Optical and Conductivity Studies of Pseudo-Doped Chitin-Polyaniline Blend

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ABSTRACT: In this article, we report the preparation and characterization of self-doped conducting chitin, polyaniline blends by solution blending method. The characterization of the blends was done by UV–vis absorption spectrum, FTIR, and conductivity studies. Conductivity of the self doped blends increases from less than $\sim 10^{-7}$ S/cm to 2.15×10^{-5} S/cm, depending on the percentage of polyaniline in the blend. Spectroscopic analysis shows interaction between chitin and polyaniline and the electronic states are similar to those of the emeraldine and protonically doped forms of polyaniline. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 309–313, 2007

Key words: blending; biopolymers; conducting polymers; chitin; polyaniline

INTRODUCTION

In recent years, polyaniline has attracted considerable attention, because of its wide spectrum of applications such as PLED, batteries, EMI shields, gas sensors, anti-corrosion agents etc., due to combination of unique properties like simple preparation and doping procedure, good environmental stability, conductivity, and low cost.[1] Unfortunately, it has rather poor mechanical, general physical properties, and processability.[1–3] Several methods have been reported to improve the processability and mechanical properties, such as electrochemical polymerization of aniline in the polymer matrix,[4,5] increasing the molecular weight,[6] synthesis of polyaniline in the presence of preformed stable colloidal particles to give conducting polymers,[7] and blending with other polymers in a cosolvent.[8] It has been observed by Siddaramaiah et al. that the thermal stability of PANI is improved after blending with polycarbonate.[9] PANI has been grafted with chitosan and doped with protonic acid to get the electrical conductivity in the range 10^{-5} to 10^{-2} S/cm.[10]

In this article, an attempt has been made to overcome these problems by blending polyaniline (EB) with chitin, a flexible polymer, by solution blending method. Polyaniline exists in different forms depending on the oxidation level. Polyaniline can be synthesized in various insulating forms such as the fully reduced leucoemeraldine base (LEB), the half oxidized emeraldine base (EB), and fully oxidized pernigraniline base (PNB). Among these three forms, EB is the most stable and widely investigated polymer. Its conductivity can be tuned via doping from 10^{-10} S/cm up to 100 S/cm and above. LEB and PNB forms cannot be made conducting. The EB form consists of equal number of reduced and oxidized repeating units as shown in Figure 1(a). The conducting emeraldine salt form (PANI) is achieved by doping with aqueous protonic doping as shown in the Figure 1(b).[1,2,11]

Chitin is a natural polysaccharide composed mainly of β-(1,4) linked 2-deoxy-2-acetamido-D-glucopyranose and partially of β-(1,4) linked 2-deoxy-2-amino-D-glucopyranose.[12–15] The structure of chitin is shown in Figure 2. It is the second most abundant natural polymer after cellulose, commonly found in exoskeletons or cuticles of many invertebrates and in the cell walls of most fungi and some algae. It is usually obtained from the shells of shellfish, crab, lobster, or shrimp. Chitin and its deacetylayted form have attracted attention because of several important advantages such as biocompatibility, biodegradability, high mechanical strength, and nontoxicity.[12,14]
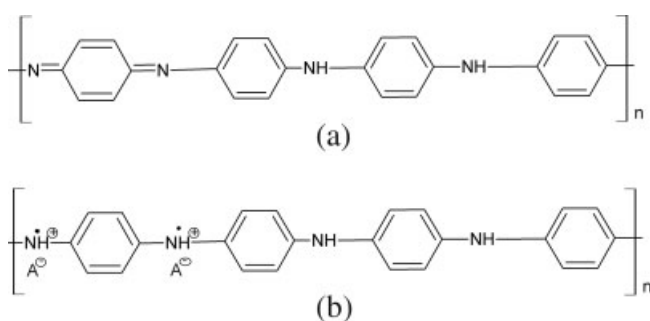
EXPERIMENTAL

Materials and chemicals

Chitin from HIMEDIA, Mumbai, with molecular weight 400,000 g/mol, *N,N*-dimethyl acetamide (DMA; AR grade) and LiCl (AR grade) from SRL,

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Figure 1 (a) Structure of emeraldine base. (b) Structure of emeraldine salt.

and ammonium peroxy disulphate (APS; GR grade) from MERCK were used as received. Aniline GR grade from MERCK was distilled under reduced pressure before use.

