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Preparation and characterization of processable electroactive polyaniline–polyvinyl alcohol composite

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Abstract

In this paper, the preparation and characterization of polyaniline–polyvinyl alcohol composites is described. The polyaniline composite was synthesized by chemical polymerization of aniline in media containing polyvinyl alcohol (10%, w/w). Oxidation of aniline results in a stable water based polyaniline dispersion, which can be cast to form a mechanically robust film.

The electrical conductivity of the films increased with increasing amount of polyaniline to a high value of 2.5 S cm^{-1}. Cyclic voltammograms revealed that the composite materials are electroactive.

Keywords: Conducting polymer composites; Polyaniline; Water based dispersions

1. Introduction

Conducting polymers exhibit a wide range of novel electrochemical and chemical properties that has led to their use in a diverse array of applications including sensors [1,2], switchable membrane [3], anti-corrosive coatings [4,5], biosensors [6], electrochromic devices [7] and rechargeable batteries [8,9].

Polyaniline is one of the most promising candidates for industrial application of conducting polymers. It is formed via simple chemical or electrochemical oxidation of aniline. However, as with other conducting polymers it is not readily processable in non-toxic solvents due to limited solubility and the fact that the materials are normally not melt processable.

A number of attempts have been made to form composites with improved processability and mechanical properties while maintaining the inherent properties of the conducting polymer. Conducting polyaniline blends and composites are prepared mostly via the chemical oxidation route, although electrochemical synthesis is also employed in some cases [10,11]. Using the chemical approach in situ polymerization of monomer in the presence of a host polymeric matrix has been reported [12–14]. Polyaniline–poly(ethylene terephthalate) [12] and polyaniline–polystyrene [13] composites were both prepared using this approach.

Emulsion polymerization in heterogeneous systems [15] has been used to prepare processable conductive composites of polyaniline–poly(alkyl methacrylate). Polyaniline composites have also been prepared via dispersion polymerization [16–18]. In such studies colloidal dispersions of electrically conductive polyaniline particles have been prepared using vinyl methyl ether [17] or methyl cellulose [19] stabilizers.

Composites of polyaniline with polystyrene [20], poly(methyl methacrylate) [21] and poly(*p*-phenylene–diphenyl ether-terephthalamide) [22] have all been prepared using a compatible solvent such as concentrated sulphuric acid solution. In more recent years, a series of polyaniline (ethylene–vinyl acetate copolymer) composites were obtained by mechanical blending; where polyaniline was chemically synthesized and then blended with melted copolymer. This simple mechanical mixing method can be employed either at room temperature or at high temperature where the host polymer is in the molten state [23].

The preparation and characterization of colloidal dispersions consisting of polyaniline and polyvinyl alcohol has been investigated in recent years. The mechanism of polymerization [24], polymerization yield [25] and the

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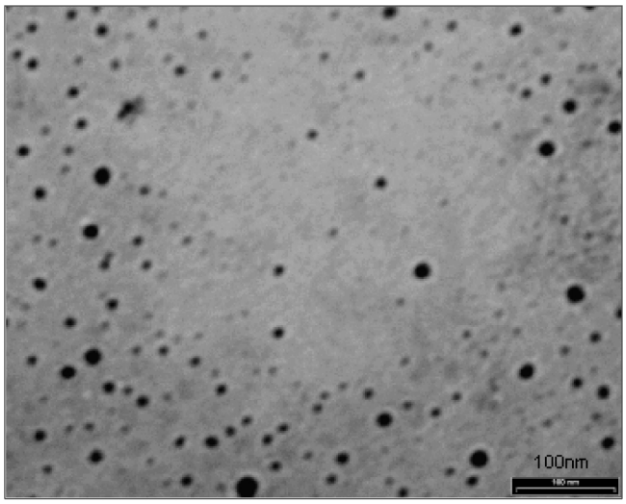

Fig. 1. Transmission electron microscopy of polyaniline particles.

size uniformity of particles [26] have been reported. Degradation mechanism [27], electrochemical behavior in non-aqueous media [28], resistivity changes in relation to dispersion concentration [29], ion exchange properties [30], photoconductivity [31] and conductivity studies [32] have all been considered in detail. The use of these PVA–PAn composites to produce a humidity [33] or carbon dioxide sensor [34] has also been reported.

