

Fabrication and Properties of Solution-Cast Polyaniline/Carboxymethylchitin Blend Films

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ABSTRACT: Blend films consisting of polyaniline in emeraldine base form (PANI EB) dispersed in partially cross-linked carboxymethylchitin (CM-chitin) were prepared by solution casting, and characterized for their physical, thermal, and electrical properties. Homogeneous and mechanically robust blend films were obtained having PANI EB contents up to 50 wt % in the CM-chitin matrix. FTIR spectra confirm intimate mixing of the two blend components. The thermal stability of the blend films increased with increase of PANI EB content, suggesting the formation of an intermolecular interaction, such as hydrogen bonding, between PANI EB and CM-chitin chains. The addition of PANI EB into the pure CM-chitin film resulted

in a decrease in electrical conductivity of the films owing to disruption of ionic conduction of the CM-chitin structure. After doping the blend films by immersion in HCl solution, the electrical conductivity of the HCl-doped films increased with increase of the PANI EB content to a maximum value of the order of 10^{-3} S/cm at 50 wt % PANI EB content. The electrical conductivity of the blend films was also dependent on the HCl concentration as well as on the type of acid dopant. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1626–1634, 2010

Key words: electrical conductivity; polyaniline; carboxymethylchitin; blend films

INTRODUCTION

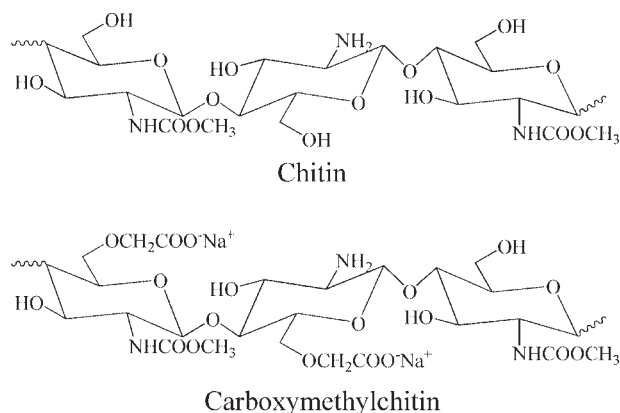
Currently, the development of conductive polymers is of interest with the expectation to replace conventional metals and semiconductors owing to their light weight, processability at relatively low operating temperature, and ease of conductivity control.¹ In the last decade, many types of conductive polymers including polyacetylene, polypyrrole, polythiophene, poly(*para*-phenylene), and polyaniline have been explored. Among these, polyaniline (PANI) has been most extensively studied, due to its facile synthesis by chemical or electrochemical methods, low monomer cost, good environmental stability, and easy conductivity control by changing the oxidation or protonation state.^{2–4} PANI has been widely applied in antistatic coatings,^{5,6} metal anticorrosion coatings,^{7,8} gas separations,⁹ artificial muscles,^{10,11} and chemical sensors.¹² Additionally, PANI was

reported to be biocompatible with cells.¹³ Thus, PANI has been considered as a candidate material for use in biomedical and pharmaceutical applications.^{14–19} Nevertheless, a low ability to process pure PANI into products with high mechanical strength, especially in the form of thin films and fibers, hinders realizing such applications. Therefore, much attention has been given to solve this drawback, and polymer blends or composites have been explored as a potential method to improve the processability and mechanical properties of the PANI, while preserving its inherent optical and electrical properties.^{20,21}

Polymer blends or composites based on PANI are normally obtained by an *in situ* polymerization of aniline in the presence of insulating polymer matrixes, such as poly(vinyl alcohol),²² poly(ethylene terephthalate),²³ and polystyrene,²⁴ or blending soluble or processable PANI with other polymer matrixes in a solution or a molten state.²⁵ Because of the ease of processing as well as avoiding the possibility to form undesirable side-reactions, the solution processing method is considered to be more effective, especially when a common solvent system can be found for both PANI and the polymer matrix. *N*-methyl-2-pyrrolidone (NMP), a well known solvent for PANI in its insulating, emeraldine base form (PANI EB), can dissolve certain polymers, such as

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Scheme 1 Chemical structures of chitin and carboxymethylchitin.

polyimide,²⁶ lignin,²⁷ and various copolymeric acids,²⁸ and also is miscible with certain other solvents, such as distilled water,²⁹ tetrahydrofuran,³⁰ and dimethyl formamide.^{28,30} Thus, NMP is an attractive candidate to prepare homogeneous blends of PANI via solution processing.

Recently, blends between PANI and naturally-occurring biopolymers, such as chitin and chitosan, have generated research interest for biomedical and pharmaceutical applications because of their biocompatibility and biodegradability.³¹ In particular, several studies have been reported on blends between PANI and chitosan^{32–34} but, to our best knowledge, few studies have focused on blends of PANI and chitin. This is likely due to the brittleness of the resulting products which limits their use in various applications. To improve the utilization of chitin, however, chemical modification of chitin can be performed.