Preparation of polyaniline

Polyaniline was prepared by chemical oxidative polymerization of aniline by ammonium peroxy disulphate (APS) in aqueous acidic medium as reported by MacDiramid et al.[16] Aniline ($0.25M$) was prepared in $1M$ HCl and cooled to 0–5°C. Precooled $0.25M$ APS solution in $1M$ HCl was added dropwise within 20-min interval and reaction mixture was maintained at 0–5°C with stirring for 1 h and was taken out of the ice/water bath and stirred for 3 more h. The green precipitate of polyaniline was filtered and washed with $1M$ HCl, then with deionized water and finally with acetone, and was dried for 24 h at 60°C. Thus obtained green flakes of PANI was powdered and treated with $0.5N$ NaOH solution for 16 h to get EB. Resultant EB powder was washed with water until neutral. Viscosity average molecular weight of polymer was found to be 50,000 g/mol.

Blend preparation

Blends of chitin and polyaniline with polyaniline 15, 30, 50, and 70% (P15, P30, P50, and P70) were pre-
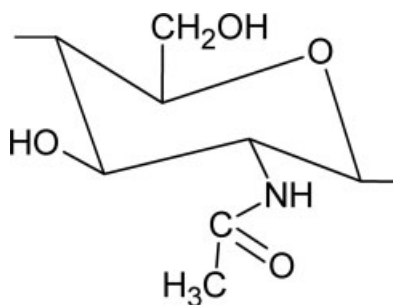

Figure 2 Structure of chitin.

pared by mixing 0.5% chitin solution in DMA with 5% LiCl and 0.5% EB solution in DMA in required proportions. Free standing films of blends were cast on glass pertridishes and dried at 70°C. The films were peeled off and washed with water, then with acetone and dried at 60°C for 24 h before being used for further studies.

Physical characterization

The blend solutions were diluted and UV–vis absorption spectra were recorded between 300–800 nm using Shimadzu spectrophotometer (model UV-3101 PC). FTIR spectra of the blend films were recorded using a Perkin–Elmer spectrophotometer (model 1000) employing the KBr pellet technique. Conductivity of various blends were recorded by two probe method using Keithley electrometer (model 6517A).

RESULTS AND DISCUSSION

The UV–vis absorption spectra of diluted chitin-polyaniline blend solutions are shown in the Figure 3. Absorptions peaks were observed at ∼330 nm and ∼630 nm. Since there is no significant absorption peak for chitin in this region and these peaks are similar to the absorption peaks observed for polyaniline, the absorption peak at ∼330 nm corresponds to π-π* transition of the benzenoid ring. The peak at ∼630 nm for P15 is assigned to polaron band transition. As the composition of the polyaniline in the blend increases, the polaron band transition absorption peak shifts to higher wavelength side. An additional peak at ∼430 nm is observed for P70 which also corresponds to polaron transition.[9,10,17] The red shift and absorption shoulder at ∼430 nm clearly
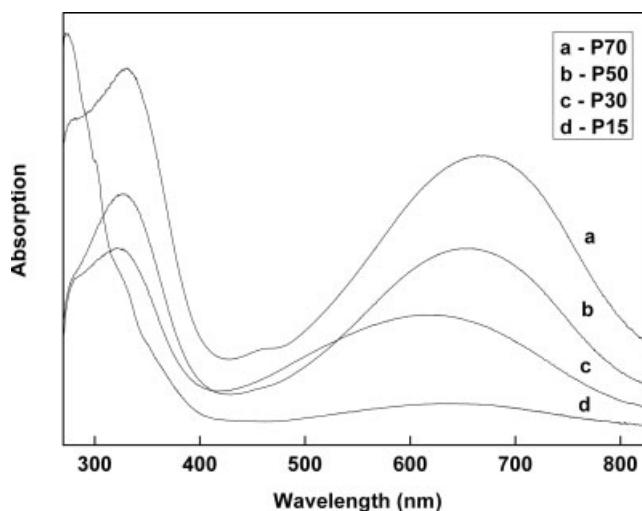
Figure 3 UV–vis spectrum of different blends.

TABLE I
Energy Gap of Different Blends

Blend	Energy gap (eV)
P15	3.77
P30	3.21
P50	3.18
P70	3.01

indicates that as the percentage of polyaniline increases, conductivity of the blend increases. Further from the energy band calculations, it is found that energy gap decreases with increase in the percentage of polyaniline in the blend (Table I).

