

Synthesis and Characterization of Novel Conducting Composites of Fe₃O₄ Nanoparticles and Sulfonated Polyanilines

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ABSTRACT: Surface charged iron oxide (Fe₃O₄) nanoparticles were used for the synthesis of sulfonated polyaniline (SPAN)-Fe₃O₄ nanocomposites (SPAN/Fe₃O₄-NCs). 2,5-diaminobenzenesulfonic acid (DABSA) and 2-aminobenzenesulfonic acid (ABSA) were independently polymerized with aniline to form SPAN. The structure of the composites was characterized by means of transmission electron microscopy (TEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectra, conductivity and magnetic properties. TEM

reveals that Fe₃O₄ nanoparticles are “glued” with SPAN in the composite. TGA indicates that SPAN/Fe₃O₄-NCs are having better thermal stability. The room temperature conductivity of SPAN/Fe₃O₄-NCs is higher than that of pristine PANI and SPAN. SPAN/Fe₃O₄-NCs exhibits magnetic behavior. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 4127–4134, 2007

Key words: sulfonated polyaniline; Fe₃O₄ nanoparticles; nanocomposites

INTRODUCTION

Studies on conducting polymers are continued to be the subject of intense investigations worldwide by many research groups.¹ Among the conducting polymers, polyaniline (PANI) has been particularly interested due to its ease of doping, simple preparation, moderate conductivity, environmental stability, and low cost. Besides that, PANI has wide applications in electronic, optical, and magnetic materials such as information storage, rechargeable batteries, electrochromic display devices, sensors, and nonlinear optics.^{2–8}

Nanocomposites consist of metal nanoparticles and conducting polymers have been synthesized and they have unique magnetic, electrical, optical, catalytic, and rheological properties.^{9–13} Besides that, applications in the areas of electrochromic devices, torque transducers, controllable dampers, sensors and actuators, and molecular engineering of nanomotors^{14–16} are envisaged for these nanocomposites. For example, Somani et al.¹⁷ synthesized PANI-TiO₂ composite by *in situ* method and probed the piezoresistive functions. Parvatikar et al.¹⁸ synthesized PANI/CeO₂ composite studied for humidity sensor

applications. Zhang et al.¹⁹ synthesized core-shell Al₂O₃/PANI composite and used in corrosion protective applications.

Nanoparticles of iron oxides (Fe₂O₃ and Fe₃O₄) have received great deal of research attention due to their utilities as magnetic materials. Magnetic polymeric particles usually are the result of covering magnetic iron oxide via physical interactions with macromolecules as well as chemical interactions between the inorganic oxide surface and the organic material.²⁰ Such particles are well-known materials and have been widely studied due to their applications in high-density data storage, ferrofluids, enzyme immobilization, bioseparation, drug delivery, immunoassays, and removal of industrial toxic waste.^{20–22} Nanocomposites of conducting polymers and Fe₃O₄ nanoparticles both electrical and magnetic properties have potential applications to electrochemical devices, electromagnetic interference shielding (EMI), electromagneto-rheological fluid, and microwave-absorbing materials. Conducting polymers can effectively shield electromagnetic waves generated from an electric source; where as, electromagnetic waves from a magnetic source, especially at low frequencies, can be effectively shielded only by magnetic materials. Thus, composite has both conducting and magnetic components particularly used as EMI shielded materials. The reports are scarce on the preparation of composites of magnetic nanoparticles with conducting polymers.^{23–26}

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Nguyen and Diaz²⁴ performed polymerization of sodium pyrrole-*N*-propylsulfonate (PyS) in the presence of FeCl₃ to obtain the Fe₂O₃/poly(PyS) composite. However, the Fe₂O₃/poly(PyS) nanocomposite was insoluble in common organic solvents. Bidan and coworkers²⁵ employed electropolymerization to embed a “chelating ligand” onto Fe₂O₃ via pre-coating the nanoparticles with polypyrrole (PPy). Polymerization of aniline using a mixture of FeCl₂ and FeCl₃ and subsequent treatment with aqueous KOH resulted in the iron oxide/polypyrrole (PPy) composite.²⁶ Annapoorni and Tandon²⁷ prepared the nanocomposites of PPy and iron oxide using ferric nitrate as an oxidant in 2-methoxy ethanol. They also studied the pressure and humidity sensitivity of polypyrrole/iron oxide.²⁸ Likewise, reports are available on the synthesis of nanocomposites of iron oxide with polymers such as polystyrene, poly(D, L-lactide), poly(styrene-*co*-maleic anhydride), etc.^{29–32}

