observed that the color of the fiber became black after a certain time. The resultant black fibers were washed using distilled water to remove excess ANI, APS and HCl from the composite fibers and then was dried in vacuum at room temperature overnight.

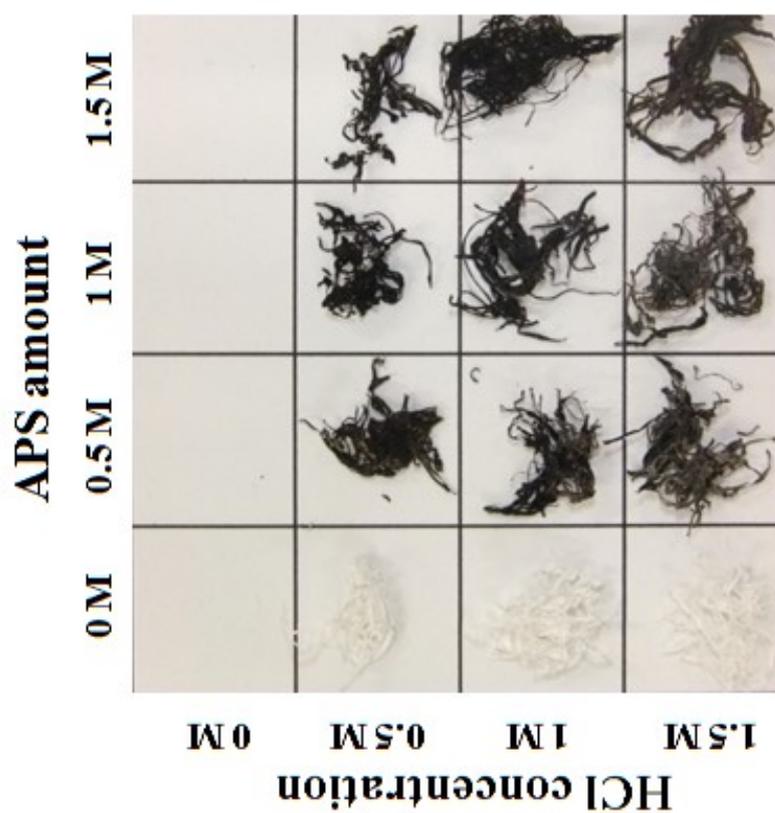


Fig. 1 Photographs of the fibers prepared by injection of the ANI-CA solution in various concentration of HCl and APS. The coagulation was carried out at room temperature for 1 minute.

3.3 Results and discussion

3.3.1 Preparation of hollow fibers having dual layers

Figure 1 shows pictures of resultant fibers prepared in aqueous solutions containing different concentration of HCl and APS. The varied concentrations of HCl and APS in the aqueous solution for the CA coagulation were in the range of 0 M – 1.5 M and 0 M – 1.5 M, respectively. The coagulation was carried out at room temperature in 1, 3, 5 and 10 min after the solution was injected into the acidic aqueous solution. It was noted that no fiber was formed, when the CA-ANI solution was kept without HCl in the aqueous solution, which contained only APS. On the other hand, when APS was absent, white fibers were formed. In this case, no black color was observed in the polymer fibers. That is, the APS was important on the formation of the black PANI. In the presence of HCl, the water soluble anilinium chloride was generated, showing high solubility to be eluted in water layer. For this reason, only the CA polymer was coagulated by the phase inversion process. However, when the HCl was absent, the high solubility of ANI to the CA seemed to be difficult to coagulate CA in water. As a result, there were no fibers in the absence of HCl in the aqueous solution. Furthermore, it was interesting to note that the black fibers were formed in the aqueous solution containing both HCl and APS. Then, there was tendency that the fiber color was changed to be a glossy black, as HCl concentration was higher.

Figures 2 (a) and (b) show SEM images of cross section of the resultant PANI-CA fibers prepared in 1 M HCl and 1 M APS for the aqueous solution. Here, the coagulation times were changed after the CA-ANI solution was injected in the range of 1 min to 5 min. It was worthy nothing that the resultant PANI-CA had hollow-shaped fiber with about 300 μm diameter (Fig. 2(a)). The

hollow fiber contained about 40 μm and 60 μm thicknesses for the outer and inner layer, respectively. In the 750 magnification (Fig. 2(b)), there was completely different inner layer and outer layer, showing dual structure in the hollow shape. The picture observation suggested that the inner layer became porous and outer layer was dense in the morphological structure. For the inner layer, the porous structure was similar to the CA matrix prepared by phase inversion method [19]. In addition, the outer layer, which showed black color, seemed to contain PANI. Figures 2 (c) and (d) show SEM images of cross section of the PANI-CA fibers formed after 3 and 5 min coagulation, respectively. With increasing the coagulation time from 1 min to 3 min, the inner hollow structure of the resultant fibers was incomplete. At 5 min in the coagulation time, the SEM data showed that the hollow structure was absent. It was interesting to note that the outer layer thickness became large with increase of the coagulation time from 1min to 5 min, meaning that degree of ANI polymerized increased with the time. The image indicated that the outer layer was bulged tightly to the layer in the fiber.