Carboxymethylchitin (CM-chitin) is obtained via the carboxymethylation reaction of chitin powder with monochloroacetic acid under basic conditions (Scheme 1). This creates a new material which is soluble in water, has good film- or fiber-forming ability, high mechanical strength, biodegradability, and biocompatibility with cells.^{31,35,36} By cross-linking with glutaraldehyde, CM-chitin exhibits hydrogel behavior that is capable of undergoing chemical and/or physical transitions in response to external stimuli such as pH,^{37,38} temperature,^{39,40} ionic strength,⁴¹ radiation,⁴² and electrical potential.⁴³ Therefore, CM-chitin hydrogels can potentially be used in applications such as soft actuators, biosensors, and controlled drug release. Unfortunately, the major drawbacks to using hydrogels in such applications are slow response time, attributed to the slow diffusion rate of activating species (such as H⁺ ions, analyzates, drug molecules etc.) and of water into and out of the hydrogels, as well as the difficulty to control the processing of responses.³² These draw-

backs are potentially solved by the incorporation of PANI particles into the hydrogel matrixes. Because of the relatively fast response of PANI upon exposure to an electrochemical potential, the presence of PANI may improve the response time of the hydrogels. In addition, whereas PANI alone exhibits a small magnitude of response, a blend of PANI with CM-chitin may generate an interesting electroactive hydrogel that combines the dual advantages of PANI and hydrogel, i.e. fast response and large magnitude of response (i.e. swelling strain), respectively; while the processing of the response can be controlled by the application of an electrochemical potential.

The aims of this work are to prepare and characterize the physical, thermal, and electrical properties of PANI EB/CM-chitin blend films. The effects of blend composition and doping conditions including HCl concentration and types of acid dopant on electrical conductivity of the obtained blend films were also investigated.

EXPERIMENTAL

Materials

Chitin with degree of deacetylation (DD) equal to 0.20, measured by the method of Baxter et al.,⁴⁴ was prepared from shrimp shell (*Penaeus merguensis*), kindly supplied by Surapon Food, Thailand.

The aniline monomer was purchased from Merck and was purified by distillation under reduced pressure. AR grade ammoniumperoxodisulfate (APS) and NMP were purchased from Merck. AR grade *p*-toluene sulfonic acid was purchased from Aldrich. AR grade glutaraldehyde, monochloroacetic acid, hydrochloric acid, nitric acid, sulfuric acid, formic acid, acetic acid, ammonia solution, acetone, ethanol, and methanol were purchased from Labscan and used as received.

Preparation of CM-chitin

CM-chitin ($M_w = 1.1 \times 10^6$ g/mole determined by GPC) was obtained using the method described by Wongpanit et al.⁴⁵ In a typical procedure, CM-chitin was prepared by suspending 5 g of chitin powder in 100 g of 42% w/w NaOH. The suspension was stored under reduced pressure for 30 min, and then pre-cooled below 5°C for 10 min with vigorous stirring. Next, 160 g of crushed ice was added to the suspension and the mixture was stirred below 5°C for 30 min. A pre-cooled solution containing 27 g monochloroacetic acid in 70 mL of 14% w/w NaOH was slowly added into the mixture solution with vigorous stirring. The reaction was maintained at 0–5°C for 30 min. After storing at room temperature overnight,

the mixture was neutralized with glacial acetic acid subsequently dialyzed in distilled water for 2 day. The dialysate was centrifuged to remove insoluble material and then precipitated in acetone. A white precipitate was washed with ethanol, filtered, and dried in vacuum at room temperature.

Synthesis of polyaniline in emeraldine base form (PANI EB)

PANI EB ($M_v = 61,282$ g/mole determined by using the method of Yang et al.⁴⁶) was synthesized according to the method described by Cao et al.⁴⁷ In a typical procedure, 20.4 g of freshly distilled aniline monomer was dissolved in 230 mL of 1.5 M HCl and the solution was cooled to below 5°C. A pre-cooled solution containing 25 g $\text{NH}_4(\text{S}_2\text{O}_8)$ in 250 mL of 1.5 M HCl was slowly added into the monomer solution for 1 h with vigorous stirring. The reaction temperature was maintained at 0–5°C for 4 h. A dark green precipitate was recovered from the reaction mixture by filtering and then washed thoroughly with a mixture of distilled water and methanol in a ratio of 80 : 20 (water to methanol) until the washing liquid was completely colorless and neutral. The precipitated product was treated with 300 mL of 3% ammonia solution at room temperature for 2 h. Upon filtering, washing with distilled water, and drying under dynamic vacuum at ambient temperature for 48 h, the dark blue powder of PANI EB was obtained.

Preparation of PANI EB/CM-chitin blend films

The PANI EB was dissolved in NMP to obtain a 1 wt % PANI EB/NMP solution. A 1 wt % solution of CM-chitin was obtained by dissolving CM-chitin powder in distilled water with vigorous stirring. Glutaraldehyde (0.005 wt %), used as the cross-linking agent for CM-chitin, was added into the CM-chitin solution and the mixture was magnetically stirred overnight. The PANI EB/NMP solution was added to the glutaraldehyde-treated CM-chitin solution in different proportions and the mixture was stirred for 12 h at room temperature. The resulting solutions were cast onto a stainless steel mold and dried at 55°C for 12 h. Finally, the blend films were removed from the mold and stored in a desiccator before use.

To study the electrical properties of the HCl-doped PANI EB/CM-chitin blend films, films with different PANI EB contents were immersed in 0.5 M HCl solution — prepared by mixing an appropriate amount of concentrated HCl into a 50 : 50 mixture of methanol and distilled water. The methanol/distilled water mixture was used instead of pure distilled water to reduce the solubility of CM-chitin.