The use of PANI for potential applications is restricted due to its poor physical and mechanical properties and it is not soluble in common solvents.^{8,33} To overcome these problems, PANI derivatives have been developed according to various methods: (1) post treatment of PANI base, (2) the incorporation of side groups into the main chain, and (3) the homopolymerization of suitable aniline derivatives or the copolymerization of aniline with the derivatives.^{34–36} Among these derivatives, sulfonated polyanilines (SPANs) has attracted much attention because of its better processability, thermal stability, self-doping, solubility, better electroactive, and optical properties.^{36–38} SPANs and its composites suitable materials for applications in rechargeable batteries, light-emitting diodes, sensors, junction devices, electromagnetic shielding materials, corrosion protection and enzymatic activity.^{38–40}

The aim of the present study is to synthesize the SPAN/Fe₃O₄ nanocomposites (SPAN/Fe₃O₄-NCs) with conducting and magnetic properties. The SPAN/Fe₃O₄-NCs were prepared by copolymerizing aniline with sulfonic acid containing aniline derivatives in the presence of Fe₃O₄ nanoparticles. 2, 5-diaminobenzenesulfonic acid (DABSA) and 2-aminobenzenesulfonic acid (ABSA) were independently used to prepare SPAN/Fe₃O₄-NCs. SPAN from DABSA and ABSA are designated as SPAN-D and SPAN-A respectively. The morphological, structural, thermal, electrical, and magnetic properties of the SPAN/Fe₃O₄-NCs are compared with the properties of pristine polymers.

MATERIALS AND EXPERIMENTAL

Materials

Aniline (reagent grade, Oriental) was distilled under reduced pressure and stored below 0°C. Other

reagents, DABSA, ABSA, iron (II) chloride tetrahydrate, iron (III) chloride hexahydrate, ammonium peroxydisulfate (APS), sodium hydroxide, hydrochloric acid, and ethanol were of analytical grade and used without further purification. Milli-Q purified water was used for all experiments.

Synthesis of surface charged Fe₃O₄ nanoparticles

Surface charged Fe₃O₄ nanoparticles were synthesized in aqueous solution via coprecipitation method. In this method, 5.2 g (0.79M) of FeCl₃·6H₂O and 2.0 g (0.40M) of FeCl₂·4H₂O were dissolved in 25 mL of 0.40M HCl. Solution of mixed iron-salts was added drop-wise into 250 mL of 1.5M NaOH under vigorous stirring for 30 min. The colloid solution was centrifuged at 4000 rpm, washed with water and dried in oven for 6 h. A brownish black powder (Fe₃O₄) was obtained.

Synthesis of SPAN/Fe₃O₄ nanocomposites [SPAN/Fe₃O₄-NCs]

DABSA and ABSA were independently used to prepare SPAN by polymerization of aniline with DABSA and ABSA.

Synthesis of SPAN-D/Fe₃O₄ nanocomposite [SPAN-D/Fe₃O₄-NC]

SPAN-D/Fe₃O₄-NC was prepared through polymerization of a mixture of DABSA and aniline in the presence of Fe₃O₄ nanoparticles. The synthetic procedure is as follows: 0.2 g of Fe₃O₄ nanoparticles were dispersed in 80 mL of ethanol/water (1 : 4 by volume) and sonicated for 20 min. To this dispersion, 0.491 g of DABSA and 1.905 g of aniline were added and polymerization was carried out by dropwise addition of 20 mL (1 : 4 v/v ethanol : water) of 1M APS solution (in 1N HCl) at 5°C for 24 h. A green colored precipitate (SPAN-D/Fe₃O₄-NC) was obtained. The precipitate was washed with ethanol/water (4:1) and dried at vacuum.

Synthesis of SPAN-A/Fe₃O₄ nanocomposites [SPAN-A/Fe₃O₄-NC]

SPAN-A/Fe₃O₄-NC was prepared as described procedure for synthesis of SPAN-D/Fe₃O₄-NC. In synthesis, 0.452 g of ABSA and 1.905 g of aniline were used.