The IR spectrum of chitin–polyaniline blend shows significant peaks of both chitin and polyaniline [Fig. 4(c)]. The peaks at $\sim$1519 cm^{-1}, $\sim$1431 cm^{-1}, $\sim$1259 cm^{-1}, $\sim$1153 cm^{-1}, and $\sim$835 cm^{-1} are charac-

teristic of polyaniline[10,17,18] [Fig. 4(b)]. All other significant peaks are due to the presence of chitin in the blend. The band at $\sim$1519 cm^{-1} is attributed to the quinoid and benzenoid unit stretching modes of PANI and the band at $\sim$1153 cm^{-1} is attributed to quinoid unit doped PANI.[10] In the IR spectrum of the chitin [Fig. 4(a)], the peak is observed at $\sim$1669 cm^{-1}, which is related to carbonyl groups.[12,15] But in the case of the blend, this peak is shifted to $\sim$1650 cm^{-1}. This may be due to the interaction between chitin and PANI.

It is known that LiCl can interact with systems containing amide groups giving rise to physically crosslinked polymers. Crosslinks derive from ion–dipole interaction between Li$^+$ ion and the principal donor site in the amide, which is the oxygen of the amide. As a consequence, an enhanced delocalization of nonbonding electron pair of the nitrogen is produced, which weakens the N—H
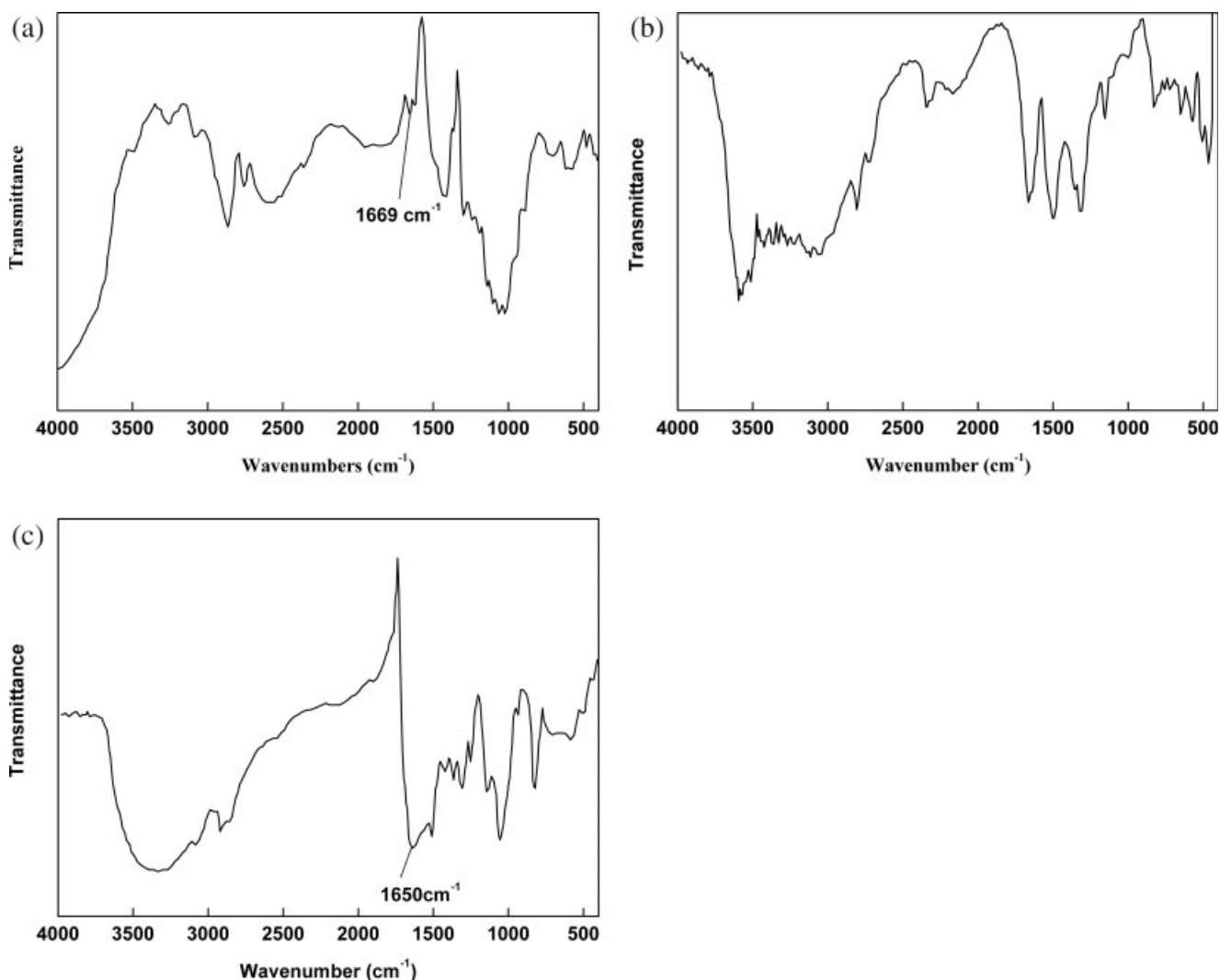
Figure 4 FTIR spectrum of (a) chitin, (b) polyaniline base, (EB) and (c) blend.
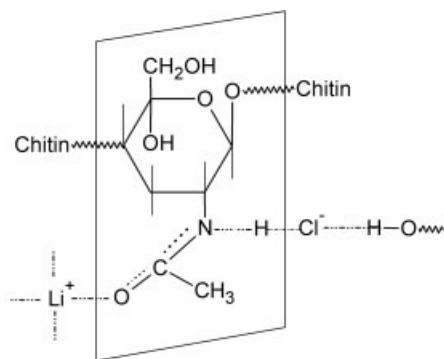
Scheme 1 Interaction of LiCl with chitin.

