

Preparation and Characterization of a Polyaniline/Poly(butyl acrylate–vinyl acetate) Composite as a Novel Conducting Polymer Composite

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ABSTRACT: This is the first report on the preparation and characterization of a polyaniline/poly(butyl acrylate–vinyl acetate) composite. The composite was prepared by the emulsion polymerization of aniline in a medium containing poly(butyl acrylate–vinyl acetate). Films prepared from the composite (cast from an aqueous medium) had excellent mechanical properties and could be stretched up to 900%. The resultant composite was soluble in common organic solvents, and a stable water-based dispersion could also be

prepared. An electrical conductivity of 2.2 S cm^{-1} was obtained. Cyclic voltammograms revealed that the composite was electroactive. It had excellent adhesion to either glass or steel plate. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2525–2531, 2003

Key words: polyaniline composites; conducting composite; vinyl acetate–butyl acrylate copolymer; electroactive materials

INTRODUCTION

Inherently conducting polymers exhibit a wide range of novel electrochemical properties. These polymers have been used in many applications, including sensors,^{1,2} switchable membranes,³ anticorrosive coatings,^{4,5} biosensors,⁶ electrochromic devices,⁷ and rechargeable batteries.^{8,9} Polyaniline (PAN) is a promising material in this respect, but its mechanical properties do not meet the requirements of a number of applications because, like other conducting polymers, it is not readily processable. Therefore, researchers have attempted to form PAN composites with improved processability and mechanical properties while maintaining the inherent electroactive properties of the polymer. Conducting PAN blends and composites are prepared mostly through the chemical oxidation of aniline in the presence of a host polymer,^{10–12} although electrochemical synthesis has also been employed in some cases.^{13,14}

Chemical synthesis has been employed with a number of approaches. Emulsion polymerization in heterogeneous systems¹⁵ was the approach used to produce processable conductive composites containing PAN and poly(alkyl methacrylate). PAN composites were also prepared via dispersion polymerization.^{16–18} Colloidal dispersions of electrically conductive PAN par-

ticles were prepared with vinyl methyl ether¹⁷ and methylcellulose¹⁹ as stabilizers.

PAN composites can also be prepared by the blending of preformed soluble PAN with other polymers. Composites of PAN with polystyrene,²⁰ poly(methyl methacrylate),²¹ and poly(*p*-phenylene/diphenyl ether–terephthalamine)²² have all been prepared via blending in solution.

In more recent years,²³ a series of poly(ethylene–vinyl acetate)/PAN composites were obtained by mechanical blending. PAN was chemically synthesized, and the solid was blended with the melted copolymer. This simple mechanical mixing method could be employed either at room temperature or at a high temperature in the molten state of the host polymer.²³

For the fabrication of new materials for industrial applications, the preparation and characterization of conducting PAN composites with poly(butyl acrylate–vinyl acetate) [poly(BuA–VAc)] were investigated. Aniline was polymerized in a medium containing poly(BuA–VAc). The mechanical and electrical properties of the polymer were investigated. The adhesion and ultraviolet–visible (UV–vis) spectroscopic properties of the composite material were also examined. The determined properties were such that these composites should find applications in a number of areas.

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EXPERIMENTAL

Reagents and materials

Ammonium persulfate, hydrochloric acid, aniline, vinyl acetate, butyl acrylate, potassium persulfate, so-

TABLE I
Recipe for the Copolymerization of Vinyl Acetate and Butyl Acrylate

Composition	Mass (g)	Percentage in composition (wt %)
Vinyl acetate	152	37.62
Butyl acrylate	48	11.88
Deionized water	200	49.5
Sodium lauryl sulfate	3	0.75
Potassium persulfate	0.3	0.075
Sodium bicarbonate	0.3	0.075

dium lauryl sulfate, and sodium bicarbonate were all purchased from Merck Chemicals.

Aniline, vinyl acetate, and butyl acrylate were all distilled before use. Other materials were used without further purification.

Instrumentation

A Wenking TG97 galvanostat/potentiostat (Bank Elektronik Co., Niedersachsen, Germany), a 654 pH meter (Metrohm, Herisau, Switzerland), a model 101 cyclic voltammeter (Sahand Pardazan, Tabriz, Iran), a UV-1601 spectrophotometer (Shimadzu, Kyoto, Japan), and a model KQPS/29 blender (Griffin and George, Ltd., Loughborough, UK) were all used for the synthesis and characterization of the composite.