In the course of this work we have investigated variations in the synthesis route that impact on the ability to produce conducting coatings and stand-alone films. The mechanical, electrochemical and physical properties of these films have been investigated in detail.

2. Experimental

2.1. Reagents and materials

Ammonium persulphate, hydrochloric acid and aniline were all purchased from BDH chemicals. Polyvinyl alcohol ($M_w = 89,000–98,000$) was obtained from Aldrich chemicals. Aniline was distilled prior to use. All other materials were used without further pretreatment.

2.2. Instrumentation

Cyclic voltammetric studies were carried out using an EG and G Princeton Applied Research Galvanostate/potentiostat Model 263A. A conventional three electrode electrochemical cell with a platinum coated working electrode ($A = 0.25\ cm^2$) in combination with a platinum counter electrode and a Ag/Ag/Cl reference electrode were used throughout the studies. Polyaniline composite was coated over the Pt electrode with an approximate thickness of 10 μm.

All UV–visible studies were carried out using a Shimadzu (UV-1601) spectrophotometer. Mechanical tests were determined by the stress–strain technique using a universal testing machine (Instron 4302) at room temperature for both dehydrated and as prepared samples. A strain rate of $3\ mm\ min^{-1}$ was employed. DC conductivity of the films was measured using a conventional four-point probe technique. All Transmission Electron Microscope (TEM) studies were carried out using Hitachi H-7000 microscope.

2.3. Procedures

2.3.1. Preparation of polyaniline–PVA composite

The polyaniline composite was synthesized by chemical polymerization of aniline in aqueous acidic (1 M HCl) media containing PVA (10%, w/w) using methods similar to those previously reported [35,36]. Specifically in this work 100 ml of the PVA (10%, w/w) was charged into the reactor. It was cooled to 0 °C while various amounts of aniline (dissolved in 50 ml of 3 M HCl) were added. While stirring vigorously, ammonium persulphate (oxidant solution) of same molar ratio as aniline was added dropwise over a period of 1 h. After 30 min the solution became green in color, indicating formation of polyaniline. The reaction mixture was stirred for 5 h while maintaining the temperature between −3 and −5 °C. A green suspension was formed. Oxidation of aniline results in a stable water based polyaniline dispersion, which can be cast to form a mechanically stable stand-alone film. A series of polyaniline–polyvinyl alcohol composites with different weight ratios of polyaniline ranging from 5 to 38% (w/w) aniline loading were prepared. For example, in the case of the 5% sample, the feed solution contained 5% (w/w) aniline and 95% (w/w) PVA.

2.4. Purification of polyaniline–PVA composite

In order to remove any unreacted chemicals, the polymer solution was dialyzed against distilled water for 48 h to ensure removal of unreacted monomers and oxidants.

2.5. Film preparation

Mechanically stable stand-alone films of polyaniline–PVA composite was formed on glass substrate using a solution casting method in 60 °C for 6 h.

2.6. Conductivity studies

PAn–PVA composite films were doped by immersing in 1:1 Acetone–HCl solution (1 M HCl) for 24 h. The film was then placed between two sheets of filter paper and was dried under high vacuum for 48 h. It was found that the conductivity reached a constant value after this period.

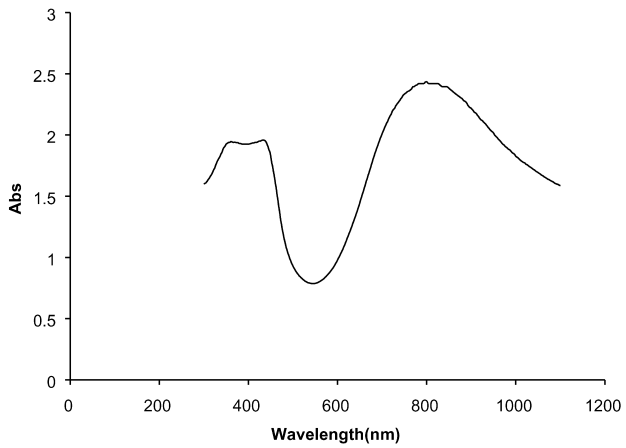

Fig. 2. UV–visible spectrum obtained for diluted aqueous solution of PAn–PVA composite when 29% (w/w) aniline was used in the feed solution.