For a comparative purpose, SPANs [SPAN-D and SPAN-A] were synthesized in the absence of Fe₃O₄ nanoparticles under similar conditions. Pristine PANI also synthesized in the absence of ABSA or DABSA monomers and Fe₃O₄ nanoparticles.

Characterization

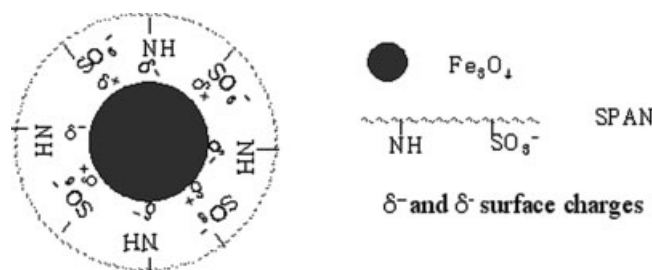
Fourier transform infrared (FTIR) spectra of fine powdered samples were recorded with a Bruker IFS 66v FTIR in the region of 400–4000 cm⁻¹ using KBr pellets. Morphology and particle sizes of composites were noticed using transmission electron microscope (TEM) operating at an accelerating voltage of 100 kV. The samples were prepared as follows: Fine powdered samples were dispersed in ethanol under ultrasonication, and then one drop of the dilute suspension of colloid was deposited on a carbon-coated copper grid and placing in the Phillips CM-30 TEM. The particle sizes in morphology were measured using a scale bar in each micrograph. Thermogravimetric analysis (TGA) of fine powdered samples was carried out on Dupont 9900/2100 TGA instrument at a heating rate of 10°C/min under a nitrogen atmosphere over a temperature range of 30–750°C. X-ray diffraction (XRD) patterns of fine powdered samples were recorded on Rigaku Diffractometer with Nickel filtered CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The conductivities of compressed pellets of the polymers and SPAN/Fe₃O₄ nanocomposites were measured by a standard four-probe vander Pauw method at room temperature. Compact discs with a diameter of 12.5 mm and a thickness of 0.25 mm were used. Conductivity was determined using the average readings taken at different points on the pressed pellets. To study the magnetic properties, as synthesized fine powdered samples were filled in gelatin capsules that have a small diamagnetic background, and M-H loop measurements were performed from -6T to +6T using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-X 1) at room temperature.

RESULTS AND DISCUSSION

We have specifically synthesized Fe₃O₄ nanoparticles having excess of surface charges to facilitate interactions between groups in SPAN and charges on Fe₃O₄ nanoparticles and to form SPAN/Fe₃O₄-NCs. Fe₃O₄ nanoparticles were prepared via coprecipitation method which involves multiple steps including deprotonation, hydrolysis, oxidation, precipitation, nucleation, crystallization, dehydroxylation and/or dehydration.⁴¹ In this process, Fe₃O₄ is obtained as a result of the coprecipitation of ions of Fe²⁺ and Fe³⁺ by the addition of solution containing the mentioned ions (molar ratio Fe⁺³/Fe⁺² = 2) to NaOH solution (pH of dispersion ~ 11) at room temperature. The process of synthesis of Fe₃O₄ nanoparticles can be described according to following Eq.



The surface charged Fe₃O₄ nanoparticles were further used to prepare nanocomposites with SPAN.



Scheme 1 Probable formation of SPAN/Fe₃O₄ nanocomposite via interactions between surface charges in Fe₃O₄ nanoparticles and groups in SPAN.

Results (discussed in the later part) demonstrate that amine or imine sites in SPAN interact with excessive negative charges (from oxygen ions) on the surface of Fe₃O₄ nanoparticles. Additionally, the oxygen-deficient shells in Fe₃O₄ nanoparticles are positively charged and favors interactions with the negatively charged sulfonic acid groups in SPAN. Hence, nanostructure for SPAN/Fe₃O₄-NCs (Scheme 1) was expected.