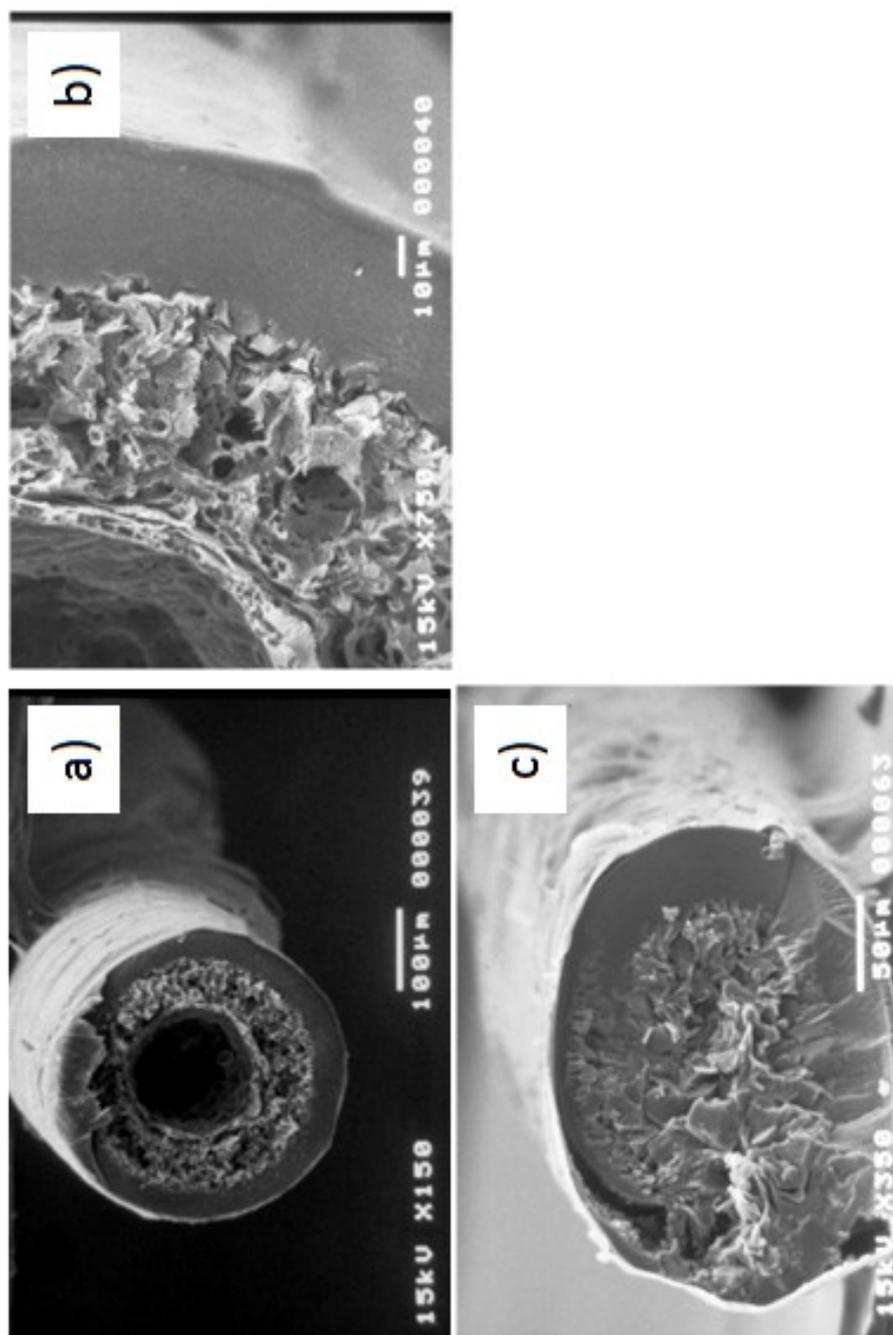


Fig. 2 SEM images of the PANI-CA fibers prepared in 1M HCl-APS in the aqueous reaction solution for a, b) 1 minute and c) 5 minutes.

