Synthesis and Characteristics of a Semi-Interpenetrating Polymer Network Based on Chitosan/Polyaniline Under Different pH Conditions

Seon Jeong Kim,[1] Su Ryon Shin,[1] Geoffrey M. Spinks,[2] In Young Kim[1] Sun I. Kim[1]

[1]*Department of Biomedical Engineering, Hanyang University, Seoul, Korea*
[2]*Intelligent Polymer Research Institute, University of Wollongong, NSW, Australia*

ABSTRACT: Chitosan/polyaniline (PANi) semi-interpenetrating network (semi-IPN) polymers were prepared under the condition of HCl aqueous solution (pH < 1). The structure and half oxidation state of emeraldine base PANi, adjusted to pH < 1, underwent changes of structure and electrical properties. Changes of structural properties were investigated using FTIR spectroscopy, solid-state ^{13}C-NMR, and wide-angle X-ray diffraction. Spectroscopic studies revealed that the PANi was converted to its pH-switched emeraldine salt form. The surface conductivity of the semi-IPN depended on the chitosan/PANi weight ratio and the pH condition. The conductivity of the semi-IPNs increased with increasing PANi content with adjusted pH < 1. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 867–873, 2005

Key words: chitosan; polyaniline; conducting polymers; pH condition; interpenetrating networks (IPN)

INTRODUCTION

Polyaniline (PANi) is an important air-stable electrically conducting polymer and has been studied extensively.[1,2] It has appeared as one of most promising organic conducting polymers because of its high thermal and chemical stability, electrical and optical properties, facile redox and pH-switching behavior, and low cost.[3–5] An important characteristic of PANi is an interesting material that undergoes two distinct redox processes as well as pH switching between unprotonated and protonated states (Fig. 1).[6] PANi can be rapidly "switched" by the addition of acids and bases that protonate and unprotonate the base sites within the polymer. This leads to the dependency of the polymer states, and thus the reactions, upon the pH of the solution. In solutions of pH > 4, PANi loses it electroactivity entirely because the emeraldine salt (ES), the only conducting form of the polymer, is dedoped to form the insulator emeraldine base (EB).[7–9] However, PANi, like many other conductive polymers, is insoluble in common solvents and infusible because it decomposes before melting.[10–12] Moreover, PANi has rather poor mechanical and general physical properties. The potential for the use of PANi in a wide range of applications has already been demonstrated. Among the most numerous applications of PANi are its uses in rechargeable batteries,[13] corrosion protection of metals,[14] gas-separation membranes,[15] and molecular sensors.[16]

PANi has four different forms, in which its repeating units contain two different entities at different relative weights: fully reduced leucoemeraldine base, half-oxidized EB, fully oxidized pernigraniline base,[17] and doped in a protonic acid that is designated ES.[18] Among other forms of PANi, EB is of particular interest because it can be rendered conductive by protonation with a sufficiently strong protonic acid such as hydrochloric acid (HCl).[19,20] However, the conductivity of the protonated PANi depends on the type of doping acid and solvent used in the protonating medium and on the processing condition. In the recent literature, simple acid–base interactions between the dopant and PANi are called primary doping,[21] with respect to the characterization of PANi-enhanced electrical conductivity by simple change of pH condition.

Chitosan, a high molecular weight carbohydrate polymer, is manufactured from chitin,[22,23] which owes it cationic nature to the free amino groups left by the partial removal of the acetyl groups of chitin. Chitosan appears to be more useful than chitin for biomedical applications and in the dehydrations of aqueous solutions because it has both hydroxyl and amino groups that can be easily modified.[24,25] Chitosan has many useful features, such as hydrophilicity, biocompatibility, and antibacterial properties.[26]

