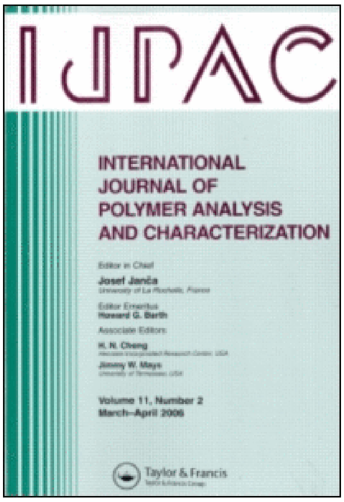

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Characterization of Chemical Grafting of Polyaniline onto Wool Fiber

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Polyaniline grafted wool fiber was prepared by a chemical polymerization method using potassium peroxydisulfate (PDS) as a lone initiator under optimized conditions. The simultaneous homopolymer formed, as well as physisorbed polyaniline (PANI) onto wool fiber, were removed by a systematic procedure. The isolation procedure was quantified through UV–visible spectroscopy. The isolated grafted PANI-wool fiber was tested by conductivity measurements cyclic voltammetry, and IR spectroscopy to provide further evidence for chemical grafting.

Keywords: Wool; Polyaniline; Grafting

INTRODUCTION

There has been considerable interest in conducting polymers, which are prepared by chemical[1,2] and electrochemical[3,4] methods because of their versatile applications in different fields.[5] Conducting polymer-coated textile fibers find use in EMI shielding.[6] Bhadani *et al.*[7] grafted conducting polymers onto various natural fibers by an electrochemical method. Conducting polymer-coated fibers are used as composite electrodes and show improved battery performance.[8] Polyacetylene has been deposited on carbon fiber to obtain a composite with high mechanical strength.[9] Polypyrrole was coated on nonconducting substrates like acrylic fibers and used for gas sensors.[10]

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Patil[11] grafted polyaniline (PANI) onto EPDM rubber and compared the thermal stability of the pure polymer, grafted polymer and the blend. Kalhori *et al.*[12] grafted PANI onto silica surfaces and characterized it through SEM, DSC and FTIR spectroscopy. Zoppi and Paoli[13] prepared a blend of polypyrrole and EPDM rubber and reported improval mechanical properties of the blend.

Mano *et al.*[14] synthesized a blend of PVC and polypyrrole and studied thermal, mechanical and electrochemical behaviors. Abraham and co-workers[15] prepared a blend of polyaniline/nylon 6 which was characterized by FTIR, XRD, TGA, conductivity measurement and UV–visible spectroscopy. Yang *et al.*16 synthesized a polypyrrole–polypropylene composite films and obtained XPS, SEM and conductivity values. Tasi *et al.*[17] grafted PANI onto nitrile rubber and characterized it in using cyclic voltammetry, IR spectroscopy, TGA and SEM. Goh and co-workers[18] prepared a blend of PANI with PVAc and characterized the blend through TGA, FTIR, XPS and electrical conductivity measurement. Ma *et al.*[19] synthesized a conductive PANI composite with a secondary doping phenomena and reported ESR, UV-visible and FTIR spectroscopic results. Paoli and co-workers[20] synthesized a conductive polymeric composite through chemical and electrochemical polymerization methods. Jin *et al.*[21] prepared a composite between PANI and PET fiber through adherent deposition method and reported SEM, WAXS, DSC and electrical conductivity results.

When aniline is polymerized in the presence of a reactive substrate, simultaneous homopolymerization of aniline is also expected. In the present study, a systematic experimental approach for the complete isolation of homopolymer from grafted fiber is made and the resulting grafted fiber is characterized.

EXPERIMENTAL

Aniline (Fischer AR) (distilled under vacuum), potassium peroxydisulfate (PDS) (CDH AR), wool fiber (a gift sample from J.K. Synthetics, Kota Rajasthan) (Soxhlet extracted with acetone to remove any organic impurities and dried at room temperature), *N*-methyl pyrrolidone (NMP), (SRL AR), formic acid (CDH AR), acetone (Ranbaxy AR) and ammonia (Fischer AR) were used.

Graft Copolymerization

Wool (W_1 g) was immersed in a given concentration of HCl (1.00 M) in a polymer tube and thermostated for 30 min. The required amount of monomer (aniline) was added and deaerated for 30 min. The time of adding the oxidizing agent, PDS, was taken as the starting time for the reaction. After a definite interval of time the reaction was arrested by blowing air into the polymer tube to freeze further reactions. The grafted wool fiber along with the homopolymer were filtered from the reaction mixture by using a G4 sintered crucible and washed well with 1.00 M HCl several times. The mixture was allowed to stand in aqueous ammonia for several hours and then dried at 80°C for 4 h and weighed. This gives the total weight of the grafted fiber (in neutral form) along with the homopolymer (W_2 g).