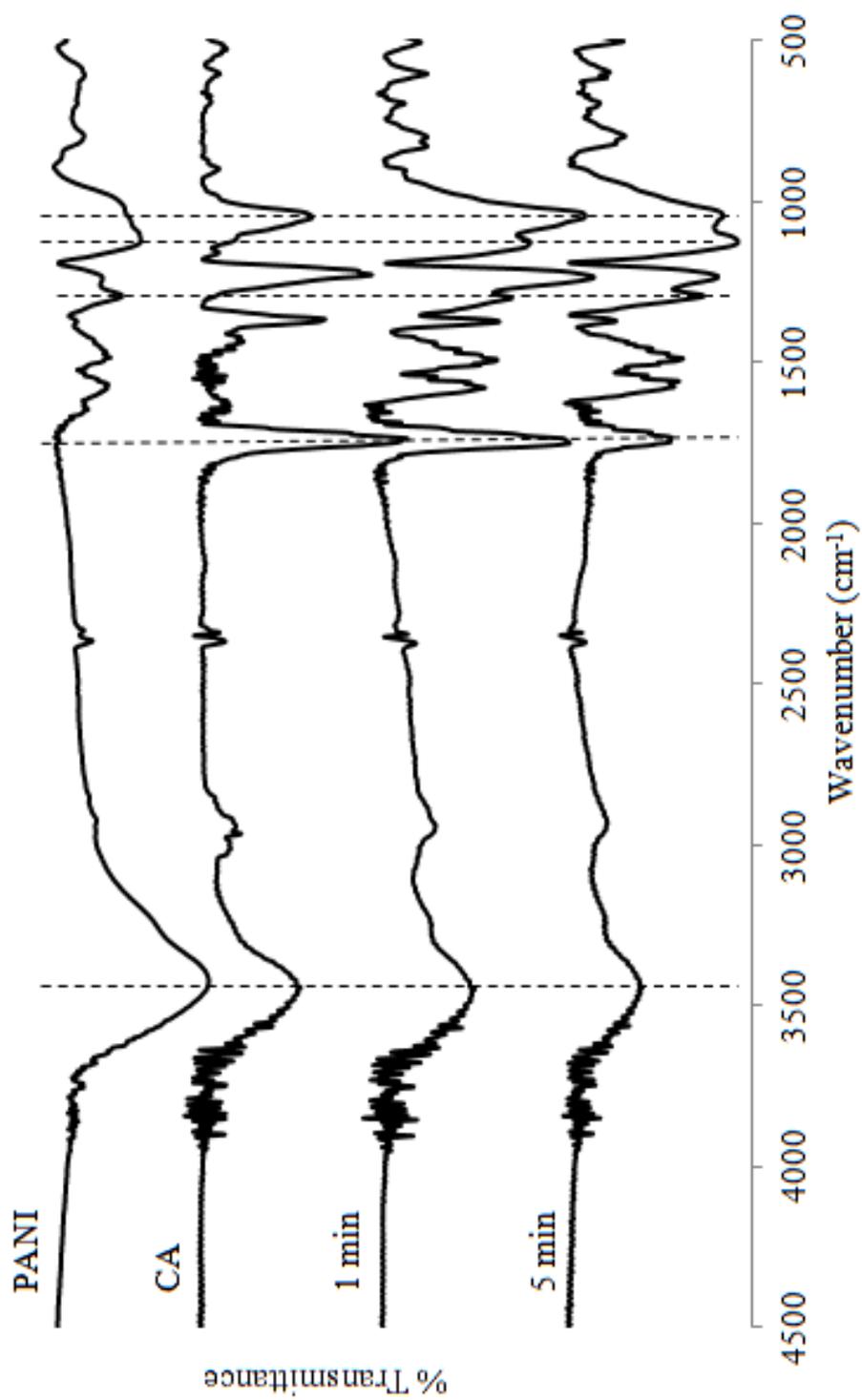


Fig. 3 FT-IR spectra of the PANI-CA fiber prepared in 1M HCl-APS solution for 1 minute and 5 minutes.

Figure 3 shows FT-IR spectra of the PANI-CA fiber prepared in 1M HCl-APS aqueous solution for 1 and 5 min in the coagulation time. These spectra were measured in terms of KBr method.

Reportedly, the characteristic peaks of CA for the carboxylate group (C=O) and the C-O group were observed at 1751 cm^{-1} and 1238 cm^{-1} , respectively, in the spectra obtained. The strong band at 1049 cm^{-1} was assigned to the C-O-C band. Also, the broad band centered at 3450 cm^{-1} was assigned to OH stretching of CA [20, 21]. In addition with their CA bands, the related PANI bonds were assigned in the quinoid rings at 1580 cm^{-1} , the C=N stretching vibration mixed with C-H bending vibration at 1492 cm^{-1} , the C-N stretch of a aromatic amine at 1296 cm^{-1} , and the C-H in plane bending modes at 1126 cm^{-1} . With the increase of the coagulation time, the 1296 cm^{-1} band became intense, indicating that the PANI formation was enhanced in the CA film [22-24]. For their spectra, since whole area of the fibers was used for their spectral measurement in KBr pellet, the information of outer and inner portions was included together in the spectra. Thus, to compare the FT-IR spectra in the each position of the PANI-CA fiber, the microscopic reflection FT-IR spectra of the PANI-CA fiber were measured. Figure 4 shows refraction FT-IR spectra at different position. As inserted by the SEM image in the figure, the positions of A-D were indicated in the picture. In comparison of these spectra, characteristic assignment was made at the different positions. The inner layer for the position D had