In general, the composites obtained by incorporating a rigid conducting polymer (such as PANi) into
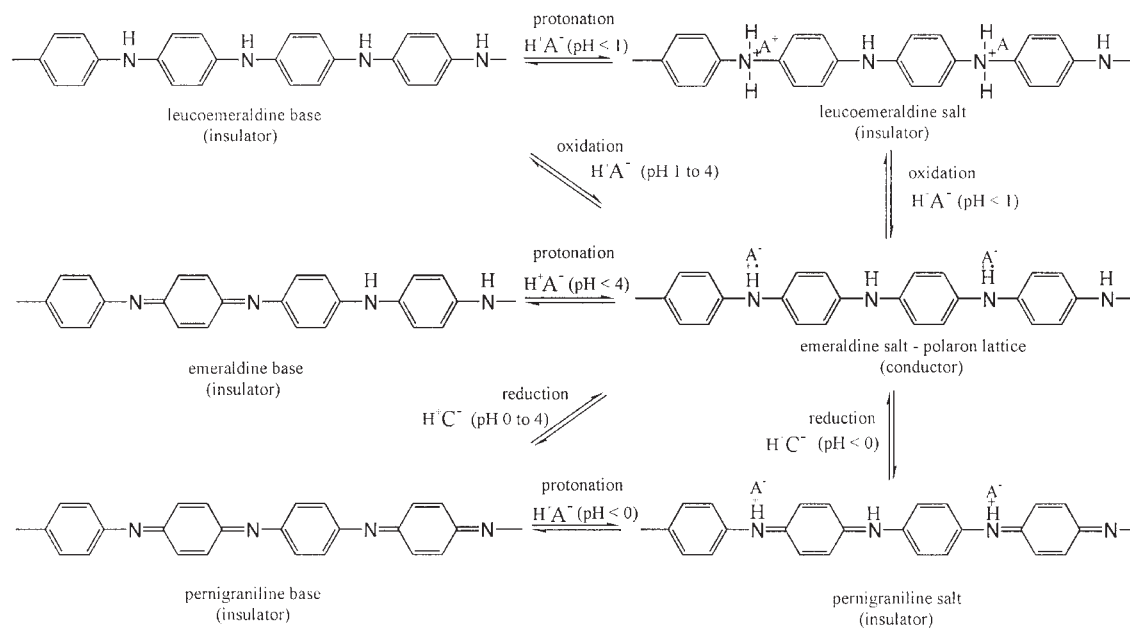
Figure 1 Protonation and redox reactions between the various forms of polyaniline (H^+A^-, H^+C^- is acidic solution).

flexible matrix can combine the good processability of the matrix and the electrical conductivity of the conductive polymer. The approach we have taken to achieve PANi with good mechanical properties and good processibility is to form a semi-interpenetrating polymer network (semi-IPN) in which the main polymer has the requisite properties of ability to form strong films and other forms, chemical stability toward dopants, thermal stability, and insolubility under readily accessible conditions. We selected the chitosan for reasons explained later. Recently, conducting polymers, such as PANi, have been considered for microelectronics applications. The combination of tunable chemical properties with the electronic properties of conducting polymer has also had a tremendous impact on the development of new sensors. The use of conducting polymers in sensors has recently been reviewed.

In this article, we report details of the effect of pH condition on the properties of a PANi/crosslinked chitosan semi-IPN. The FTIR spectrum, solid-state ^{13}C-NMR, and WAXD were used to characterize the structures of the resulting chitosan/PANi semi-IPN. It is expected that, with respect to the surface conductivity of these samples, there is an increase in electrical conductivity when adjusted to pH < 1.

EXPERIMENTAL

Materials

The chitosan (average molecular weight = 2.0×10^5; degree of deacetylation = 76%) was provided from Jakwang Co. (Ansung, Kyonggi, Korea). Glutaralde-

hyde (GA; 25 wt % solution in water) was purchased from Yakuri Chemical Co. (Osaka, Japan). Acetic acid and methanol were supplied by Duksan Pure Chemical Co. Ltd. (Ansan, Korea). PANi EB [average molecular weight = 6.5×10^4 (undoped form, minimum assay 99.5%)], HCl, and NMP (1-methyl-2-pyrrolidone) were purchased from Aldrich Chemical Co. (Milwaukee, WI).

Doping of PANi EB powder

PANi EB powder was doped by immersion in dopant solutions, HCl aqueous solution (pH < 1), for 24 h, followed by drying under dynamic vacuum at room temperature.[27]