The direct-current conductivity of the films was measured with a conventional four-point-probe technique. Cyclic voltammetry studies were carried out with a conventional three-electrode electrochemical cell with a gold-film-coated working electrode (area = 0.25 cm²) in combination with platinum counter and Ag/Ag/Cl reference electrodes. The PAn composite was coated on the gold-film electrode to a thickness of 25 μm.

Mechanical tests were determined by the stress-strain technique with a universal testing machine (model 1435, Zwick, Germany) at room temperature. A strain rate of 1 mm/min was employed

Procedures

Copolymer preparation

Poly(BuA-VAc) was synthesized according to previously reported methods.^{24,25} The copolymer latex was

prepared by emulsion polymerization with recipes given in Table I.

The polymerization was carried out in a 500-mL, glass reactor. At the beginning of the reaction, 120 mL of water, 40 mL of a monomer mixture, and all the emulsifier and sodium bicarbonate solution were charged into the reactor. The reactor was heated to 70°C. The remaining amount of the monomer and a potassium persulfate solution (0.3 g in 80 mL of water) were fed into the reactor at rates of 1 and 0.4 mL min⁻¹, respectively. The reaction was completed after 6 h. The solution was stirred at 100 rpm during the reaction. A milky latex dispersion was obtained.

With solvent extraction followed by precipitation, the percentages of the copolymer, homopolymers, and unreacted monomer in the product were obtained (Table II). Methanol (50 mL) was added to 7.5 g of the emulsion. Methanol only dissolved the poly(vinyl acetate) homopolymer; poly(BuA-VAc) and poly(butyl acrylate) were extracted. Finally, with the addition of 35 mL of tetrahydrofuran, poly(butyl acrylate) was dissolved, and poly(BuA-VAc) was extracted. Each portion was dried at 105°C, and the mass of each was measured. The percentage of each component was then determined (the copolymer and homopolymers). The concentration of the copolymer in the emulsion was approximately 40 wt %.

Purification of the poly(BuA-VAc) latex

The latex was purified with a steam distillation method for the removal of the residual monomer and remaining initiator.

Preparation of the PAn/poly(BuA-VAc) composite

The PAn composite was synthesized by the chemical polymerization of aniline in an emulsion containing poly(BuA-VAc) (40.2 wt %). The oxidation of aniline was initiated with a similar method used to obtain pure PAn.²⁶ The emulsion (65 mL, 40.2 wt %) was diluted with 65 mL of water and then charged into the reactor. It was cooled to 5°C, and then aniline (dissolved in 70 mL of 0.5M HCl) was added. Under vigorous stirring, ammonium persulfate (oxidant) was added (in the same molar ratio with aniline) dropwise. After 30 min, the solution became dark green, and this indicated the formation of PAn. The reaction mixture

TABLE II
Product Composition for the Emulsion Copolymerization of Vinyl Acetate and Butyl Acrylate

Poly (BuA-VAc)	Poly(butyl acrylate) (wt %)	Poly(vinyl acetate) (wt %)	Unreacted monomers (wt %)
80.5	9.9	4.6	5

Analysis was based on total monomers used.