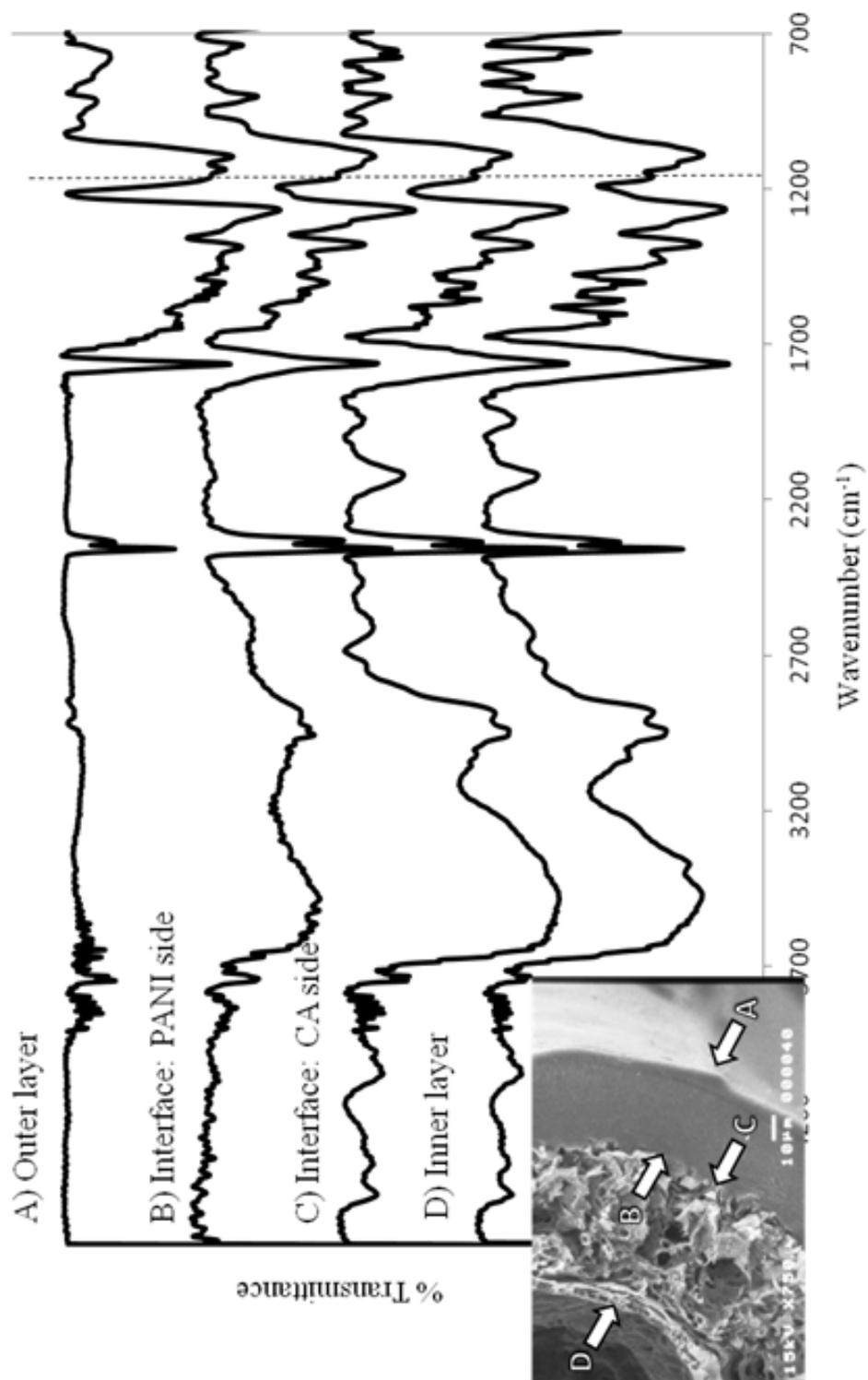


Fig. 4 Reflection FT-IR spectra of the PANI-CA fiber of each positions for the hollow fiber prepared with 1M HCl-APS aqueous reaction solution for 1 min.

high CA band for OH band at 3450 cm^{-1} and C=O at 1751 cm^{-1} . Therefore, this strongly suggested that the inner layer contained the coagulated CA. In the outer layer at the position A, the characteristic peak of CH in plane bending modes of PANI at 1126 cm^{-1} was appeared strongly. Although the OH peak of the CA appeared in the inner side interface at the position B, the outer layer was present in less peak intensities for the $>\text{C}=\text{O}$ and OH attributed with CA. These results meant that the outer layer contained mainly a number of PANI polymerized from ANI. In addition, comparison indicated that the CA amounts were decreased when the observed position was changed from the D to A.