Preparation of semi-IPN hydrogels

The chitosan was dissolved completely in 2 wt % acetic acid (the solid content in solution was 2 wt %) for 24 h. PANi was dissolved in NMP (0.5 wt %) and adjusted to acidity of pH < 1 by HCl aqueous solution. An amount of chitosan/PAN mixed solution, adjusted to pH < 1 by HCl aqueous solution, was obtained by mechanical stirring for 24 h. The detailed composition and designation of the chitosan/PANi semi-IPNs are listed in Table II (see below). The mixed solutions were poured into petri dishes and dried in a vacuum oven at 50°C for 48 h. Crosslinking of a sample was carried out by immersing the film in glutaraldehyde solution (methanol : deionized water = 1 : 1, adjusted to pH < 1) at room temperature. The residual NMP in the film and residual material was further
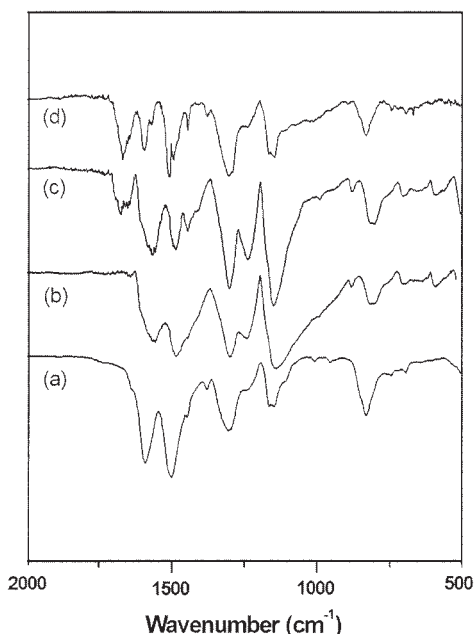
Figure 2 FTIR spectra of (a) PANi EB; (b) PANi doped with HCl; (c) CP-31 semi-IPN, adjusted to pH < 1; and (d) CP-31 semi-IPN, unadjusted.

washed by methanol solution (methanol : deionized water = 1 : 1 adjusted of pH < 1) and dried under vacuum for more than 24 h.

Characterizations

FTIR spectroscopy of the samples was carried out on a Nicolet Model Magna IR 550 spectrometer (Nicolet Instrument Technologies, Madison, WI) for which samples were pelletized with KBr powder. Solid–state ^{13}C-NMR spectra were obtained by using a Varian Unity Inova 300 spectrometer (Varian Associates, Palo Alto, CA), with a solids accessory. Experimental conditions were: ^{13}C (300-MHz frequency); zircon cell (length: 2 cm; internal diameter: 5 mm). Wide-angle X-ray diffraction (WAXD) scans for samples were obtained using a D/MAX Rint 2000 diffractometer model (Rigaku, Tokyo, Japan). Nickel-filtered copper radiation (K_α) was incident on the sample, which was scanned at the rate of 1°/min in the reflection mode over a range of 2θ from 5 to 50. The surface conductivities of chitosan/PANi semi-IPN films were measured using a custom-built dc linear four-point probe apparatus with a CMT-SR1000N sheet resistance measurement system. Under these conditions the surface conductivity σ can be calculated using the following equation[28]:

$$\sigma = \left[\left(\frac{\pi}{\ln 2} \right) t \left(\frac{V}{I} \right) \right]^{-1} \qquad (1)$$

where t is the film thickness, V is the voltage drop across the inner two probes, and I is the current driven through the sample.

RESULTS AND DISCUSSION

The FTIR spectra of PANi EB, doped PANi, and CP-31 semi-IPNs, adjusted to pH < 1 and unadjusted, are shown in Figure 2. The prominent absorption peaks at 1589 and 1500 cm^{-1} are attributed to the quinoid and benzenoid unit stretching modes of EB [curve (a)] and the relative intensity of these two bands gives an indication of the oxidation state of EB. The band at 1164 cm^{-1} is attributed to the quinoid unit stretching mode of EB and the vibrations at 1240 and 1303 cm^{-1} are attributed to C—N stretching and the benzenoid unit stretching mode of EB, respectively. The band at 829 cm^{-1} in the spectrum from EB is from the C—H bending mode of benzenoid unit. The FTIR spectrum of the CP-31 semi-IPN [curve (d)] is similar to the spectrum from the EB form of PANi [curve (a)]. The new absorption peaks of curves (c) and (d) are attributed to the chitosan in semi-IPN.