Subsequently, the HCl-doped blend films were placed between two sheets of the filter paper and dried under vacuum at ambient temperature for 48 h.

Characterization methods

The UV-visible spectrum of the synthesized PANI EB in NMP was obtained from a Shimadzu UV-Visible spectrometer model 2550 in the wavelength range 200–800 nm.

FTIR spectra of the samples were recorded using a Thermo Nicolet Nexus 670 FTIR spectrometer in the absorbance mode with 32 scans at a resolution of 4 cm^{-1} . Spectra of frequency range of 4000–400 cm^{-1} were measured using a deuterated triglycerinesulfate detector (DTGS) with specific detectivity of $1 \times 10^9 \text{ cm} \cdot \text{Hz}^{1/2} \cdot \text{w}^{-1}$.

The morphologies of the samples were investigated using a scanning electron microscope (JOEL, model JSM-5800LV) at 10 or 15 kV after gold sputtering on the samples. The cross-sectional fracture surfaces of the blend films were obtained by cooling in liquid nitrogen followed by breaking the specimens.

Differential scanning calorimetry (Mettler-Toledo DSC 822) of the samples was carried out in the temperature range 30–600°C at a heating rate of 10°C/min under a nitrogen atmosphere.

Thermogravimetric analysis (DuPont Instrument TGA 5.1, model 2950) was used to evaluate the thermal stability and to determine the decomposition temperature of the samples. The temperature range studied was 30–600°C at a heating rate of 10°C/min under a nitrogen atmosphere.

The electrical conductivities of the samples were measured at ambient temperature using a custom-made two-point probe with an electrometer/high resistance meter (Keithley, model 7517A). The measured electrical conductivity was calculated from the slope of the I-V plot and was averaged based on three samples.

RESULTS AND DISCUSSION

UV-visible spectrum

UV-visible spectroscopy was used to investigate the electronic state of the soluble-fraction of the synthesized PANI EB in NMP (data not shown). The PANI EB shows two absorption peaks at ~320 and 620 nm which can be assigned to the π - π^* transition of the benzenoid ring and the exciton absorption of the quinoid ring, respectively.² The integral areas under these two peaks specify the concentration of the imine and the amine structural units, as expected for the emeraldine oxidation state of PANI EB.²⁶

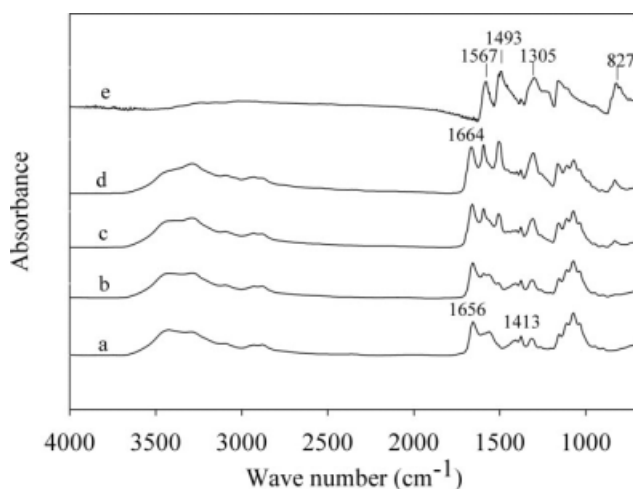


Figure 1 FTIR spectra of (a) CM-chitin; PANI EB/CM-chitin blend films containing (b) 10 wt % PANI EB, (c) 30 wt % PANI EB, and (d) 50 wt % PANI EB, and (e) PANI EB powder.

FTIR spectra

FTIR spectra were used to characterize the chemical composition of CM-chitin, PANI EB, and their blend films, as shown in Figure 1. In the spectrum of the pure CM-chitin [Fig. 1(a)], the characteristic peaks of O—H and N—H stretching at 3200–3500 cm^{-1} , carbonyl stretching of the acetamido group at 1656 cm^{-1} , and asymmetric and symmetric stretching of the carboxylate anion at 1563 cm^{-1} and 1413 cm^{-1} were observed, consistent with previous results.⁴⁵ Likewise, characteristic peaks of PANI EB were observed [Fig. 1(e)] at 1567 cm^{-1} , 1493 cm^{-1} , 1305 cm^{-1} , and 827 cm^{-1} corresponding to C=N stretch-

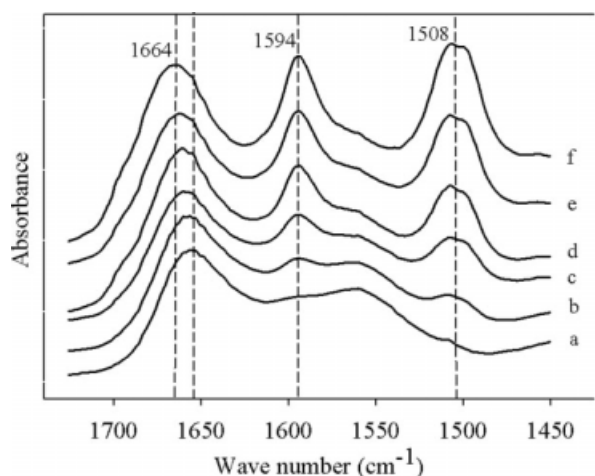


Figure 2 Expanded view of the FTIR spectra shown in Figure 1 in the range 1450–1725 cm^{-1} to illustrate the shift of the carbonyl stretching band from 1656 cm^{-1} in pure CM-chitin to 1664 cm^{-1} in the 50 : 50 CM-chitin/PANI EB blend: (a) CM-chitin; PANI EB/CM-chitin blend films containing, (b) 10 wt % PANI EB, (c) 20 wt % PANI EB, (d) 30 wt % PANI EB, (e) 40 wt % PANI EB, and (f) 50 wt % PANI EB.