3.3.2 Properties of ANI-CA fibers

Fig. 5 shows UV-Vis spectra of the PANI-CA fiber prepared in the 1M

Figure 5 shows UV-Vis spectra of the PANI-CA fiber prepared in the 1M HCl-APS aqueous solution at room temperature for different coagulation times. To measure the UV-vis spectra, the resultant fiber was dissolved in N,N-dimethylformamide (DMF) and then, measured by a transmission method using a quartz cell. In the UV-vis spectra of the PANI-CA prepared for 1 min coagulation, the two strong absorption bands were observed; One was with maximum at 590 nm corresponding to molecular exciton

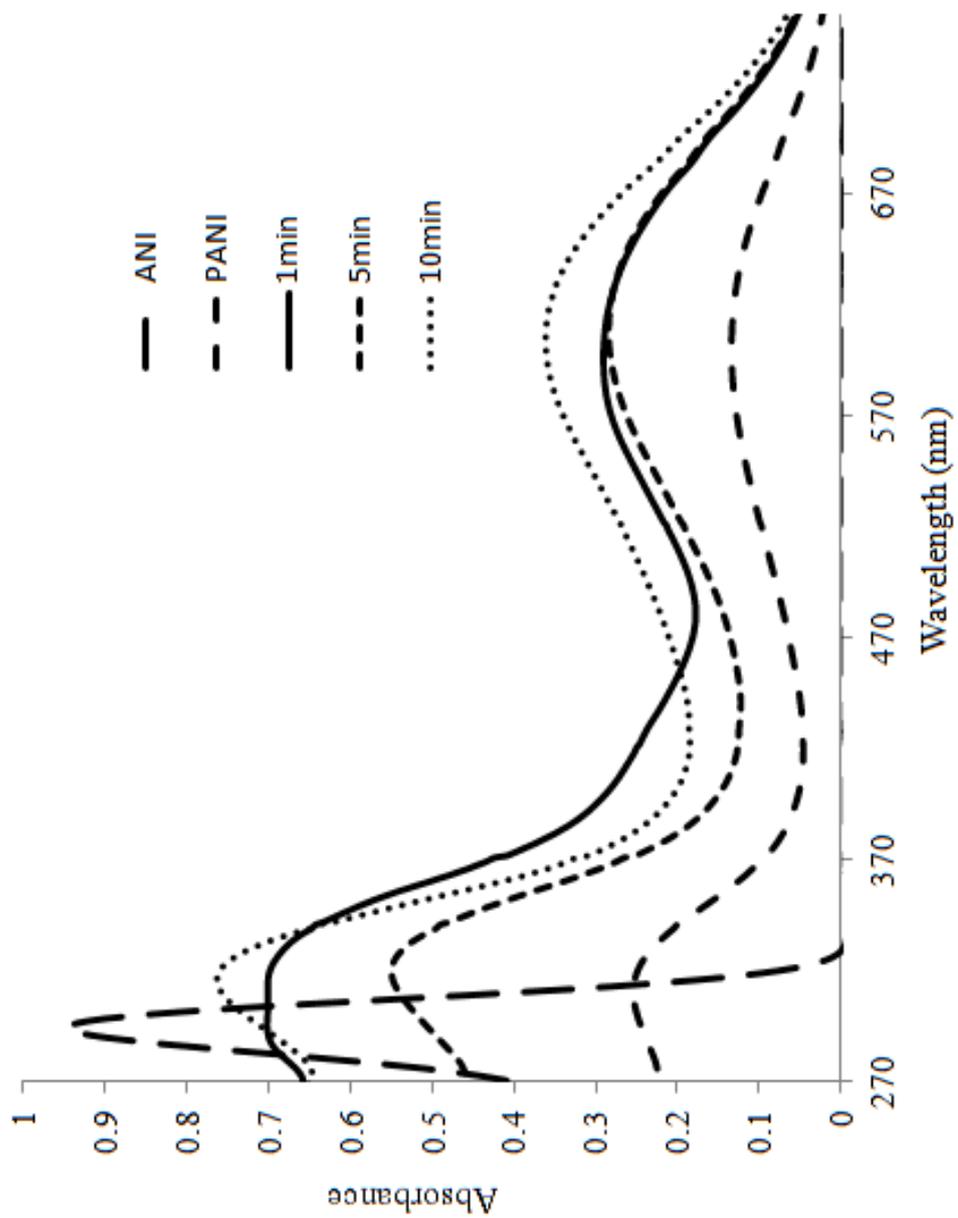


Fig. 5 UV-vis spectrum of PPY-CA film prepared from 10 mM to 100 mM of FeCl₃ aqueous solutions



Fig. 6 DCS curves of PANI-CA fiber prepared in the 1M HCl-APS aqueous solution at room temperature for 1, 5 and 10 min.

transition and another at 320 nm, $\pi \rightarrow \pi^*$ transition [22, 25, 26]. The spectrum implied that both oxidized and reduced species also were exhibited in the 320 nm transition. Moreover, there was absorption band at 427 nm in the spectra [27, 28]. This indicated the presence of aniline oligomers. In addition, when the coagulation time extended to be 5 min, the latter peak was shifted toward 634 nm, suggesting that the PANI was oxidized. From these results, when the aniline in the CA-ANI solution was added to the 1 M HCl-APS solution, the monomer formed PANI oligomers at the earlier coagulation time. Thereafter, the ANI was polymerized on the surface of the CA fiber to form PANI. With increase of the coagulation time, there was tendency that the formed PANI was oxidized to be the EB form in the inner layer.