bond and allows the hydrogen atom to interact with the chloride anion. Such interactions will be active in the solution of chitin/DMA-LiCl, because of the presence of the amide group in chitin. In the case of solutions, these interactions give a macromolecular fluctuating network and a more viscous solution. The interaction between chitin and LiCl is shown in Scheme 1.[19] In the case of chitin–cellulose blend film prepared from DMA/LiCl, the miscibility of the blend is predicted in terms of the interaction of Cl^- ion which links NH of chitin with OH of cellulose.[19] Similar explanation can be given for the interaction between chitin with polyaniline blend. The interaction may be between the Cl^- ion of chitin with NH of polyaniline. Interaction between chitin and polyaniline is further verified by dissolution study. Solubility of blend films were studied in DMA, DMF, NMP, and chloroform. Even after a week, only a very small portion of polyaniline dissolved in the solvent.

DC electrical conductivity values of various blends were recorded by two probe method using a Keithley electrometer (model 6517A). Conductivity of various blend compositions is shown in the Table I. The conductivity of blend films increase with increase in the percentage of polyaniline in the blend. This is because of more and more LiCl getting doped with polyaniline. Highest conductivity observed is 2.15×10^{-5} S/cm (Table II). Doping of EB with LiCl is already reported by Saprigin et al.,[20,21] and they obtained the maximum conductivity of the order of

10^{-8} S/cm. In chitin–polyaniline (EB) blend, during the preparation of the blend, LiCl gets attached to both chitin and EB. Even though we used 5% LiCl for solution preparation, the effective doping concentration is less, as residual LiCl was found on the surface of the film. Rejection of excess LiCl has also been reported by Saprigin et al.[20,21] Thus, LiCl is responsible for the interaction between chitin and polyaniline increase in DC electrical conductivity. P30 blend is further doped with $1M$ HCl for 16 h and the conductivity of HCl doped P30 is found to be $\sim 2.15 \times 10^{-3}$ S/cm. Thus, by increasing the concentrations of polyaniline and HCl, conductivity of the blend can be further improved.

CONCLUSIONS

Self-doped blends of chitin and polyaniline with various compositions were prepared by solution blending technique. The free standing films of blends are stable under ambient condition. The red shift and absorption shoulder at ~ 430 nm clearly indicates that as the percentage of polyaniline increases, conductivity of the blend increases. FTIR study shows interaction between chitin and polyaniline in the blend. Conductivity achieved through self doping with LiCl used as solvent, is 2.15×10^{-5} S/cm. The conductivity achieved is high enough to make them interesting materials. Even though conductivity is several orders below what is achieved just by doping polyaniline, during preliminary experiments, we observed that by doping with other doping agent conductivity can be improved further. We are working on the doped chitin/polyaniline system in detail and the results will be reported later.

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TABLE II
Conductivity Variation of Blends

Blend	Conductivity (S/cm)
P0	$\sim 10^{-9}$
P15	1.1×10^{-7}
P30	8.3×10^{-7}
P50	1.79×10^{-6}
P70	2.15×10^{-5}
P100	$\sim 10^{-10}$

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