ing of quinoid structure, the C—N stretching of benzenoid structure, the C—H bending (conjugated bond), and the vibration of symmetrically substituted benzene, respectively.⁴⁸ In the spectra of the PANI EB/CM-chitin blend films [Fig. 1(b–d)], characteristic peaks of both CM-chitin and PANI EB were observed in all spectra and, moreover, the characteristic peaks of PANI EB became increasingly dominant with increasing PANI EB content. Additionally, no new peaks were observed in these blends, indicating that no new chemical bonds were formed between the CM-chitin and the PANI EB structure. However, as illustrated in Figure 2, it is clear that the characteristic peak due to carbonyl stretching of CM-chitin (1656 cm^{-1}) shifts to a significantly higher wave number (1664 cm^{-1}) in the blend film with increase of PANI EB content up to 50 wt % [see Fig. 1(d)]. This strongly implies intimate mixing between the two blend components, and possibly that an interaction occurs between PANI EB and CM-chitin, for example, hydrogen bonding between carbonyl and hydroxyl groups in CM-chitin may be replaced by bonding between carbonyl groups of CM-chitin and less electropositive amine and imine groups of PANI EB. A similar effect has been reported in the IR spectra of blends of polyaniline with polyurethane.⁴⁹

Morphology

The visible characteristic of the PANI EB/CM-chitin blend films is that of a homogeneous dark blue color, the color of PANI EB particles. Scanning electron microscopy (SEM) was used to investigate the morphology of the synthesized PANI EB particles (Fig. 3) as well as the prepared PANI EB/CM-chitin blend films. Pure CM-chitin film shows a smooth surface, whereas the roughness of the surface of the

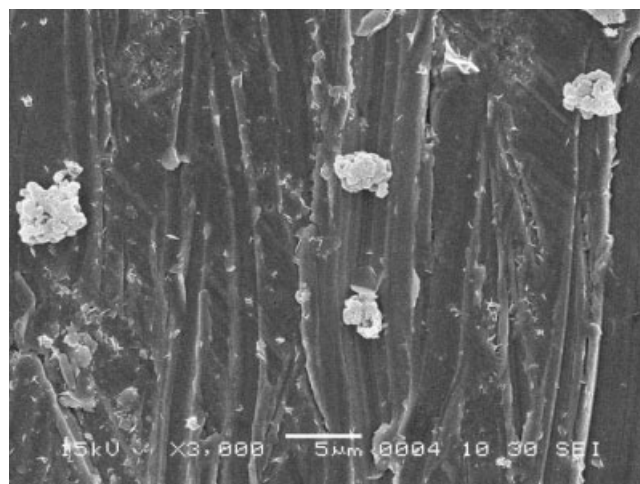


Figure 3 SEM image of the synthesized PANI EB particles.

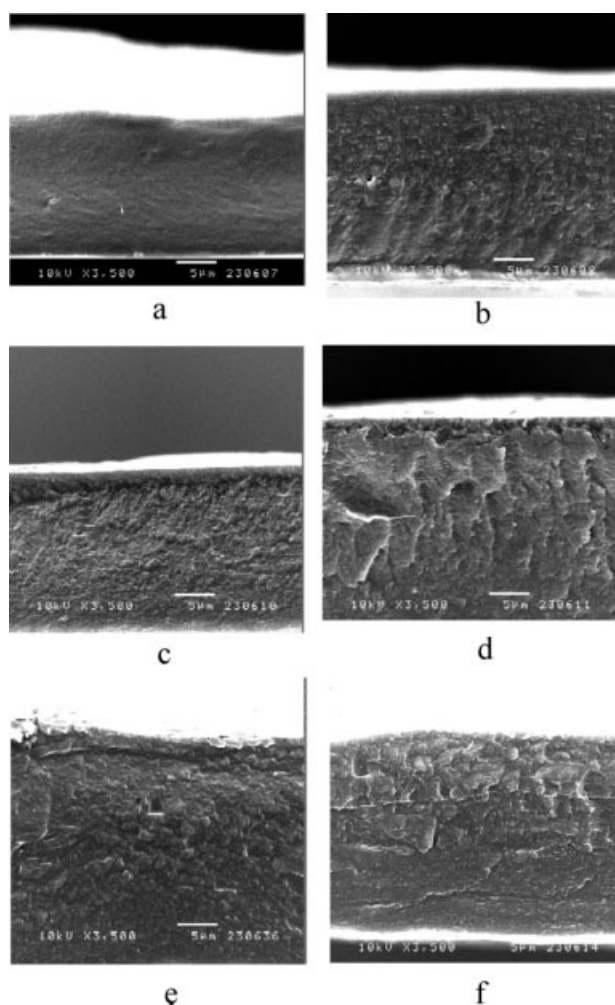


Figure 4 Cross-sectional morphology of (a) CM-chitin films and PANI EB/CM-chitin blend films containing (b) 10 wt % PANI EB, (c) 20 wt % PANI EB, (d) 30 wt % PANI EB, (e) 40 wt % PANI EB, and (f) 50 wt % PANI EB.