Figure 6 shows DSC curves of the PANI-CA fibers prepared in the 1M HCl-APS aqueous solution at room temperature. The DSC curves of the PANI powder and CA powder were also contained as references. The T_{max} appeared in about 103 °C for the fibers obtained with the 1 min coagulation. This meant that the evaporation of water molecules from the fibers was observed in the curves. It might be due to that waters were trapped inside of the polymer fiber or bound to the polymer backbone [29, 30]. In these curves, it was observed that the value of T_{max} was shifted to the higher temperature side, when the fibers were prepared at longer coagulation times. This could be suggested that the increase of the

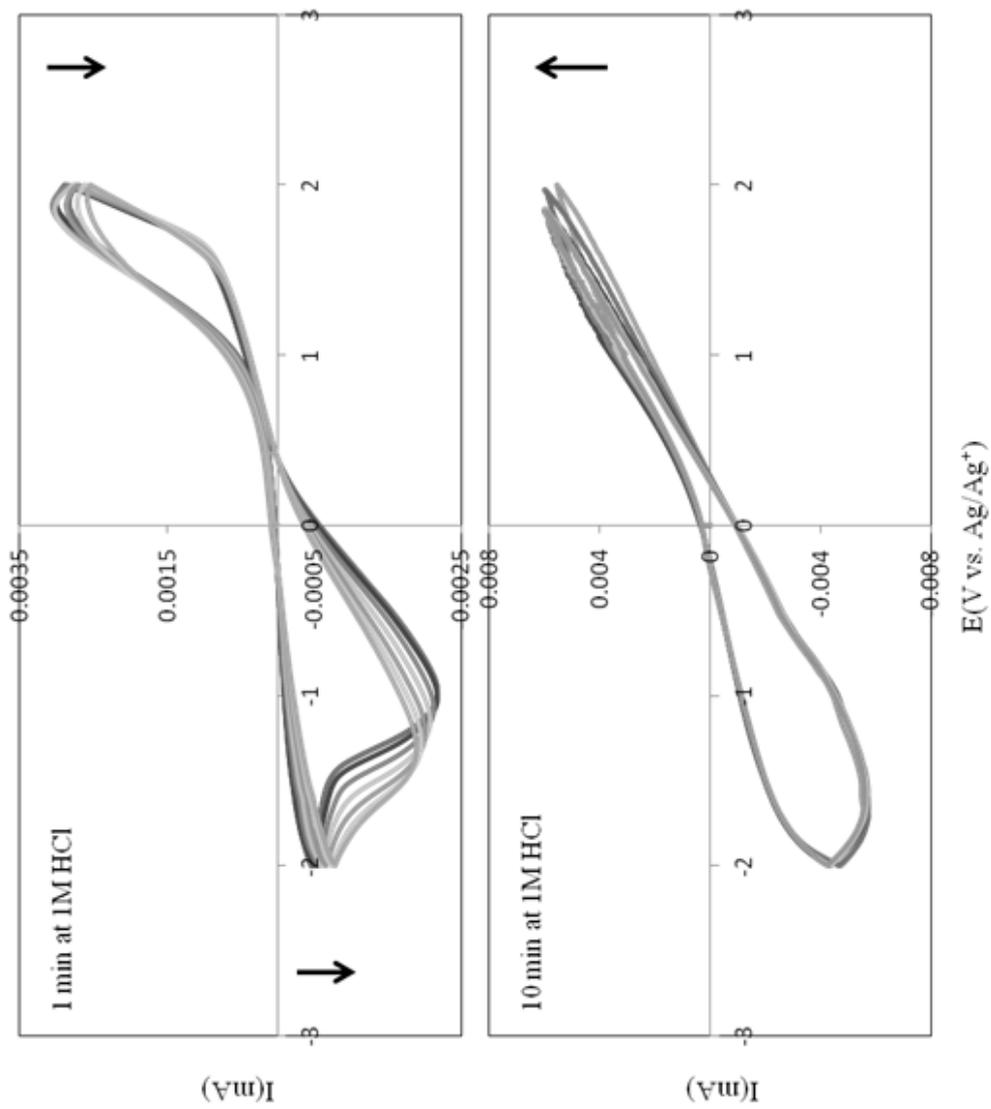


Fig. 7 Cyclic voltammograms of PANI-CA fiber prepared in the 1M HCl-APS aqueous solution for 1 and 10 min immersion 1 M HCl solution.

coagulation time increased the formation of the PANI in the CA scaffold fibers.