3. Results and discussions

Polyaniline dispersions were prepared as described in the Section 2 with special attention paid to maintaining the temperature during polymerization at −3 to −5 °C. In all cases, a stable polyaniline dispersion was obtained with TEM revealing particles of the size 5–10 nm (Fig. 1).

3.1. UV–Visible spectra

The dispersion obtained was diluted (40 times) and the UV–visible absorption spectra obtained (Fig. 2). Two characteristic absorption peaks attributed to the conducting emeraldine salt were observed. That at 390 nm was assigned to the $\pi-\pi^*$ transition, the other at about 800 nm is assigned to the polaron band. This spectrum suggests that the composite had a compact coil structure as described previously for polyaniline [37].

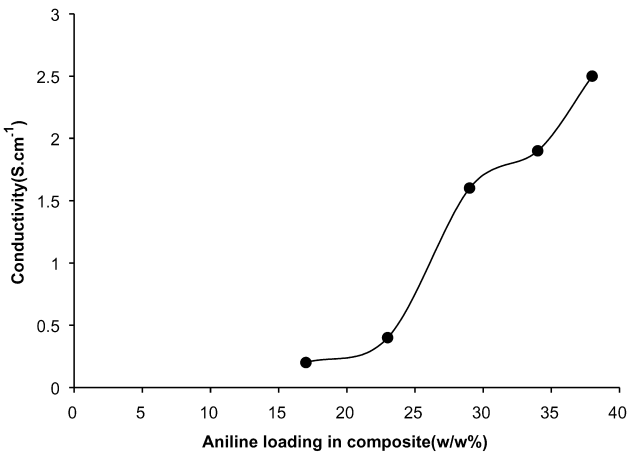

Fig. 3. Four point probe conductivity of PAn–PVA composite films as a function of aniline loading (during synthesis). Temperature: 23 °C. Samples were subjected to conductivity measurements immediately after dehydration (see Section 2 for details). Aniline percentages were calculated based on aniline and PVA composition in feed solution.

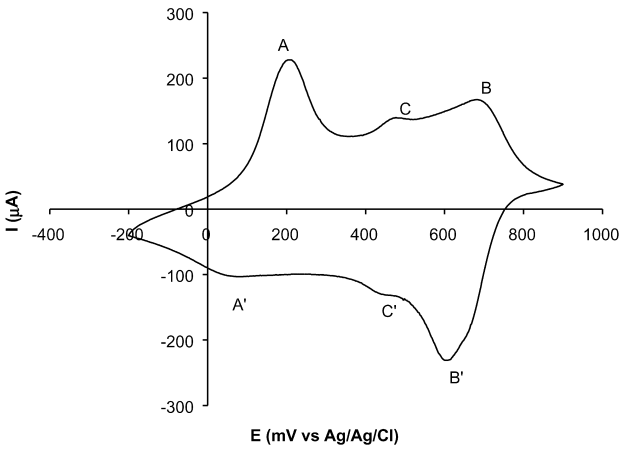

Fig. 4. Cyclic voltammograms showing oxidation–reduction of a PAn–PVA film cast from water based dispersion of the composite onto a platinum disk electrode. Polymer thickness: approximately 10 μm. Aniline concentration in feed solution: 29% (w/w), scan rate = 10 mV s^{-1}. Couples A/A′, B/B′ and C/C′ discussed in text.

3.2. Conductivity

Stand-alone films with different weight fractions of polyaniline were prepared by casting the solution onto a glass slide. The conductivity of each film was measured and found to depend strongly on the fraction of polyaniline in the composite (Fig. 3). Conductivities in the range 0.2–2.5 S cm^{-1} were obtained. The maximum was of the same order of magnitude (1.3 S cm^{-1}) as results previously reported [36]. With aniline concentrations in the feed solution beyond 40% (w/w) the conducting polymer precipitated from solution.

3.3. Electroactivity

The cast films were then subjected to cyclic voltammetry (CV) in 0.5 M HCl (Fig. 4). It is well known that polyaniline undergoes two separate oxidation and reduction processes.