Morphology

Figure 1 represents the TEM images of nanocomposites [Fig. 1(a,b)] and Fe₃O₄ nanoparticles [Fig. 1(c)]. As shown in Figure 1(c), Fe₃O₄ nanoparticles are existing as agglomerates due to high surface area and magneto dipole–dipole interactions between the particles. Figure 1(c) shows that the diameter of Fe₃O₄ particles is around 5 nm. TEM images of SPAN-D/Fe₃O₄-NC [Fig. 1(a)] and SPAN-A/Fe₃O₄-NC [Fig. 1(b)] indicate that Fe₃O₄ nanoparticles (dark shaded) are entrapped into the matrix of conducting polymer (light shaded). After addition of oxidant (APS) to dispersion containing Fe₃O₄ and monomers, polymerization starts, SPAN with amino and sulfonic groups interacts with surface charges of Fe₃O₄ nanoparticles. As a result, SPAN encapsulated Fe₃O₄ composite can be formed. We compared the structural, thermal, electrical and magnetic properties of SPAN/Fe₃O₄ nanocomposites with that of pristine polymers (SPANs and PANI) (see in the next section).

XRD

Figures 2 and 3 present the XRD patterns of the SPAN-D/Fe₃O₄-NCs, SPAN-A/Fe₃O₄-NCs, pristine SPAN-D, SPAN-A, PANI, and Fe₃O₄ nanoparticles. XRD pattern of Fe₃O₄ nanoparticles [Fig. 2(d)] displays several relatively strong reflection peaks. Main diffraction peaks are assigned: $2\theta = 17.7^\circ, 30.3^\circ, 35.7^\circ, 43.2^\circ, 53.4^\circ, 57.1^\circ, \text{ and } 63.0^\circ$.⁴² The average diameter of the Fe₃O₄ nanocrystal was estimated by using the Scherrer's equation.⁴³