The doped PANi [curve (b)] causes a slight shift of all bands and a change in intensities of the bands. The characteristic peaks of doped PANi appear in the composite, at 1558, 1484, 1289, 1241, 1117, and 802 cm^{-1}, respectively, and the band at 1117 cm^{-1} is attributed to quinoid unit doped PANi. The FTIR spectrum of the doped PANi with HCl aqueous solution [curve (b)] is similar to that reported previously for doping PANi (PANi emeraldine salt)[29] as well as being very similar to the FTIR spectrum from the CP-31 semi-IPN, adjusted to pH < 1 [curve (c)]. These character-
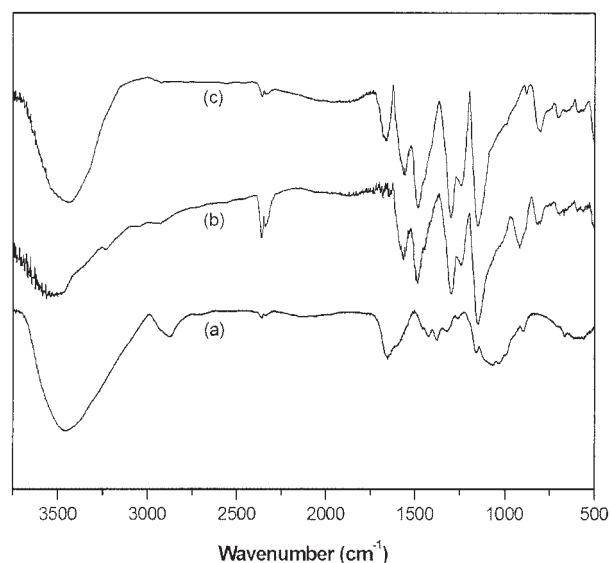

Figure 3 FTIR spectra of (a) chitosan; (b) CP-31 blend, adjusted to pH < 1; and (c) CP-31 semi-IPN, adjusted to pH < 1.
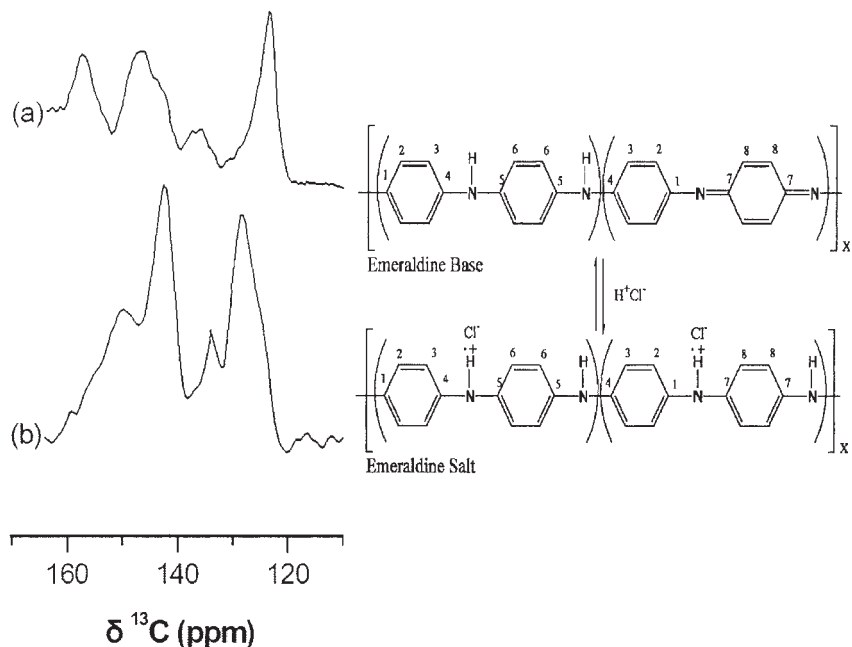
Figure 4   Solid-state ^{13}C-NMR spectrum and structure of (a) PANi EB and (b) PANi doped with HCl.

istic peaks are identical to those of doped PANi and CP-31 semi-IPN, adjusted to pH < 1, prepared in a common condition. On the other hand, PANi in CP-31 semi-IPN, adjusted to pH < 1, shows a structure similar to that of the proposed chemical structure of doped PANi.