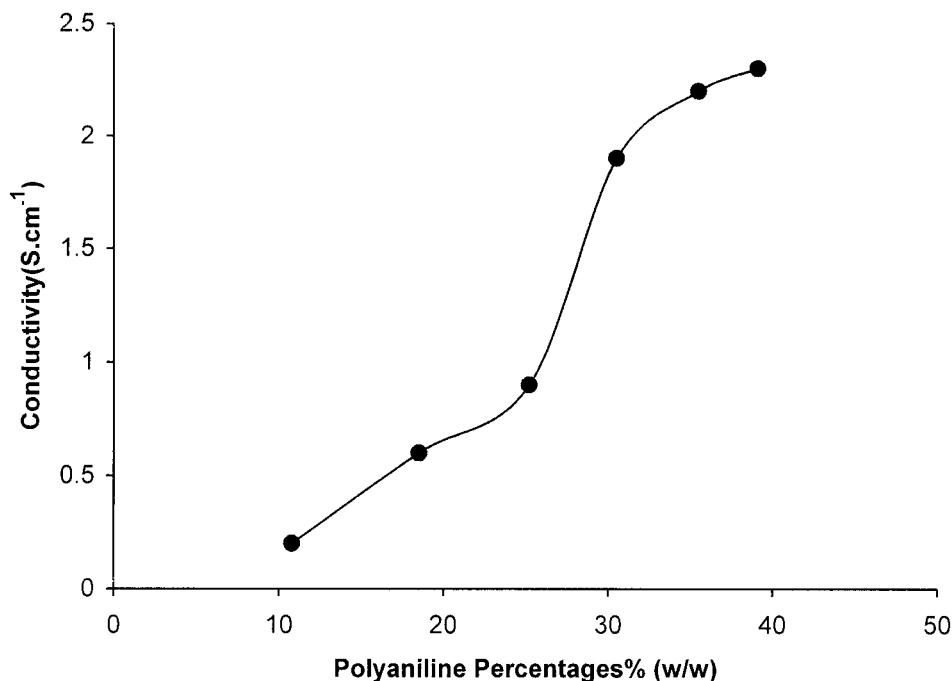


Figure 1 Four-point-probe conductivity dependence of PAN/poly(BuA-VAc) composite films versus the PAN percentage at 23°C.

was stirred for 5 h, with the temperature kept between 0 and -3°C . An emulsion with the appearance of a gel was formed.

Purification of the PAN/poly(BuA-VAc) composite

For the removal of any unreacted chemicals, the product was washed with three portions of 100 mL of deionized water. After each wash, the product was centrifuged at 2400 rpm for 15 min. The percentages of PAN in the composite matrix were determined by the elemental analysis of a highly dried powder of the composite.

Film preparation

A purified composite material of PAN and poly(BuA-VAc) was redispersed in 1.0M HCl. The prepared solution was cast over a piece of a glass substrate with a solution-casting method. The films were dried at 60°C for 6 h.

The prepared films were 25 μm thick in all the studies.

Conductivity studies

PAN/poly(BuA-VAc) composite films were doped by immersion in a 1M HCl solution for 24 h. The films were then placed between two sheets of filter paper

and dried under a high vacuum for 48 h. The conductivity reached a constant value after this period.

Adhesion measurements by tape testing

An X-cut was made in each film to the substrate (a stainless steel plate) according to ASTM Standard D 3359-95a. The cuts (six in all) were 20 mm long and 2 mm apart from one another. A pressure-sensitive tape was applied over the cut and then removed, and the adhesion was assessed qualitatively on a 0-5 scale.

RESULTS AND DISCUSSION

Stand-alone films with different percentages of PAN ranging from 10 to 40 wt % were prepared by the casting of the solution onto a glass slide. The conductivity of each film was measured (Fig. 1). Each test was carried out six times, and the results were found to vary within 5% of the average value. It was also found that the conductivity depended strongly on the fraction of PAN in the composite; conductivities in the range of $0.2\text{--}2.2\text{ S cm}^{-1}$ were obtained. The conductivities were relatively high even when the PAN content was low. For example, the composite containing only about 10 wt % PAN had a conductivity of 0.2 S cm^{-1} . Conductivities as high as 2.2 S cm^{-1} were observed when the PAN fraction was 40 wt %.

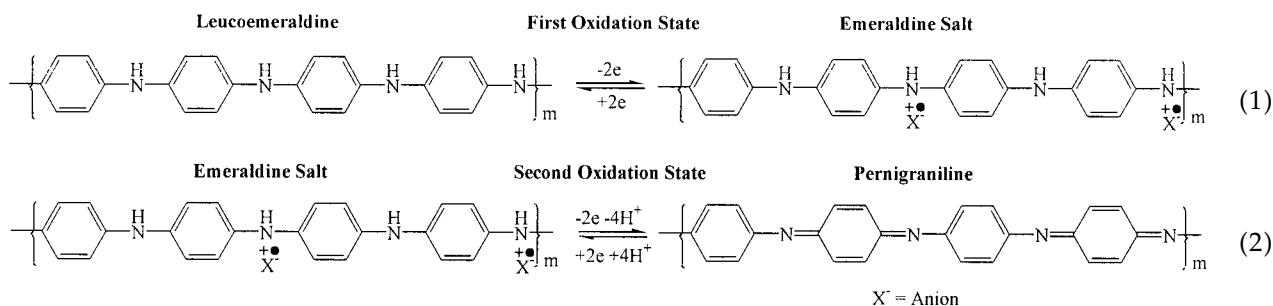
It is assumed that a connected interpenetrated network was formed with PAN chains as charge-transfer species throughout the network.