$$D = K\lambda/\beta \cos \theta$$

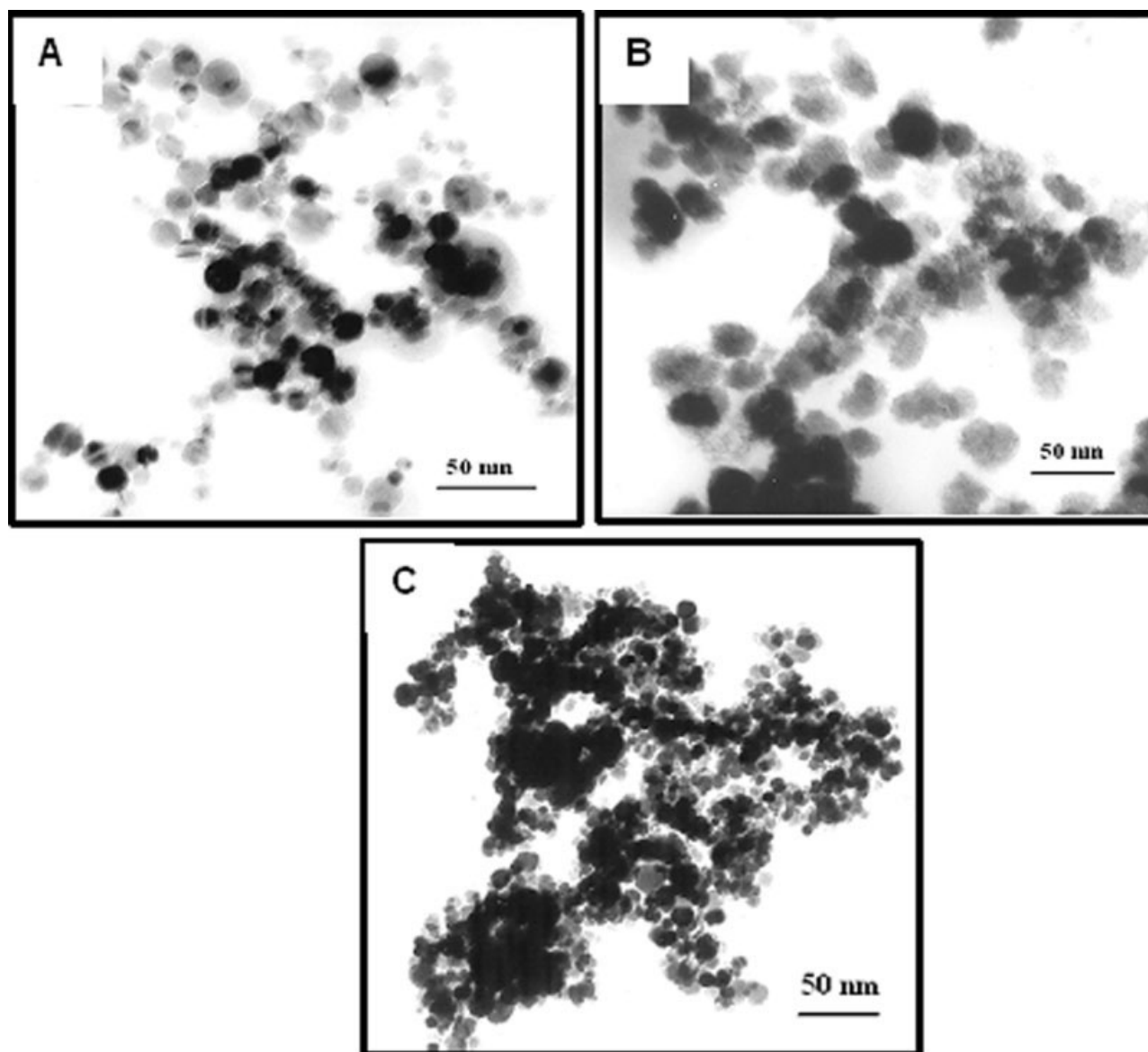


Figure 1 TEM images of (a) SPAN-D/Fe₃O₄-NC, (b) SPAN-A/Fe₃O₄-NC, and (c) Fe₃O₄ nanoparticles.

where λ is the X-ray wavelength (1.5406 Å), K is the shape factor, D is average diameter of the crystals (in angstroms), θ is the Bragg angle (in degrees), β is the full width at half-maximum (fwhm) expressed in units of 2θ . The value of “ K ” depends on several factors, including the Miller index of the reflecting plane and the shape of the crystals.^{44,45} If the shape is unknown, K is often assumed as 0.89. The reflecting peak at $2\theta = 35.7^\circ$ is used to estimate the average size (~ 5 nm) of the Fe₃O₄ nanoparticles. It is consistent with TEM results [Fig. 1(c)].

XRD patterns of SPAN-D/Fe₃O₄-NC [Fig. 2(a)] and SPAN-A/Fe₃O₄-NC [Fig. 3(a)] are different from that of pristine polymers [Figs. 2(b,c) and 3(b)]. Pristine PANI has three broad peaks at $2\theta = 15.3^\circ$, 21.0° , and 25.3° [Fig. 2(c)] that are characteristics of amorphous PANI. The peaks observed in X-ray pattern of

PANI were somewhat changed in the position of diffraction pattern of SPANs. SPAN-D/Fe₃O₄-NC and SPAN-A/Fe₃O₄-NC [Figs. 2(a) and 3(a)] show additional peaks at 35.7° , 43.2° , 57.1° , and 63.0° indicates existence of Fe₃O₄ nanoparticles in the composites. These peaks are absent in the diffraction pattern of pristine SPAN-D, SPAN-A, and PANI [Figs. 2(b,c) and 3(b)].

Structural characterization

A comparison of FTIR spectra (Figs. 4 and 5) of SPAN/Fe₃O₄-NCs, SPANs, PANI informs that there are differences in the molecular level interactions between the components in the composites. PANI [Fig. 4(c)] shows the absorption peaks at 3410, 1571, 1480, 1302, 1239, 1133, and 805 cm⁻¹.⁴⁶ The peaks at

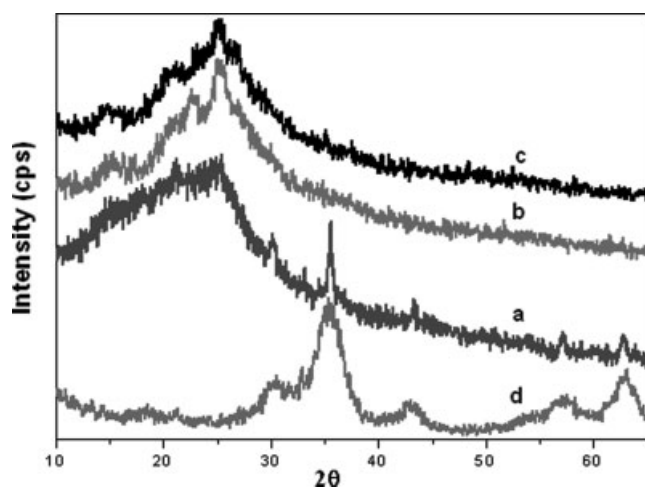


Figure 2 XRD patterns of (a) SPAN-D/Fe₃O₄-NC, (b) SPAN-D, (c) PANI, and (d) Fe₃O₄ nanoparticles.