Figure 3 shows the FTIR spectra of crosslinked chitosan and CP-31 blend adjusted to pH < 1 and CP-31 semi-IPN adjusted to pH < 1. Characteristic peaks of crosslinked chitosan [curve (a)] are located at 3500– 3450 cm^{-1}, attributed to stretching peaks of the –NH$_2$ and hydroxyl group, 1637 and 1313 cm^{-1} for amide I and amide III, respectively. A peak at 1637 cm^{-1} is attributed to the amide I band caused by the remaining acetamide group in chitosan. In a comparison of the CP-31 semi-IPN [curve (c)] with the CP-31 blend [curve (b)], a new peak appears at 1654 cm^{-1}, attributed to imine bonds (C=N) formed by a crosslinking reaction between amino groups in chitosan and aldehyde groups in glutaraldehyde. The Schiff's reaction of glutaraldehyde with primary amine groups to pro-

duce covalent glutaraldehyde crosslinking has been studied in many circumstances to discover the presence of free amine organic functions in simple or complex inorganic and organic compounds.[25,30]

The ^{13}C-NMR spectra of PANi EB powder and doped PANi powder are shown in Figure 4. Table I shows the assignments for CP-31 blends, adjusted to pH < 1 and unadjusted, PANi EB, and doped PANi, respectively. The spectrum from PANi EB [curve (a)] has peaks near 124 ppm from the protonated benzenoid unit, peaks near 144 ppm from nonprotonated benzenoid unit, a peak at 137 ppm the protonated carbons of the quinoid unit, and a peak at 159 ppm from the imine carbon (unprotonated quinoid unit). The doped PANi [curve (b)] causes a slight shift of all peaks. Doping PANi and CP-31 semi-IPN (adjusted to pH < 1) results in acidic doping in the intensity of the peak from the imine carbons (159 ppm) with a concomitant increase and shifts in the peak from the protonated carbons of the quinoid unit (138 ppm).[31] PANi can be doped by protonic acids, leading to a

TABLE I
Observed Solid-State ^{13}C-NMR Chemical Shifts and Peak Assignments of EB PANi, PANi Adjusted to pH < 1, and Chitosan/PANi Semi-1PNs

Assignment (polyaniline)	PANi EB (ppm)	PANi (adjusted to pH < 1)	CP-31 semi-IPN (unadjusted pH < 1)	CP-31 semi-IPN (adjusted to pH < 1)
C-6, C-2, C-3	124	126	125	126
C-1, C-4, C-5	144	144	143	142
C-7	159	—	158	—
C-8	137	132	136	131

TABLE II
Observed Solid-State ^{13}C-NMR Chemical Shifts and Peak Assignments of Chitosan, CP-31 Blend (Adjusted to pH < 1) and CP-31 Semi-IPN (Adjusted to pH < 1)
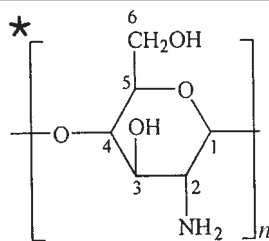
Chitosan

Assignment (chitosan)	Chitosan (ppm)	CP-31 blend (adjusted to pH < 1)	CP-31 semi-IPN (adjusted to pH < 1)
C-1	105	102	104
C-2	58	57	—
C-3, C-5	75	76	72
C-4	79	79	—
C-6	63	62	61
Imine bond (–N=CH–)	—	—	141

conductive form, the ES. PANi is doped by protonic acid, leading to a conductive form, the emeraldine salt. Consistent with the FTIR data, the spectrum from the doping PANi film shows characteristics of a chemical structure that are identical to those of the CP-31 semi-IPN, adjusted pH < 1.

Usually, PANi EB consists of amine (–NH–) and imine (=N–) sites in equal proportions. The imine sites are protonated by HCl acid to the bipolaron (dication salt) form. Although theoretical calculations have predicted that the bipolaron state is energetically more favored than the polaron, it is widely agreed that polarons are the charge carriers responsible for the high conductivity in PANi. It has been proposed that the presence of coulombic interactions, dielectric screening, and local disorder in the PANi lattice act to stabilize the delocalized polaron state. On the other hand, this undergoes a further rearrangement to form the delocalized polaron lattice, which is a polysemiquinone radical-cation salt. It has also been shown that bipolaron states do exist in PANi, but they are few in number and are not associated with the conducting regions of the polymer.[6]

Table II shows the assignments for chitosan, CP-31 blend (adjusted to pH < 1), and CP-31 semi-IPN (adjusted to pH < 1), respectively. The ^{13}C-NMR pattern of crosslinked chitosan in semi-IPN is less well resolved than that of its raw form. The signals observed on the spectra, at 25 and 173 ppm, were attributed to the signals of –C=O and –CH₃, respectively. Moreover the C-1 signal is broad, and C-3 and C-5 signals overlap, forming a shoulder at the bottom of the C-4 signal. The C-2 and C-6 signals are also less well resolved and it appears that the C-2 signal decreases. With the crosslinking of chitosan, C-1, C-3, C-5, and