blend films increases somewhat, with increasing the PANI EB content in the CM-chitin matrix (data not shown). To explore the distribution of PANI EB particles throughout the blend films, the cross-section of freeze-fractured films with different PANI EB contents was imaged by SEM, and compared to that of the pure CM-chitin film, as shown in Figure 4. For the pure CM-chitin film, a smooth fracture surface was observed [Fig. 4(a)]. With the addition of different PANI EB contents (10, 20, 30, 40, 50 wt %) into the CM-chitin matrix, the roughness of the fracture surface of the blend films increased as shown in Figure 4(b–f). However, localized aggregation or agglomeration of the PANI EB particles could not be distinguished throughout the blend films. This suggests that a homogeneous blend is formed between the PANI EB and the CM-chitin matrix. This homogeneity can be explained in that an intermolecular interaction, such as hydrogen bonding, between the PANI EB and CM-chitin molecules combined with

the small sizes of NMP-soluble PANI EB particles promotes a high dispersion efficiency and homogeneous incorporation of the PANI EB particles into the CM-chitin matrix during the blending process.⁵⁰ In addition, the present result can be contrasted with our previous investigation of the blend between PANI EB and a chitosan with a DD of 0.80.³³ It was reported that partial aggregation of PANI EB particles in chitosan matrix occurred at 50 wt % PANI EB contents. Therefore, our present finding implies better compatibility between the PANI EB particles and the CM-chitin matrix, compared to the chitosan matrix. However, the precise source of the difference in miscibility of these two blending systems remains unclear. It seems likely that various parameters, such as the charge of the polymer matrixes (i.e. negatively-charged CM-chitin versus positively-charged chitosan), the DD, and the ionic strength, will influence the dispersion efficiency of PANI EB in the blends. Therefore, future studies are planned to gain more insight into the effects of these parameters.

Differential scanning calorimetry (DSC)

DSC thermograms of CM-chitin, PANI EB, and their blend films are shown in Figure 5. Pure CM-chitin exhibits an endothermic peak at $\sim 80^{\circ}\text{C}$ and an exothermic peak at 283°C [Fig. 5(a)]. These peaks correspond to the loss of water and the degradation of the CM-chitin chains, respectively.⁵¹ In contrast, PANI EB shows an endothermic peak at around 120°C followed by two broad exothermic peaks at around $200\text{--}400^{\circ}\text{C}$, [Fig. 5(g)] which have been identified as due to the elimination of water, and

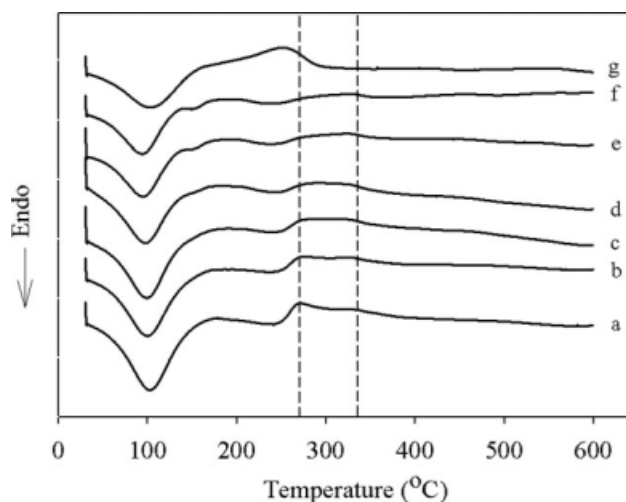


Figure 5 DSC thermograms of (a) CM-chitin; PANI EB/CM-chitin blend films containing (b) 10 wt % PANI EB, (c) 20 wt % PANI EB, (d) 30 wt % PANI EB, (e) 40 wt % PANI EB, and (f) 50 wt % PANI EB; and (g) PANI EB powder.