3410 cm⁻¹ is attributed to N-H stretching mode, 1571 and 1480 cm⁻¹ are attributed to the characteristic C=C stretching of the quinoid and benzenoid rings, the peaks at 1302 and 1239 cm⁻¹ are assigned to C-N stretching modes of the benzenoid ring, the broad and strong peak around 1133 cm⁻¹ is associated with vibrational modes of -N=quinoid=N (Q refers to the quinoid ring), and 805 cm⁻¹ is attributed to C-H out of plane vibration. The striking difference between the spectra of SPANs [Figs. 4(b) and 5(b)] and pristine PANI [Fig. 4(c)] explained as follows. The formation of sulfonated polyanilines (SPAN-D and SPAN-A) is confirmed by appearing of new bands near 695 and 1040 cm⁻¹. These bands were absent in the spectra of PANI [Fig. 4(c)]. The bands were present in the spectra of SPAN-D and SPAN-A at 1040 cm⁻¹ is attributed to the stretching

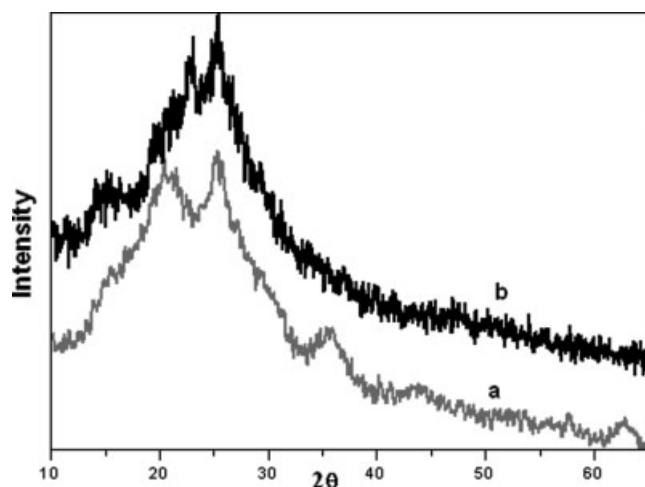


Figure 3 XRD patterns of (a) SPAN-A/Fe₃O₄-NC, and (b) SPAN-A.

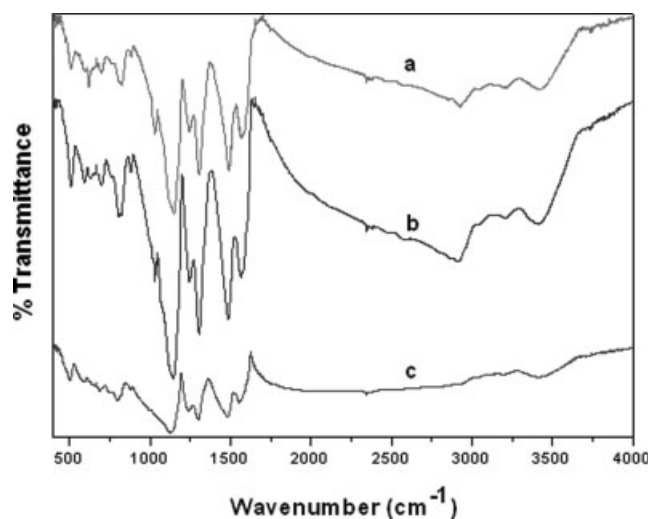


Figure 4 FTIR spectra of (a) SPAN-D/Fe₃O₄-NC, (b) SPAN-D, and (c) PANI.

vibrations of the SO₃ moiety.⁴⁷ The band at 695 cm⁻¹ is attributed to the C=S aromatic stretching vibration. Similarly, these bands were present in the spectra of SPAN/Fe₃O₄-NCs [Figs. 4(a) and 5(a)]. The bands 1570, 1480, 1040, and 695 cm⁻¹ observed in the spectrum of SPAN-D or SPAN-A are shifted to lower wave numbers by 5 cm⁻¹, respectively, in the spectra of nanocomposites [Figs. 4(a) and 5(a)]. This is due to change of degree of electron delocalization by the interaction of Fe₃O₄ nanoparticles with SPANs.