C-6 peaks are enlarged and there is decreased overlapping in the neighboring C-2 and C-4 peaks. Glutaraldehyde grafting produces new alkyl groups that cause the appearance of a new broad peak. Thus, additional signals appear at 141 ppm. This band is related to the appearance of new bonds between amine functions and aldehyde groups.[32] Crosslinked chitosan is produced by Schiff's base reaction of amino groups in chitosan and aldehyde groups in glutaraldehyde.[10]

WAXD patterns of PANi EB and doped PANi, as well as those of CP-31 semi-IPNs (adjusted to pH < 1 and unadjusted) are shown in Figure 5. For the PANi EB, there is only one broad amorphous single peak at $2\theta = 20°$. The peak centered at $2\theta = 20°$ may be ascribed to periodicity parallel to the polymer chain, whereas the latter peaks may be attributed by the periodicity perpendicular to the polymer chain.[33] After doping with HCl, PANi became more crystalline and its XRD pattern showed peaks of increasing intensity. With the doped PANi, the PANi EB became more crystalline and was reflected in the presence of several diffraction peaks at $2\theta = 9, 22, 26,$ and $31°$, indicating a crystalline structure. It was reported that emeraldine salt (PANi–HCl) was partly crystalline, whereas emeraldine base (undoped PAN) was essentially an amorphous polymer.[27] It was also reported that n-methyl-2-pyrrolidone (NMP)-p-PAN films, doped with aqueous HCl solution, were partly crystalline. The disappearance of the two WAXD peaks for semi-IPN confirms that in those cases the PANi was completely embedded in the chitosan matrix.

WAXD patterns of chitosan/PANi semi-IPNs of various contents are shown in Figure 6. The X-ray diffractograms of the semi-IPN show distinct crystal-
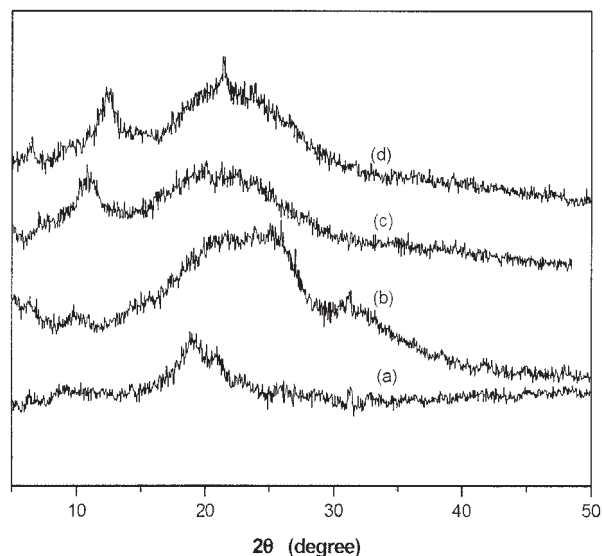
Figure 5 WAXD patterns of (a) PANi EB; (b) PANi doped with HCl; (c) CP-31 semi-IPN, adjusted to pH < 1; and (d) CP-31 semi-IPN, unadjusted.

line peaks attributed to the chitosan and PANi, indicated by the presence of a broad peak at 12.8°, in agreement with the characteristic diffractogram of the original chitosan.[31] The wide peak, appearing at about 20°, was assigned to overlapping of chitosan and PANi, and the peak became sharp with increasing content of PANi in the semi-IPN. The crystallinity decreased with increasing amount of crosslinked chitosan by glutaraldehyde in the solid gel formed in the semi-IPN.
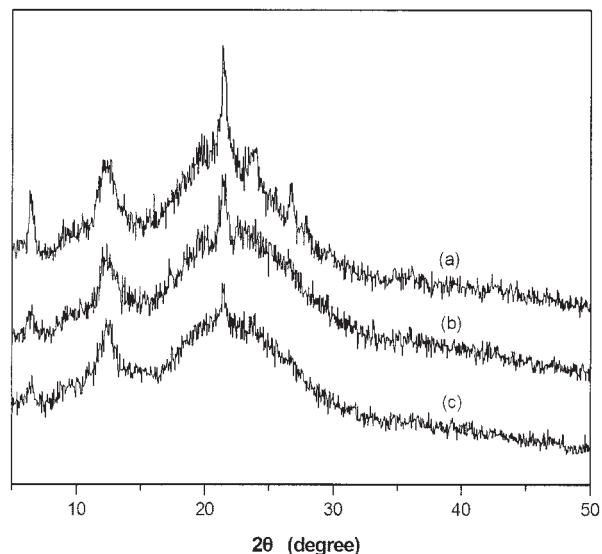

Figure 6 WAXD patterns of (a) CP-21 semi-IPN, adjusted to pH < 1; (b) CP-31 semi-IPN, adjusted to pH < 1; and (c) CP-21 semi-IPN, unadjusted.