This is clearly found to be occurring in the films prepared here. The well defined oxidation–reduction responses indicate that the composite is electroactive. The first response (A and A′) is due to oxidation–reduction of leucoemeraldine to emeraldine and vice-versa. The second response (B and B′) is due to oxidation of emeraldine to pernigraniline (fully oxidized form) and vice-versa. Peaks C and C′ are attributed to polyaniline breakdown products obtained upon excursion to the potentials necessary to observe the B, B′ couple.

Oxidation–reduction peak currents were recorded for the composites containing various aniline content (Fig. 5). It was found that as the polyaniline loading in the cast films increased, the peak current observed during CV also increased. A sharp increase in peak current was observed for films prepared from mixtures that had aniline concentrations of 30% or more. As the polyaniline concentration in the feed solution was decreased a significant loss in

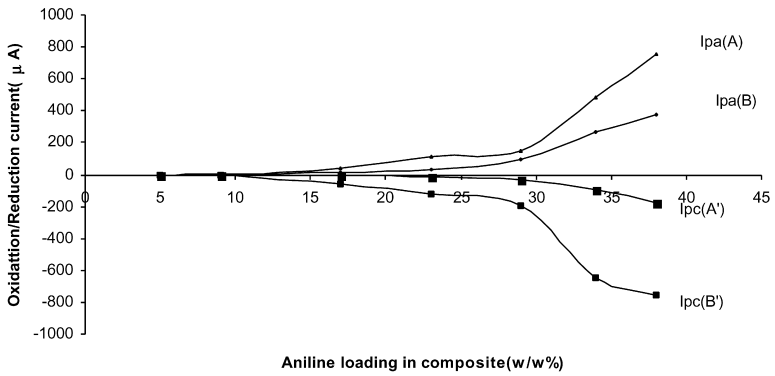

Fig. 5. Oxidation(ipa)–reduction(ipc) peak currents obtained (during CV) for PAn–PVA composites, containing various aniline loading. Cyclic voltammograms obtained in 0.5 M HCl. For A, A′, B and B′ see Fig. 4. Potential range −0.2 to −0.9 V (vs. Ag/Ag/Cl). Scan rate = 10 mV s^{-1}. Aniline percentages were calculated based on aniline and PVA composition in feed solution.

electroactivity was observed (Fig. 6). With polyaniline loadings of less than 9% the redox responses were no longer observed.

3.4. Hygroscopic properties of PAN–PVA

In order to measure the moisture capacity of the films, all samples were dehydrated (Table 1) and moisture loss was measured. It was found that the moisture content of the samples increased on increasing the aniline concentration in the feed solution, up to 29% (w/w) then it decreased slightly. A similar trend was observed when the samples regained moisture under 70% humidity. It should be noted that under similar experimental conditions dried PVA films did not significantly absorb moisture. A similar trend has been reported by previous researchers [36].

3.5. Mechanical properties

The solution casting method was used to prepare free-standing films of PAn–PVA. Smooth, flexible, mechanically robust films were obtained. The mechanical properties of the films containing various polyaniline–PVA ratios were determined (Table 2). PVA itself forms good quality films with appreciable tensile strength and Young's modulus (Table 2). On introducing polyaniline, the tensile strength decreased however, it increased to some extent with an increasing fraction of polyaniline. Small amounts of polyaniline must disturb the PVA network resulting in a lower value for the tensile strength. On increasing the polyaniline fraction (Table 2) a more uniform combination of PAn–PVA results in increased tensile strength. Upon introducing further aniline in the feed solution the strength decreases again. Elongation at break was also improved significantly upon introducing polyaniline to PVA.

The value obtained for elongation at break (Table 2) indicates that the films can be stretched up to 190% with no failure of mechanical properties. This is a significant improvement over the previously reported value of 55% [36]. This can be attributed to the impact the polymerization conditions employed has on mechanical properties.