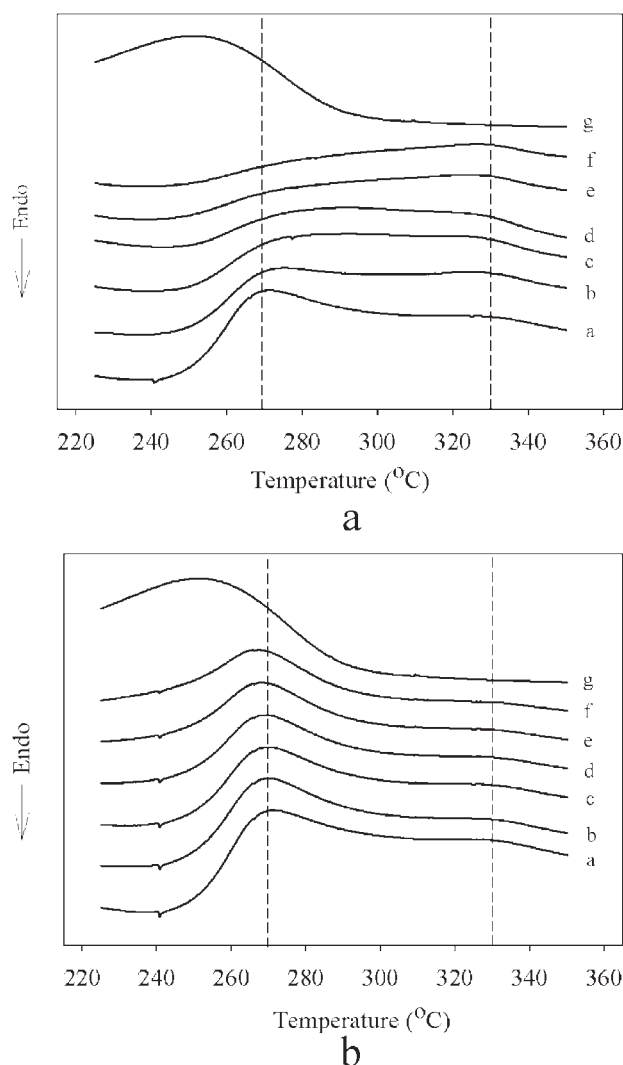


Figure 6 (a) Expanded view of the DSC thermograms shown in Figure 5, (b) simulated DSC thermograms of CM-chitin, PANI EB and their blends based on weighted average of the thermograms of the pure constituents.

interchain cross-linking of PANI EB.⁵² A third peak observed at 500°C in previous studies, due to degradation of the PANI EB structure,⁵³ was not observed in our DSC experiments. Apparently, this peak was too broad to be resolved in the samples studied. For the PANI EB/CM-chitin blend films [Fig. 5(b–f)], an apparent increase in the degradation temperature of the pure CM-chitin film from 283°C to ~330°C in the blend was observed with increasing of the PANI EB content in the CM-chitin matrix up to 50 wt %. This is made more evident in Figure 6(a), which highlights the region in the DSC thermograms from 225 to 350°C. In Figure 6(b), we show a crude simulation of what might be obtained, if the blend thermograms were a weighted average of those of the pure constituents. Comparing Figure 6(a,b), we interpret our results as further support for the presence of an intermolecular interaction between the

PANI EB and the CM-chitin chains.³³ Apparently, the interaction diminishes the cross-linking reaction observed in pure PANI, and also improves the thermal stability of the CM-chitin, so that most of it degrades at a higher temperature. With increase of the PANI EB content, the number of amine and imine groups available to participate in hydrogen bonding with the CM-chitin structure increases, which may explain the improved thermal stability of the blends.

Thermogravimetric analysis (TGA)

Thermogravimetric behaviors of CM-chitin, PANI EB, and their blend films were examined, as shown in Figure 7. PANI EB shows two discrete weight losses at ~80°C and 500°C [Fig. 7(g)] assigned to the evaporation of water and degradation of the PANI EB structure, respectively. In the case of pure CM-chitin, two discrete weight losses at ~80°C and 283°C [Fig. 7(a)] reflect the loss of water and the degradation of the CM-chitin chains, respectively. Thus, consistent with the DSC results, the CM-chitin chains degrade before the PANI EB structure. The blend films exhibit three discrete weight losses [Fig. 7(b–f)], representing the combined thermal behaviors of the PANI EB and the CM-chitin, at around 80°C, 290°C, and 500°C, owing to the evaporation of water, the degradation of the CM-chitin chains, and the degradation of the PANI EB structure, respectively. However, it was confirmed that the degradation temperature of CM-chitin (at 283°C) increases, substantially, on increasing the PANI EB content in the blend films up to 50 wt %, and, moreover, the residual mass of the blend films is higher than that

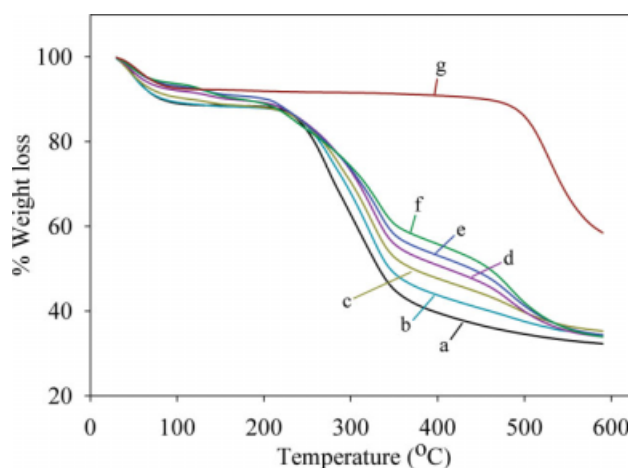


Figure 7 TGA thermograms of (a) CM-chitin; PANI EB/CM-chitin blend films containing, (b) 10 wt % PANI EB, (c) 20 wt % PANI EB, (d) 30 wt % PANI EB, (e) 40 wt % PANI EB, (f) 50 wt % PANI EB, and (g) PANI EB powder. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