TABLE III
Conductivities of PANi EB and Chitosan/PANi Sample

Sample	Weight ratio [chitosan/PANi]	at pH < 1[a]	Conductivity (S/cm)
PANi EB[b]	—	×	$\sim 10^{-10}$
CP-21 semi-IPN	2 : 1	○	1.0×10^{-4}
CP-31 semi-IPN	3 : 1	○	2.9×10^{-5}
CP-41 semi-IPN	4 : 1	○	2.1×10^{-6}
CP-31 blend	3 : 1	○	3.4×10^{-5}
CP-31 blend	3 : 1	×	3.9×10^{-7}

[a] ×, adjusted to pH < 1; ○, adjusted to pH < 1.
[b] From Lee et al.[15]

Table III shows the surface conductivity of the PANi EB, chitosan/PANi blend, and semi-IPNs, adjusted to pH < 1 and unadjusted. The values of surface conductivity of the chitosan/PANi samples are within the range 10^{-7} to 10^{-4} S cm^{-1}, which is much higher than that of PANi EB. This is because the acidification of the chitosan/PANi samples that were adjusted to pH < 1 becomes greater. The CP-21 semi-IPN shows the highest surface conductivity. The conductivity of the semi-IPN samples increased with increasing weight content of PANi in the semi-IPNs. The increase in the surface conductivity, caused by interaction of the components, also reflects the charge transfer being associated with the acidic doping of PANi. When the semi-IPN is compared with blend, the lower conductivity value found for the crosslinked semi-IPN may be explained by two distinct reasons. The first is related to the lower HCl diffusivity inside the more compact three-dimensional structure of the material, which may result in being partially doped. The other reason is related to the different morphology assumed by the polymer.[34]

A conducting polymer, such as PANi, can be useful for sensor application, where the conductivity ranges from 10^{-7} to 10^3 S/m. The combination of chemical properties with the electrical properties of the chitosan/PANi semi-IPN system is expected to promote the development of new sensors. The electrical signals measured can be current flow, change in capacitance, or change in resistance. The area of biosensors has proven particularly interesting in this regard because conducting polymer systems have been shown to be capable of *in situ* control of antibody–antigen interactions, making them reversible under selected conditions.[6]

CONCLUSIONS

The effects of pH condition of chitosan/PANi semi-IPNs on the changes in chemical and conductivity properties were investigated. The semi-IPNs based on PANi and crosslinked chitosan were found to depend strongly on the synthesis conditions, such as the pH condition. FTIR and NMR studies also revealed that

the structure of the semi-IPNs, adjusted to pH < 1 by HCl aqueous solution, is similar to that observed for doping PANi (emeraldine salt form). WAXD patterns show a greater degree of crystallinity of HCl-treated samples than that of the untreated sample. The conductivity of the semi-IPNs increases with increasing PANi contents, adjusted to pH < 1, formed a blended structure. The observed increase in the electrical conductivity caused by interaction of the components also reflects the charge transfer being associated with the acidic doping of PANi. As a result, PANi EB can be switched by protonic acid solution (adjusted to pH < 1 by HCl aqueous solution), leading to a conductive form, the emeraldine salt form. Therefore, the present chitosan/PANi semi-IPN system can be useful for microelectronics applications such as biosensors, chemical sensors, and molecular sensors.