Upon introducing enough polyaniline (over 17%, w/w) the Young's modulus of the samples decreased. These

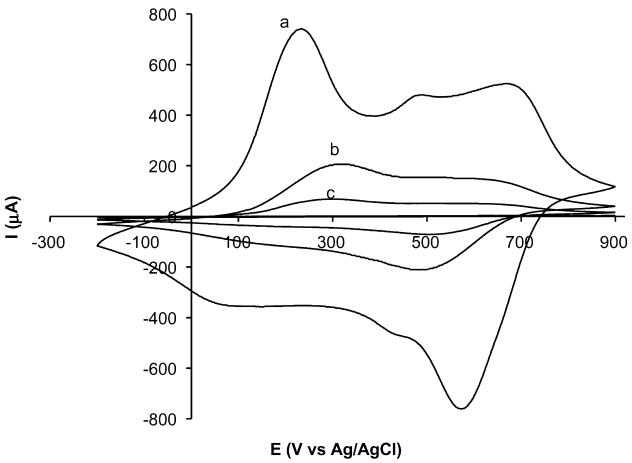

Fig. 6. Electroactivity of the composites with varying polyaniline content. (a): aniline loading = 34% (w/w), (b): aniline loading = 23% (w/w), (c): aniline loading = 9% (w/w). Aniline percentages were calculated based on aniline and PVA composition in feed solution. Scan rate = 10mV $sec^{-1.}$

Table 1
Hygroscopic properties of PAn–PVA films

Aniline loading in composite (w/w%)	Moisture loss[a] (w/w%) upon dehydration	Moisture gain[b] (w/w%) in 70% humidity
5	5.2	0.9
9	5.4	1.1
17	7.7	1.2
23	9.7	3.1
29	13.2	8.0
34	12.9	7.8
38	12.4	3.7

Aniline percentages were calculated based on aniline and PVA composition in feed solution.

[a] All samples were dehydrated under vacuum using silica gel for 48 h.

[b] Hydration of samples was carried out under laboratory conditions (temperature 20 °C).

Table 2
Mechanical properties of films

Aniline loading in composite (w/w%)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Yield stress (MPa)
0	1.5	22.8	95	No yield point
5	1.6	20.9	150	No yield point
9	1.8	12.9	150	No yield point
17	2.0	20.2	185	15
23	1.7	18.7	130	18
29	1.5	11.9	150	10
34	1.2	8.5	125	7
38	1.1	10.1	155	No yield point

Aniline percentages were calculated based on aniline and PVA composition in feed solution. The mechanical properties of the samples were measured as described in Section 2.

Table 3
Mechanical properties of films after dehydration

Aniline loading in composite (w/w%)	Tensile strength (MPa) before dehydration	Tensile strength (MPa) after dehydration	Young's modulus (MPa) before dehydration	Young's modulus (MPa) after dehydration
5	20.9	39.5	1.6	2.8
9	12.9	20.2	1.8	3.7
17	20.2	22.4	2.0	6.8
23	18.7	33.4	1.7	5.1
29	11.9	15.8	1.5	3.2
34	8.55	12.9	1.2	1.6
38	10.1	14.6	1.1	1.4

Aniline percentages were calculated based on aniline and PVA composition in feed solution.

values are much improved on those reported previously [36].

It was also found that the moisture content of the composite has a significant effect on both tensile strength and modulus (Table 3). Dehydrated samples are more mechanically robust. Regardless of polyaniline content of the composite, the tensile strength increased when dehydrated. Similarly Young's modulus of the samples increased upon dehydration. These results are consistent with water acting as a plasticizer causing a reduced Young's modulus and tensile strength in the hydrated polymer.

3.5.1. Elemental analysis

Selected samples were subjected to elemental analyses in order to determine the polyaniline content of the composite. Feed content of aniline to PVA (%w/w) of 5, 17, 34 and 38 gave compositions of 4, 15, 33 and 39% (w/w) polyaniline, respectively, in the final product.

4. Conclusions

A series of polyaniline–polyvinylalcohol dispersions with different polyaniline contents were prepared.

Films prepared from these dispersions have excellent mechanical properties. They are flexible (as verified by modulus values) and can be stretched up to 190%. A tensile strength value as high as 40 MPa was obtained.

The electrical conductivity of the composites was improved with increasing amount of polyaniline and reached a high value of 2.5 S cm^{-1}. Cyclic voltammograms revealed that the composite materials are electroactive.

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