Isolation of Grafted Fiber from Homopolymer

The mixture of the grafted wool and PANI, the homopolymer, was Soxhlet extracted with NMP for 24 h to separate the homopolymer. The extraction process was repeated until the separation of the homopolymer from the grafted sample was completed and was ascertained by a colorless filtrate. The fiber was dried in vacuum to constant weight (W_3 g). The difference between W_3 and W_1 gives the weight of the grafted polymer. The difference between W_2 and W_3 gives the weight of the homopolymer. With the use of the mixture of grafted PANI and homopolymer obtained in the graft copolymerization, a similar procedure was used of following the weight of the mixture (W_2) without adding ammonia (to neutralize the doped polymer).

Rate Measurements

The percentage grafting and percentage efficiency were calculated as follows:

$$\%\ \text{grafting} = \frac{W_3 - W_1}{W_1} 100$$

$$\%\ \text{efficiency} = \frac{W_3 - W_1}{\text{Weight of monomer used}} 100$$

where W_1 is the weight of pure wool fiber and $W_3 - W_1$ is the weight of grafted polymer.

Cyclic Voltammetric Study

Cyclic voltammograms were recorded by using BAS 100 A Electrochemical Analyzer. The PANI-grafted wool fiber was washed again with NMP to remove any possible adhering PANI homopolymer and dried in vacuum. It was made into a paste by dissolving it in formic acid and was dip coated onto a Pt-working electrode. Cyclic voltammograms were recorded for the dip-coated wool-*g*-PANI film on the Pt electrode at various sweep rates by sweeping the potentials in the range 0.00–0.90 V vs. Ag/AgCl reference by using 1.00 M HCl as the background electrolyte.

Conductivity Measurements

Conductivity of both the grafted and pure backbone (wool) was measured by using Keithley 617 programmable electrometer instrument. Approximately 1-cm length of wool fiber (grafted or ungrafted) was taken and its two ends were connected to two poles of the Keithley electrometer. Current was impressed across these poles and the conductivity value was noted from the programmable instrument.

UV–Visible Study

UV–visible spectra were recorded by using Shimadzu UV 2401 PC model instrument for the PANI-grafted wool fiber at various Soxhlet extraction time intervals during the isolation of the grafted fiber.

IR Spectroscopy

IR spectrum was recorded using an FT-IR Bruker Equinox 55 model instrument for both grafted and pure wool fiber using pressed KBr pellets.

RESULTS AND DISCUSSIONS

Graft copolymerization of PANI onto wool fiber was carried out in 1.00 M HCl under a nitrogen atmosphere. The preliminary experiments indicated the simultaneous formation of homopolymer, PANI. This was evident from the formation of a green-color powder of PANI along with the transformed green-colored wool fiber. Earlier workers doing electrochemical graft copolymerization of PANI onto different substrates have not made any attempt to systematically separate such PANI homopolymer from the reaction medium and determining physisorbed PANI on the fiber. The quantitative nature of the isolation method was verified by following the course of PANI during the extraction procedure using UV–visible spectroscopy. Aliquots after different time intervals of extraction were analyzed for the PANI content from the spectrum.[22] The visible spectra of the aliquot sample recorded for various extraction time intervals are presented in Figure 1. The extent of change of PANI content was measured at 624 nm. After 24 h of repeated extraction, PANI was absent, indicating the complete

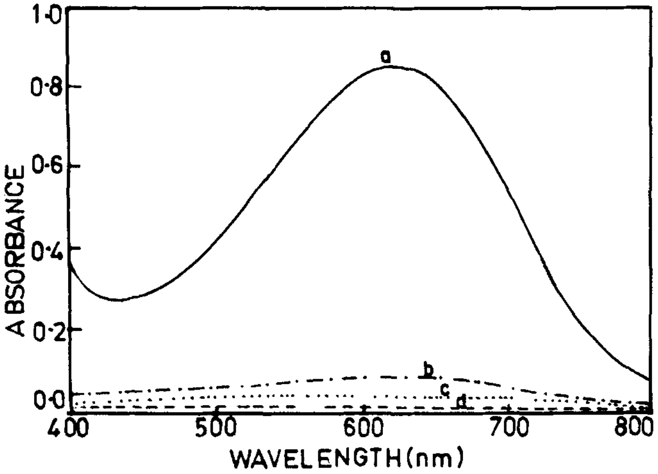

FIGURE 1 Visible spectrum of polyaniline solution after different time intervals of Soxhlet extraction with NMP. (a) 1 h; (b) 3 h; (c) 5 h; (d) 12 h.

removal of both homopolymer and physisorbed PANI on the grafted fiber.