Cyclic voltammograms are compared in Figure 7 for the PANI-CA fibers prepared in the 1M HCl-APS aqueous solution. In the CV data of (a), reduction potential peak was shown at -1V. In addition, when the cycles of the CV measurement were increased, the reduction potential peak was shifted toward low voltage side. This meant that the PANI-CA fiber prepared in the 1 min coagulation time contained PANI component, showing a low oxidation degree. Furthermore, the reduction potential peak was shifted toward -1.5 V side, when the cycle number was increased. This suggested that the increased coagulation time made PANI-CA oxidation in the fibers. Especially, for the 10 min of the coagulation time, the sample showed no shift of the reduction potential. This might be due to that the formed PANI had high oxidation degree in the obtained fibers [3, 31 - 34].

In the CV profiles, the area of the voltammograms corresponded to electrical capacity (C). Therefore, the CV data for their PANI-CA fibers could calculate to obtain values of electrical capacity [35, 36]. The resultant electrical capacity for the PANI-CA fibers prepared at coagulation times of 1 and 10 min is plotted against cyclic numbers in Figure 8. When the coagulation time was increased from 1 min to 10 min, the values of the electrical capacity increased. In the case of the fiber prepared at 1 min, the value of the electrical capacity was almost constant at 3.3×10^{-3} C, but, that for the 10

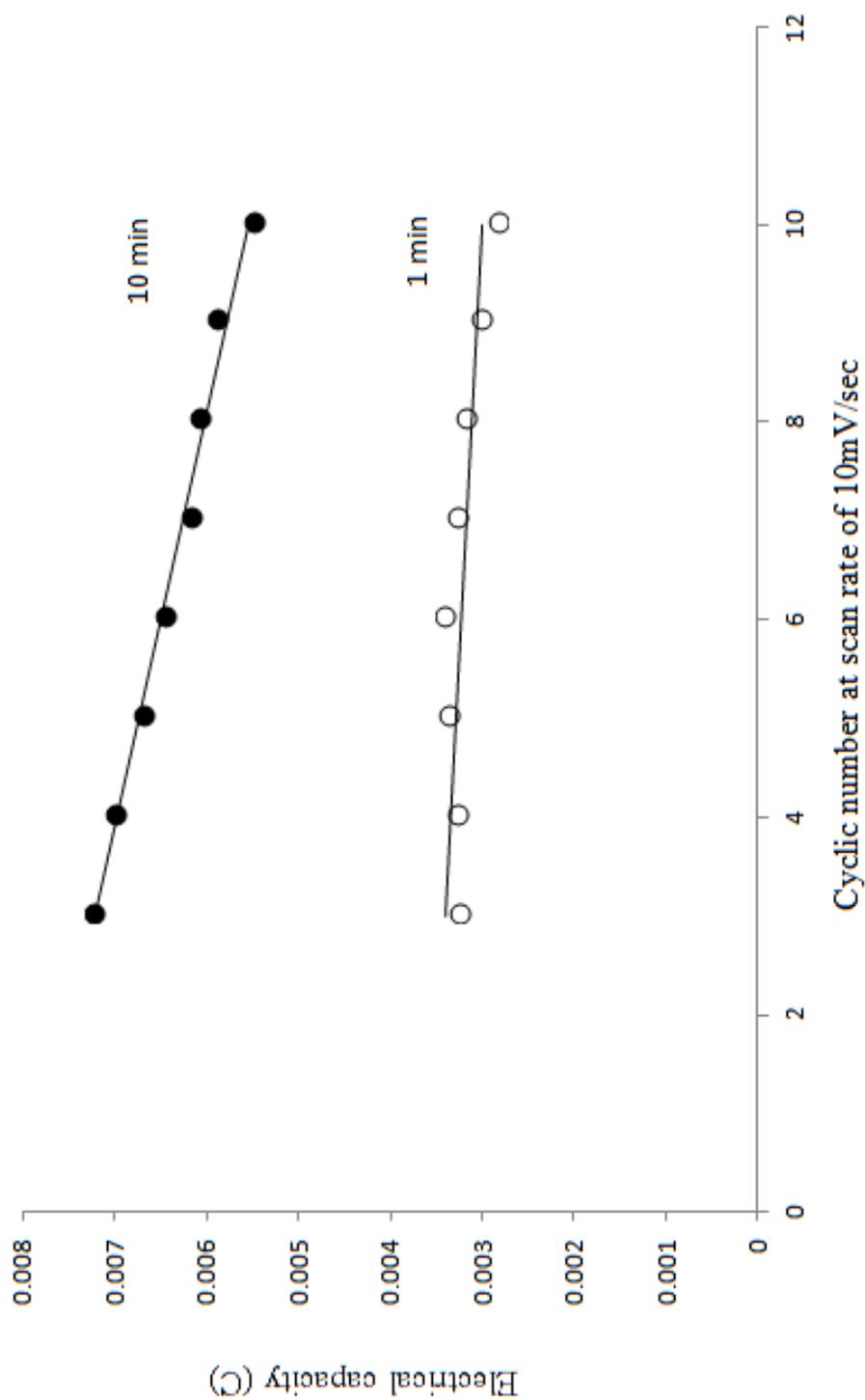


Fig. 8 Electrical capacity calculated from CV data of each PAN-CA fiber.

min sample was slightly decreased from 7.2×10^{-3} C to 5.5×10^{-3} C, as the cycle number was changed from 3 to 10, respectively. The decreased electrical capacity at each cycle number indicated that the sample used contained PANI in the PANI-CA layer. Thus, during the CV measurement, the cycle might change the chain conformation in PB by oxidation of the PANI [37, 38].