Characterization of the composite

Electroactivity

PAn composite coatings were prepared on the working electrode, as described in the Experimental section, and cyclic voltammograms were recorded.

Well-defined responses attributed to the oxidation and reduction of PAn (A/A' and B/B'), as shown in eqs. (1) and (2), respectively, were observed (Fig. 2). It is well known that during every scan, a polymer undergoes two separate oxidation and reduction processes:



The first response (A/A') is due to the oxidation of leucoemeraldine to emeraldine and vice versa. The response B/B' may be attributed to the oxidation and reduction of emeraldine to pernigraniline (fully oxidized form) and vice versa [as shown in eq. (1)]. The separation²⁶ between the redox couples was about 600 mV, larger than that observed for PAn (500 mV). Also, a linear dependence of the peak current on the scanning rate in the range of 25–100 mV S⁻¹ was observed, indicating that the reaction was not diffusion-controlled but was due to surface bond species.

As observed previously, responses due to PAn breakdown products were observed upon excursion to the potentials necessary to fully oxidize PAn.²⁷

The oxidation–reduction peak current was recorded for composites containing different percentages of PAn (Fig. 3). As the percentages of PAn increased, the peak currents (both anodic and cathodic) also increased. With PAn percentages of over 30 wt %, no significant change in the electroactivity was observed. However, when the percentage of PAn was reduced to 20 wt % or less, a significant loss in electroactivity was observed (Fig. 3).

UV–vis spectra

The UV–vis spectrum of PAn/poly(BuA–VAc) in an aqueous medium exhibited overlapping bands be-

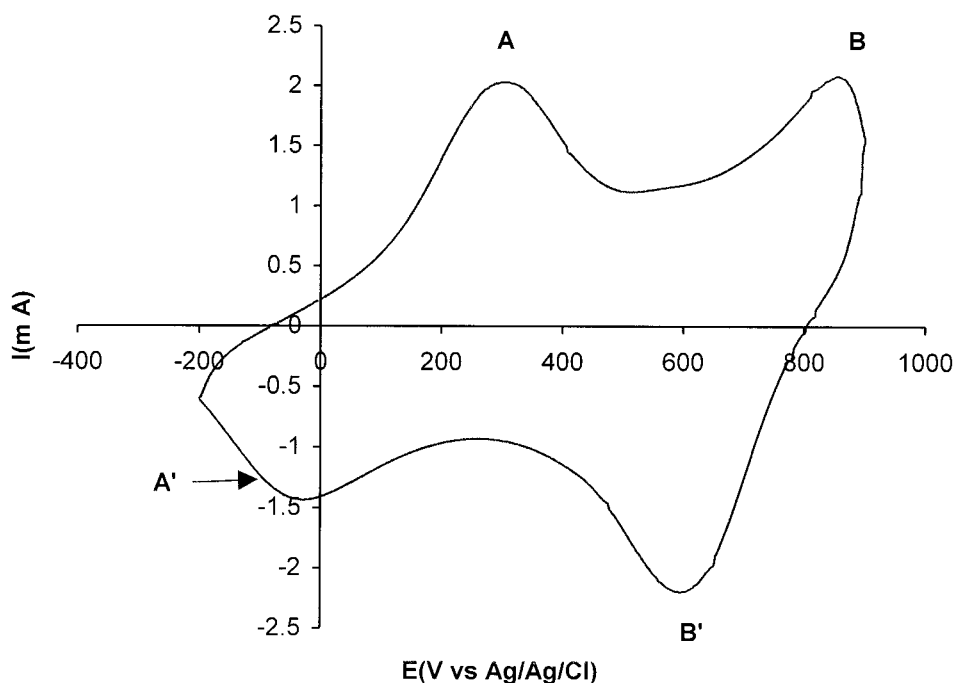


Figure 2 Typical cyclic voltammogram showing oxidation–reduction PAn/poly(BuA–VAc) composite films cast from a water-based dispersion of the composite on a gold-film electrode. The polymer was scanned in a 0.5M HCl solution (polymer thickness $\approx 25 \mu\text{m}$; amount of PAn in the composite = 25/2 w/w; scanning rate = 100 mV S⁻¹).