References

1. Fan, J.; Wan, M.; Zhu D. J Polym Sci Part A: Polym Chem 1998, 36, 3013.
2. Yang, S.; Tirmizi, S. A.; Burns, A.; Barney, A. A.; Risen, W. M. Synth Met 1989, 32, 191.
3. Jin, Z.; Su, Y.; Duan, Y. Synth Met 2001, 122, 237.
4. Yuan, G. L.; Kuramoto, N.; Takeishi, M. Polym Adv Technol 2003, 14, 428.
5. Rao, P. S.; Subrahmanya, S.; Sathyanarayana, D. N. Synth Met 2003, 139, 397.
6. Wallace, G. G.; Spinks, G. M.; Kane-Maguire, L. A. P.; Teasdale, P. R. Conductive Electroactive Polymers, 2nd ed.; CRC Press: Boca Raton, FL, 2003; pp 121–177.
7. Mathew, R.; Yang, D.; Mattes, B. R.; Espe, M. P. Macromolecules 2002, 35, 7575.
8. Kababya, S.; Appel, M.; Haba, Y.; Titelman, G. I.; Schmidt, A. Macromolecules 1999, 32, 5357.
9. Espe, M. P.; Mattes, B. R.; Schaefer, J. Macromolecules 1997, 30, 6307.
10. Yin, W.; Li, J.; Li, Y.; Wu, Y.; Gu, T. Polym Int 1997, 42, 276.
11. Lee, Y. M.; Kim, J. H.; Kang, J. S.; Ha, S. Y. Macromolecules 2000, 33, 7341.
12. Yang, D.; Mattes, B. R. Synth Met 1999, 101, 746.
13. Venkatachalam, S.; Prabhakaran, P. V. Synth Met 1998, 97, 141.
14. Chen, C. H. J Appl Polym Sci 2003, 89, 2142.
15. Lee, Y. M.; Nam, S. Y.; Ha, S. Y. J Membr Sci 1999, 159, 41.
16. Agbor, N. E.; Petty, M. C.; Monkman, A. P. Sens Actuators B 1995, 28, 173.
17. Li, Z. F.; Ruckenstein, E. J Colloid Interface Sci 2003, 264, 362.
18. Hobaica, S. C. J Polym Sci Part B: Polym Phys 2003, 41, 807.
19. Mav, I.; Žigon, M.; Šebenik, A.; Vohlidal, J. J Polym Sci Part A: Polym Chem 2000, 38, 3390.
20. Baibarac, M.; Mihut, L.; Louarn, G.; Lefrant, S.; Baltog, I. J Polym Sci Part B: Polym Phys 2000, 38, 2599.
21. Cochet, M.; Louarn, G.; Quillard, S.; Boyer, M. I.; Buisson, J. P.; Lefrant, S. J Raman Spectrosc 2000, 31, 1041.
22. Park, S. B.; You, J. O.; Park, H. Y.; Haam, S. J.; Kim, W. S. Biomaterials 2001, 22, 323.
23. Mehrdad, Y. P.; Jaime, R.; Raul, Q. Macromol Chem Phys 2000, 201, 923.
24. Kang, D. W.; Choi, H. R.; Keon, D. K. J Appl Polym Sci 1999, 73, 469.
25. Peniche, C.; Waldo, A. M.; Davidenko, N.; Sastre, R.; Gallardo, A.; Roman, J. S. Biomaterials 1999, 20, 1869.
26. Lee, W. F.; Chen, Y. J. J Appl Polym Sci 2001, 82, 2487.
27. Chaudhari, H. K.; Kelkar, D. S. J Appl Polym Sci 1996, 62, 15.
28. Chen, Y.; Imrie, C. T.; Cooper, J. M.; Glidle, A.; Morris, D. G.; Ryder, K. S. Polym Int 1998, 47, 43.
29. Li, X.; Chen, W.; Bian, C.; He, J.; Xu, N.; Xue, G. Appl Surf Sci 2003, 217, 16.
30. Oyrton, A. C.; Monteiro, J. R.; Claudio, A. Int J Biol Macromol 1999, 26, 119.
31. Sapurina, I. Y.; Gribanov, A. V.; Mokeev, M. V.; Zgonnik, V. N.; Trchova, M.; Stejskal, J. In: Proceedings of the Vth International Workshop, Fullerenes and Atomic Clusters, St. Petersburg, Russia, July 2–6, 2001.
32. Guibal, E.; Milot, C.; Eterradossi, O.; Gauffier, C.; Domard, A. Int J Biol Macromol 1999, 24, 49.
33. Zhang, Z.; Wei, Z.; Wan, M. Macromolecules 2002, 35, 5937.
34. Abbati, G.; Carone, E.; D'iiario, L.; Martinelli, A. J Appl Polym Sci 2003, 89, 2516.