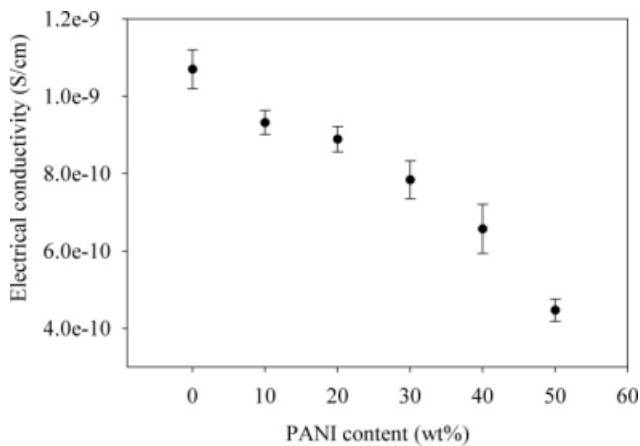


Figure 8 Electrical conductivity of undoped PANI EB/CM-chitin blend films as a function of PANI content.

of the pure CM-chitin. Thus, consistent with the DSC thermograms, the TGA data support the existence of a favorable intermolecular interaction, indicating compatibility between the PANI EB and the CM-chitin chains.

Electrical property

The electrical conductivities of both undoped and HCl-doped PANI EB/CM-chitin blend films as a function of the PANI EB content is presented in Figures 8 and 9, respectively. From Figure 8, it was found that the electrical conductivity of the pure CM-chitin film is 1.07×10^{-9} S/cm, whereas the pelletized PANI EB, the insulating form of PANI, exhibits an electrical conductivity of 3.72×10^{-11} S/cm. After adding the PANI EB into pure CM-chitin in amounts from 10 to 50 wt %, the electrical conductivity of the blend films gradually decreases from 9.32×10^{-10} S/cm to 4.47×10^{-10} S/cm,

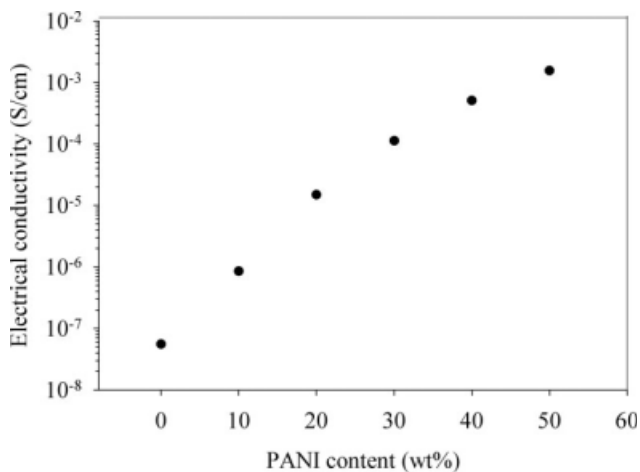


Figure 9 Electrical conductivity of PANI EB/CM-chitin blend films after doping with 0.5 M HCl for 2 h as a function of PANI content.

respectively. The decrease is apparently due to a disruption of ionic conduction of the CM-chitin chains when the insulating PANI EB is added.³³ CM-chitin film shows a superior electrical conductivity compared to the PANI EB/CM-chitin blend films due to its large number of high polarity groups, viz. amino ($-\text{NH}_2$), hydroxy ($-\text{OH}$), and carboxymethylated ions ($-\text{COO}^-\text{Na}^+$), which generate ionic conduction. An ionic conduction mechanism in polyelectrolytes such as CM-chitin has been described by Shriver et al.⁵⁴ who reported that ionic conduction occurs via dissociation of electrostatic bonds between counterions and the polyelectrolyte chain, and formation of new bonds with other groups. This causes motion of the counterions along the polyelectrolyte chain resulting in the electrical conduction. On addition of PANI EB into the CM-chitin matrix, the ionic mobility between the polar groups of CM-chitin and their counterions is disrupted by the presence of the insulating PANI EB particles, resulting in a decrease of electrical conductivity of the blend films. In contrast, after doping the pure CM-chitin film as well as the PANI EB/CM-chitin blend films by immersion in 0.5 M HCl for 2 h, the electrical conductivity of all film samples significantly increases. The increasing of electrical conductivity of the HCl-doped CM-chitin film (up to 5.59×10^{-8} S/cm) is attributed to an increase in polarity of the CM-chitin functional groups, after treatment with HCl solution. In the case of the HCl-doped PANI EB/CM-chitin blend films, in contrast, the increase of electrical conductivity (up to the order of 10^{-3} S/cm at 50 wt % PANI EB content) mainly results from the conversion of the incorporated PANI EB particles in the CM-chitin matrix to the emeraldine salt form (PANI ES) of highly π -conjugated PANI ES.⁵⁵ Additionally, it was found that the electrical conductivity of the HCl-doped PANI EB/CM-chitin blend films (PANI ES/

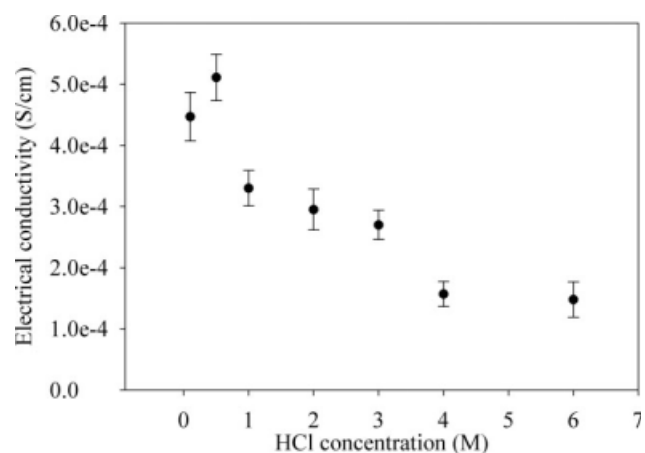


Figure 10 Electrical conductivity of PANI EB/CM-chitin blend films containing 40 wt % PANI EB content after doping with different HCl concentrations for 2 h.