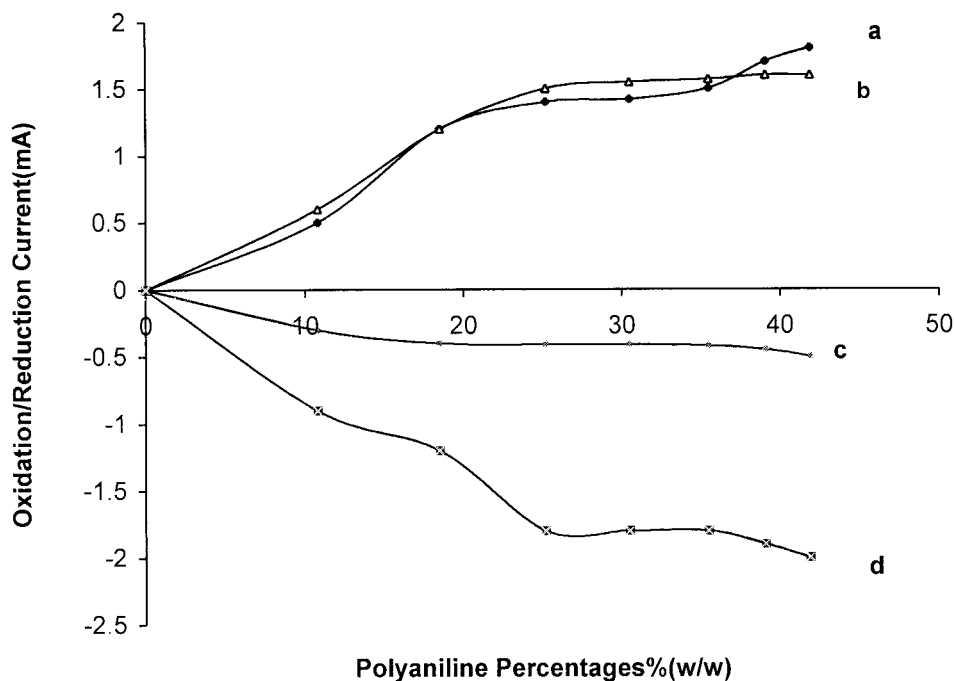


Figure 3 Oxidative–reductive peak currents obtained for PAN/poly(BuA–VAc) composite films with different PAN percentages: (a) first anodic peak current, (b) second anodic peak current, (c) first cathodic peak current, and (d) second cathodic peak current. The films were cast from a water-based dispersion of the composite on a gold-film electrode. The polymer was scanned in a 1M HCl solution (scanning rate = 50 mV s^{-1} ; polymer thickness $\approx 25 \mu\text{m}$).

tween 300 and 400 nm that could be assigned to the π – π^* transition (Fig. 4). Another strong peak at about 750 nm suggests that PAN in this composite material was in a compact-coil conformation.²⁸

Mechanical properties

Smooth, flexible, mechanically robust films were obtained by the casting of freestanding films of PAN/