3.4 Conclusion

As a unique technique, PANI-CA fibers were prepared using wet cast method, when CA-ANI solution was used. The PANI-CA fibers obtained by the 1 min coagulation time had dual layer hollow fiber structure. The outer layer mainly contained the dense PANI layer and the inner CA layer, which was formed by the coagulation. When the coagulation time was changed in the range of 1 to 10 min, the hollow structure in the PANI-CA fiber was broken and dual layer without the inner hollow was formed. The electrochemical properties were measured using cyclic voltammetry. Changing the oxidation and reduction potential peak position indicated that the preparation conditions of the coagulation time depended on the oxidation and reduction condition of the resultant PANI in the fibers.

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Chapter 4

Summary

In the present thesis, preparation of composite materials of the electrically conductive polymer and scaffold material with new phase inversion methods and these characterizations were studied for PPy-CA conductive films and PANI-CA dual layer hollow fiber.

In Chapter 1, introduction of several conductive polymers and CA as a scaffold material were mentioned in their remarkably properties and applications. Furthermore, general phase inversion methods and new phase inversion method were described. Additionally, the purpose of this thesis was described for electrically conductive composite materials, which prepared by new phase inversion methods.

Chapter 2 described for conductive PPy-CA composite film which were prepared using wet cast technique, when Py-CA solution was used. In the method proposed, the resultant composite CA included PPy particles having about 1 μm diameters. The amounts of PPy changed from 3.6×10^{-6} g/g_{CA} to 8.0×10^{-3} g/g_{CA}, when FeCl₃ concentration was from 10 mM to 100 mM, respectively. At 100 mM FeCl₃, resultant film expressed 3.6×10^1 S/cm electrical conductivity on the solution side of the film. Also, electrical conductivity was observed depending on the preparation conditions like immersion time, and immersion temperature in addition with FeCl₃ concentration.

In Chapter 3, PANI-CA fiber was prepared using wet cast method, when

ANI-CA solution was used. In the method proposed, The PANI-CA fiber obtained by the short reaction time has dual layer hollow fiber structure. The outer layer has formed by the densely PANI, and the inner layer has formed by the porous CA scaffold. When the reaction time was extended, center of the PANI-CA fiber also formed densely PANI. The electrochemical properties were measured using cyclic voltammetry were changed the oxidation and reduction potential peak position that depending on the preparation conditions like reaction time of ANI-CA solution with 1M HCl-APS solution.

In conclusion, this thesis is specially characterized in following originalities in new phase inversion method of preparation of conductive composite materials. Features of this method, the monomers of conductive polymer could be used as a solvent for dissolving the scaffold material, and oxidation polymerization of conductive polymer was observed to proceed simultaneously with the coagulation of scaffold material for formation of composite material by contained polymerization initiator into the coagulation water in advance. Thus, it is possible to prepare the composite material easily and simply. In addition, it could be control the shapes of composite materials. ; 1) PPy-CA composite films were prepared using wet cast method, when Py-CA solution was used. The resultant composite films were characterized, showing good film fabrication and electrical conductivity of around 6.9×10^{-4} to 3.6×10^1 S/cm. 2) PANI-CA fibers were founded to show dual layers structure, when wet technique was applied for using syringe injection to acidic water in the ANI polymerization process.

I expect that these techniques of preparing composite material could become interest and attractive in future industrial applications.

List of publications

Duel layer hollow fiber of polyaniline-cellulose acetate prepared with simple wet technique of chemical polymerization of aniline_

Tsubasa Takano, Motohiro Tagaya, Takaomi Kobayashi

Polymer Bulletin, Accepted.

Conductive Polypyrrole Composite Films Prepared Using Wet Cast Technique with a Pyrrole-Cellulose Acetate Solution

Tsubasa Takano, Aya Mikazuki, Takaomi Kobayashi

Polymer Engineering & Science Accepted.

Presentation in International Conference and Symposium

1. **The 1st International GIGAKU Conference in Nagaoka**, Nagaoka, Japan,
“CONDUCTIVE POLYPYRROLE COMPOSITE FILMS PREPARED
WITH WET CAST TECHNIQUE” Tsubasa Takano, Aya Mikazuki, Takaomi
Kobayashi (February, 2012)