TABLE I
Electrical Conductivity of PANI EB/CM-Chitin Blend Films Containing 40 wt % PANI Contents Doped with 0.5 M of Different Types of Acid for 2 h

Type of acid	Pk _a	Electrical conductivity of undoped PANI/CM-chitin (S/cm)	Electrical conductivity of doped PANI/CM-chitin (S/cm)
Hydrochloric acid	-6.1	$6.57 \times 10^{-10} \pm 6.34 \times 10^{-11}$	$5.11 \times 10^{-4} \pm 3.80 \times 10^{-5}$
Sulfuric acid	-3	$6.57 \times 10^{-10} \pm 6.34 \times 10^{-11}$	$7.05 \times 10^{-4} \pm 4.30 \times 10^{-5}$
Nitric acid	-1	$6.57 \times 10^{-10} \pm 6.34 \times 10^{-11}$	$3.43 \times 10^{-4} \pm 3.75 \times 10^{-5}$
<i>p</i> -toluene sulfonic acid	-2.8	$6.57 \times 10^{-10} \pm 6.34 \times 10^{-11}$	$3.49 \times 10^{-4} \pm 3.34 \times 10^{-5}$
Formic acid	3.75	$6.57 \times 10^{-10} \pm 6.34 \times 10^{-11}$	$2.24 \times 10^{-6} \pm 2.48 \times 10^{-7}$
Acetic acid	4.7	$6.57 \times 10^{-10} \pm 6.34 \times 10^{-11}$	$3.06 \times 10^{-6} \pm 1.52 \times 10^{-7}$

CM-chitin blend films) significantly increases from 8.54×10^{-7} S/cm to 1.56×10^{-3} S/cm with increase of PANI EB contents from 10 wt % to 50 wt %, respectively, as seen in Figure 9. Finally, it should be noted that PANI EB/CM-chitin blend films with PANI EB contents higher than 50 wt % could not be fabricated due to the excessive film brittleness.

To investigate the effect of HCl concentration on electrical conductivity of the blend films, Figure 10 shows the electrical conductivity of the HCl-doped PANI EB/CM-chitin blend films loaded with 40 wt % PANI EB contents after doping with different HCl concentrations for 2 h. From this result, it was found that the electrical conductivity of the blend films does not significantly change when increasing the HCl concentration from 0.1 M (4.47×10^{-4} S/cm) to 0.5 M (5.11×10^{-4} S/cm). However, on further increasing the HCl concentration up to 6 M, the electrical conductivity of the blend films gradually decreases, to a value of 1.48×10^{-4} S/cm. This result is attributed to over-protonation of PANI ES (the protonated form of PANI EB) chains causing a decrease in the delocalization length of the PANI ES. Additionally, it should be noted that the higher HCl concentration may lead to the degradation of the CM-chitin chains, and hence result in inferior mechanical strength of the resulting blend films.^{56,57} Moreover, it was further established that the electrical conductivity of the blend films is influenced by the type of acid dopant used, as shown in Table I. The results suggest that a greater acid strength, e.g., H₂SO₄, HCl, *p*-toluene sulfonic acid, and HNO₃, compared to a lower acid strength, such as CH₃COOH and HCOOH, results in a superior electrical conductivity. This is likely due to a greater degree of protonation of the imine group of PANI ES.

CONCLUSION

PANI EB/CM-chitin blend films can be easily fabricated by solution casting, producing smooth, flexible, and mechanically robust materials. SEM observation reveals a homogeneous blend film morphology, with increase of the PANI EB content

up to 50 wt %. FTIR spectra of the blend films confirm the presence of PANI EB particles in the CM-chitin matrix and further indicate the presence of an intimate mixing between the CM-chitin and the PANI EB. TGA and DSC thermograms evidence an improvement in thermal stability of the blend films with increased incorporation of PANI EB into the CM-chitin matrix. Together with the FTIR evidence, this suggests a compatibilizing interaction between CM-chitin and PANI EB. On the addition of PANI EB into the CM-chitin, a decrease in electrical conductivity of the blend films occurs, attributed to the disruption of the ionic conduction of the CM-chitin by the presence of the insulating PANI EB. After doping the blend films by immersion in HCl solution, the electrical conductivity of the HCl-doped films increased with increasing PANI EB content. Moreover, we demonstrated that the magnitude of the electrical conductivity of the blend films can be manipulated by varying the doping conditions such as HCl concentration and type of acid dopant. Despite their relatively poor electrical conductivity level (of the order of 10^{-3} S/cm for the 50 wt % PANI loaded CM-chitin blend film) compared to that of conventional metals ($\geq 10^2$ S/cm), it is clear that the blend films, which combine the electroactive property of the PANI with the hydrogel property of the CM-chitin, are promising materials for diverse applications, such as artificial muscles, biosensors, and drug controlled release.

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