After isolation, the grafted fiber was kept in NMP for several hours and the weight changes in the grafted fiber were followed. It is interesting to observe that there was no weight loss after this treatment. The percentage grafting and efficiency are presented in Table I. The isolation procedure adopted without ammonia treatment gave similar results, except for an initial 15–20% weight changes for the ammonia treated samples.

Cyclic Voltammetric Study

Cyclic voltammograms were recorded for the wool-*g*-PANI film coated on a Pt-working electrode at potentials between 0.00 and 0.90 V vs. Ag/AgCl reference electrode in 1.00 M HCl as a background electrolyte at various sweep rates. The cyclic voltammograms are given in Figure 2. For the purpose of identifying PANI, the cyclic voltammograms recorded for the PANI homopolymer films on the Pt-working electrode are also presented in Figure 3. A close comparison of these cyclic voltammograms show characteristics of PANI in the grafted fiber. The steady increase in peak current of grafted fiber with sweep rate indicates the stable nature of PANI-grafted film on the Pt surface, similar to PANI homopolymer film.

FTIR Spectral Study

The FTIR spectrum of pure wool fibre is shown in Figure 4a. The FTIR spectrum of the PANI-grafted wool fiber (Figure 4B) exhibited strong absorption throughout the range 4000–500 cm^{-1}. NH stretching vibrational mode and aromatic CH stretching vibrational mode are found at 3300 and 3040 cm^{-1}, respectively. The vibrational bands of secondary aromatic amine and imine nitrogen appear at 1300 and 1160 cm^{-1} respectively. This assignment has already been made for PANI by earlier workers.[23] The presence of PANI in the grafted fiber hence adds evidence for the chemical grafting of PANI onto wool. There are other peaks observed in the spectrum (Figure 4b) which corresponds to the vibrational spectrum of wool backbone fiber.

TABLE I Effect of aniline concentration, PDS concentration and weight of fiber on percentage grafting and efficiency

$[ANI]^a$ (mol L^{-1})	*Grafting* (%)	*Efficiency* (%)	$[PDS]^b$ (mol L^{-1})	*Grafting* (%)	*Efficiency* (%)	*Weight of fiber*^{c} (W_1 g)	*Grafting* (%)	*Efficiency* (%)
0.20	0.80	0.80	0.005	0.40	0.06	0.10	0.90	0.06
0.30	0.95	0.56	0.010	0.65	0.09	0.15	1.53	0.16
0.40	1.25	0.48	0.015	1.55	0.22	0.25	1.60	0.28
0.50	1.75	0.36	0.020	2.30	0.33	0.30	1.70	0.37
0.60	2.70	0.28	0.025	2.55	0.37	0.35	1.91	0.48

[a,b] Weight of fiber = 0.20 g; [b,c] [Aniline] = 0.30 mol L^{-1}; [a,c] [PDS] = 0.01 mol L^{-1}; [a,b,c] [HCl] = 1.00 mol L^{-1}, Temperature = 45°C.

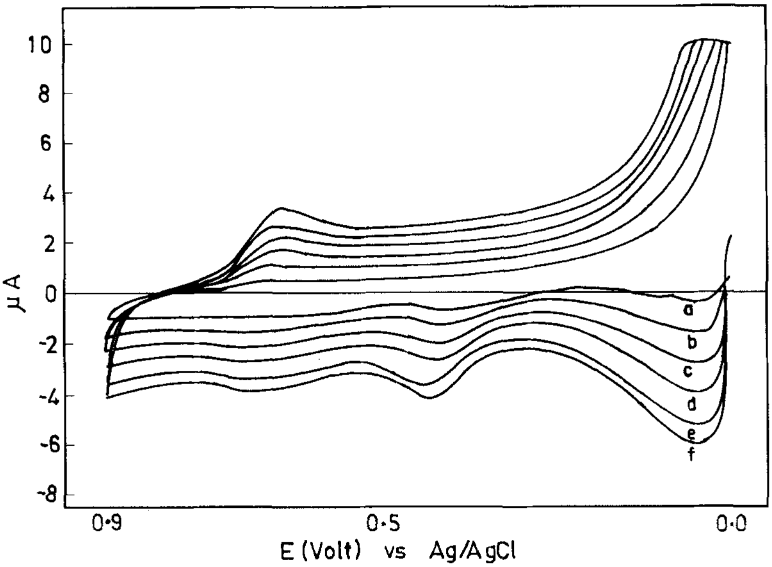

FIGURE 2 Cyclic voltammograms of polyaniline-grafted wool fiber film on Pt-working electrode in 1.00 M HCl as a background electrolyte using Ag/AgCl reference electrode at various sweep rates. (a) 200 mV/s; (b) 400 mV/s (c) 600 mV/s; (d) 800 mV/s; (e) 1000 mV/s; (f) 1200 mV/s.