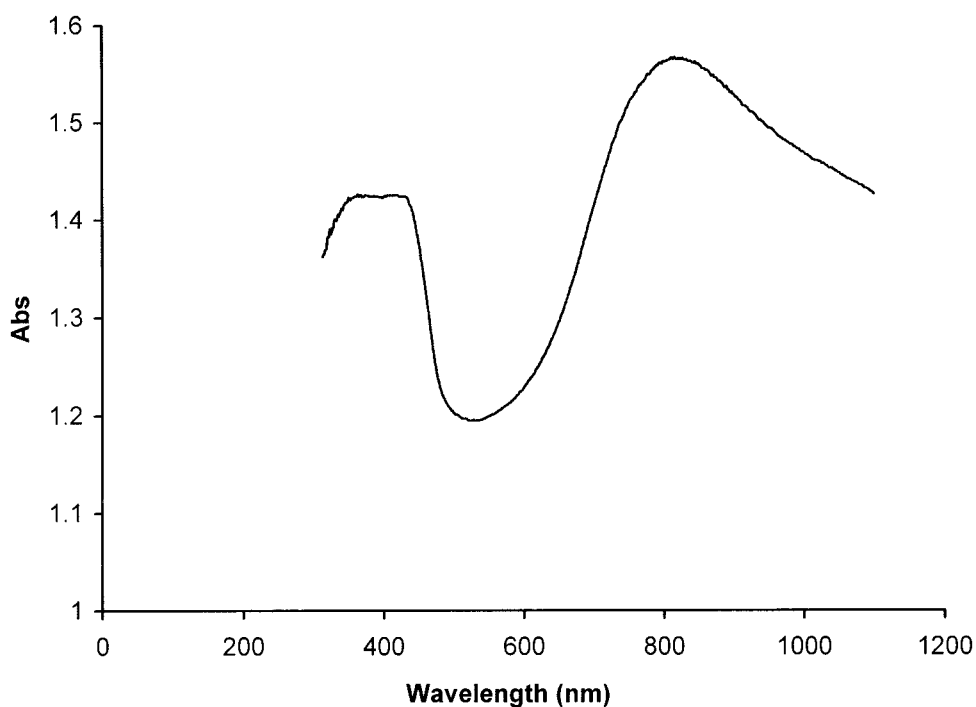


Figure 4 UV–vis spectrum obtained for a diluted aqueous solution of the PAN/poly(BuA–VAc) composite with a PAN percentage of 30.5 wt %.

poly(BuA-VAc). The mechanical properties of the films with different percentages of PAN were determined (Table III). As the PAN content of the composite increased, the tensile strength decreased. Small amounts of PAN disturbed the poly(BuA-VAc) network, and this resulted in lower values for the tensile strength. With the PAN percentages increasing further (Table III), a more uniform combination of PAN/poly(BuA-VAc) resulted in an increased tensile strength. A similar trend for other PAN composites has also been reported.²⁹

The value obtained for the elongation at break (Table III) indicated that the films could be stretched up to 900%, and so the composite could be considered elastomeric. The values of Young's modulus obtained for the composite were very low, indicating that the materials were very soft and flexible. However, with increasing PAN content, the films became less flexible, as verified by the values of Young's modulus (Table III).

Adhesion testing

The adhesion of the PAN-containing composite was determined after a film was cast onto a steel plate. With a tape testing method, the adhesion of each sample was assessed qualitatively on a 0–5 scale (Table IV). The adhesion was affected by the PAN content of the composite. Pure PAN adhered weakly to the steel surface (Table IV), but the adhesion was significantly improved by the introduction of poly(BuA-VAc). Composite coatings containing up to 35% PAN could be classified as 5B, with 0% of the area removed during the adhesion test. However, films with more PAN failed to adhere strongly to a steel surface. The composites with PAN loadings as low as 20% retained their conductivity and electroactivity and showed excellent adhesion performance.

CONCLUSIONS

PAN/poly(BuA-VAc) composites were prepared through the chemical polymerization of aniline in an

TABLE III
Mechanical Properties of PAN/Poly(BuA-VAc) Composite Films

PAN (wt %)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
0.0	0.150	5.2	—
10.8	0.014	3.2	900
18.5	0.039	3.7	850
25.2	0.050	4.4	460
30.5	0.143	6.6	240
35.5	0.100	4.8	120

The mechanical properties of the samples were measured as described in the Experimental section.

TABLE IV
Adhesion Properties of PAN/Poly(BuA-VAc) Composite on a Steel Plate

PAN (wt %)	Classification	Area removed
10.8	5B	0%T(none)
18.5	5B	0%T(none)
25.2	5B	0%T(none)
30.5	5B	0%T(none)
35.5	5B	0%T(none)
39.1	4B	<5%T(none)
41.9	3B	5–15%
43.8	2B	15–35%
46.4	1B	35–65%
49.0	0B	>65%
Pure Copolymer	5B	0%T(none)
Pure PAN	5B	>65%

The adhesion properties of the samples were measured as described in the Experimental section.

emulsion containing poly(BuA-VAc). The conductivity of the films cast from dispersions depended on the PAN percentages of the composite. Conductivities of 0.2–2.2 S cm⁻¹ were obtained. The procedure produced an elastomeric material that could be stretched up to 900%. The elastomeric material had good electrochemical properties resembling those of pure PAN, as confirmed by cyclic voltammetry studies. The composite films showed excellent adhesion to steel.

Because there is no similar report in the literature, the direct comparison of our results with other composites of PAN is impossible. Although a similar level of conductivity was observed in comparison with that of other composites of PAN,^{20–22,29} processability, superior mechanical properties, and excellent adhesion were the main features of the composite. These features are expected to introduce more applications for conducting PAN in the future.

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