Conductivity Measurements

Conductivity data are presented in Table II for wool and PANI-grafted wool fiber. The conductivity was found to be higher for the PANI-grafted wool fiber and proportionally increases with increase in percentage grafting. The conductivity measurement confirms the chemical grafting of PANI onto wool fiber. On comparison of the conductivity of the already reported PANI,[24,25] the value obtained for the grafted sample was found to be much lower. This is quite reasonable since these PANI units are being grafted onto an insulating backbone (wool) which can substantially lower the conductivity values.

CONCLUSION

The homopolymer, PANI, which is physisorbed on the grafted fiber can be successfully separated completely after 24 h of repeated Soxhlet

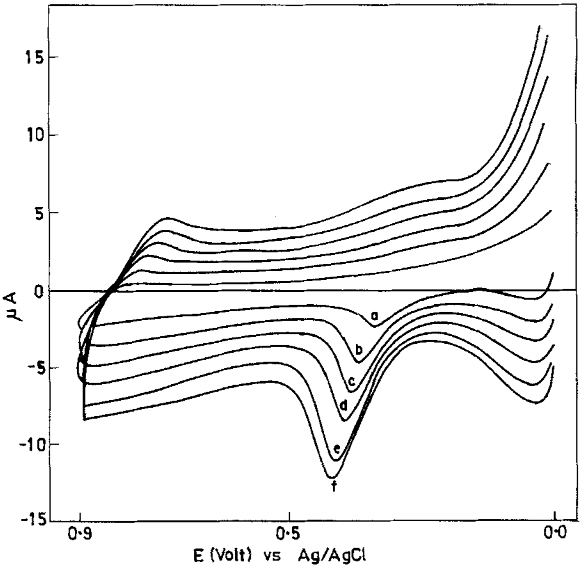

FIGURE 3 Cyclic voltammograms of PANI film on Pt-working electrode in 1.00 M HCl as a background electrolyte using Ag/AgCl reference electrode at various sweep rates. (a) 200 mV/s; (b) 400 mV/s; (c) 600 mV/s; (d) 800 mV/s; (e) 1000 mV/s; (f) 1200 mV/s.

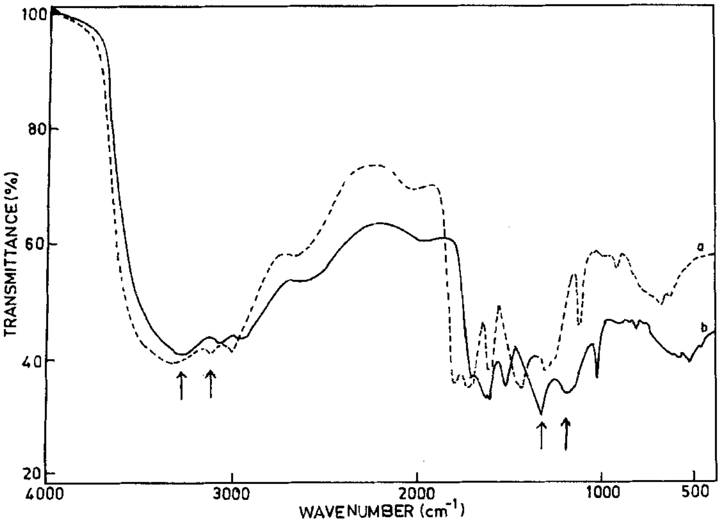

FIGURE 4 (a): FTIR spectrum of pure wool fiber (-----). (b): FTIR spectrum of PANI-grafted wool fiber (—).

TABLE II Conductivity measurements

Polymer	*Grafting* (%)	*Conductivity* × 10^6 ($Ohm^{-1} cm^{-1}$)
Wool	—	0.0012
Wool-*g*-PANI	0.65	120
	2.50	300

Polymerization conditions: [aniline] = 0.30 mol L^{-1}, [PDS] = 0.01 mol L^{-1}, Weight of wool = 0.20 g, [HCl] = 1.00 mol L^{-1}, Time = 30 min, Temperature = 45°C.

extraction with NMP and the conductivity of the textile was improved by graft copolymerization. The cyclic voltammetry, IR spectroscopy add evidence for chemical grafting of PANI onto wool.

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