Elemental analysis results shows that the sulfonated degree (S/N ratio) of SPANs (SPAN-D or SPAN-A) and SPAN/Fe₃O₄ composites is around 0.25, which is much higher than that of PANI (<0.01). Very low level sulfonation of ANI units induced by the oxidant takes places during polymerization. Higher S/N ratio indicates that formation of SPANs.

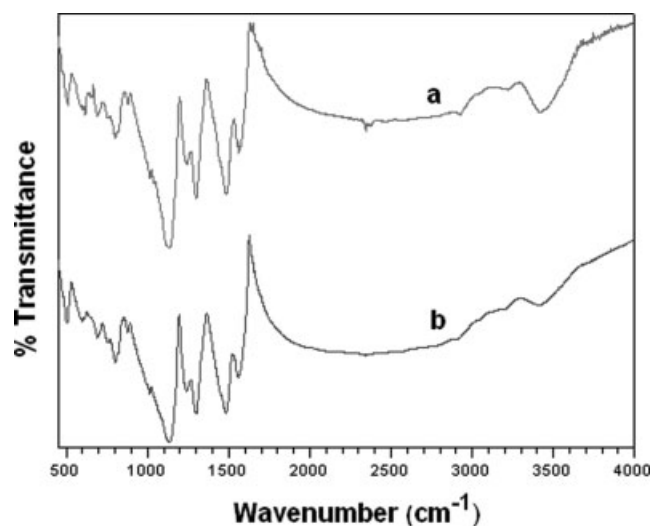


Figure 5 FTIR spectra of (a) SPAN-A/Fe₃O₄-NC, and (b) SPAN-A.

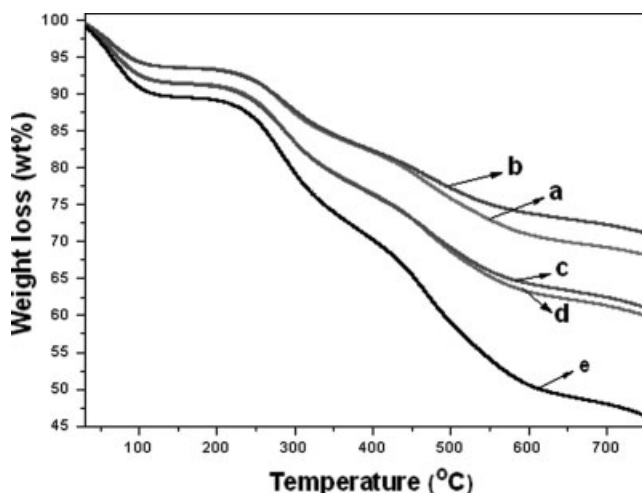


Figure 6 Thermograms of (a) SPAN-D/ Fe_3O_4 -NC, (b) SPAN-A/ Fe_3O_4 -NC, (c) SPAN-D, (d) SPAN-A, and (e) PANI.

Thermal behavior

The thermal stability of the polymers and composites were evaluated with the help of TGA. Figure 6 represents the thermograms of (a) SPAN-D/ Fe_3O_4 -NC,

(b) SPAN-A/ Fe_3O_4 -NC, (c) SPAN-D, (d) SPAN-A and (e) PANI. PANI or SPANs can undergo degradation via two or three steps: loss of water/moisture, decomposition of dopants or SO_3^- units, and decomposition of polymer chains.^{48,49} SPAN/ Fe_3O_4 -NCs, SPANs (SPAN-D or SPAN-A) and PANI show 3–10% weight loss at the temperature between 60 and 110°C, which is attributed to the loss of water/moisture. The amount of water present in the polymer or composites was not considered for determining onset and decomposition temperatures. Onset temperature was determined according to previous reports.⁵⁰ The onset temperatures (5% weight loss) of the SPAN/ Fe_3O_4 composites [Fig. 6(a,b)], SPANs [Fig. 6(c,d)], and PANI [Fig. 6(e)] are 279, 268, and 259°C, respectively. Composites lost weight 5.63% in the temperature between 280 and 480, whereas SPANs and PANI lost 8.12 and 9.83% at the same temperature range. Less decomposition of SPANs (SPAN-D or SPAN-A) over the PANI is due to presence of sulfonic groups in the SPANs backbone. 64.3% of original weight is stable upto 750°C in the case of SPAN/ Fe_3O_4 -NCs, whereas SPANs and PANI have original weight of 52.7 and 36.75%, respectively. This indicates that SPAN/ Fe_3O_4 composites have better

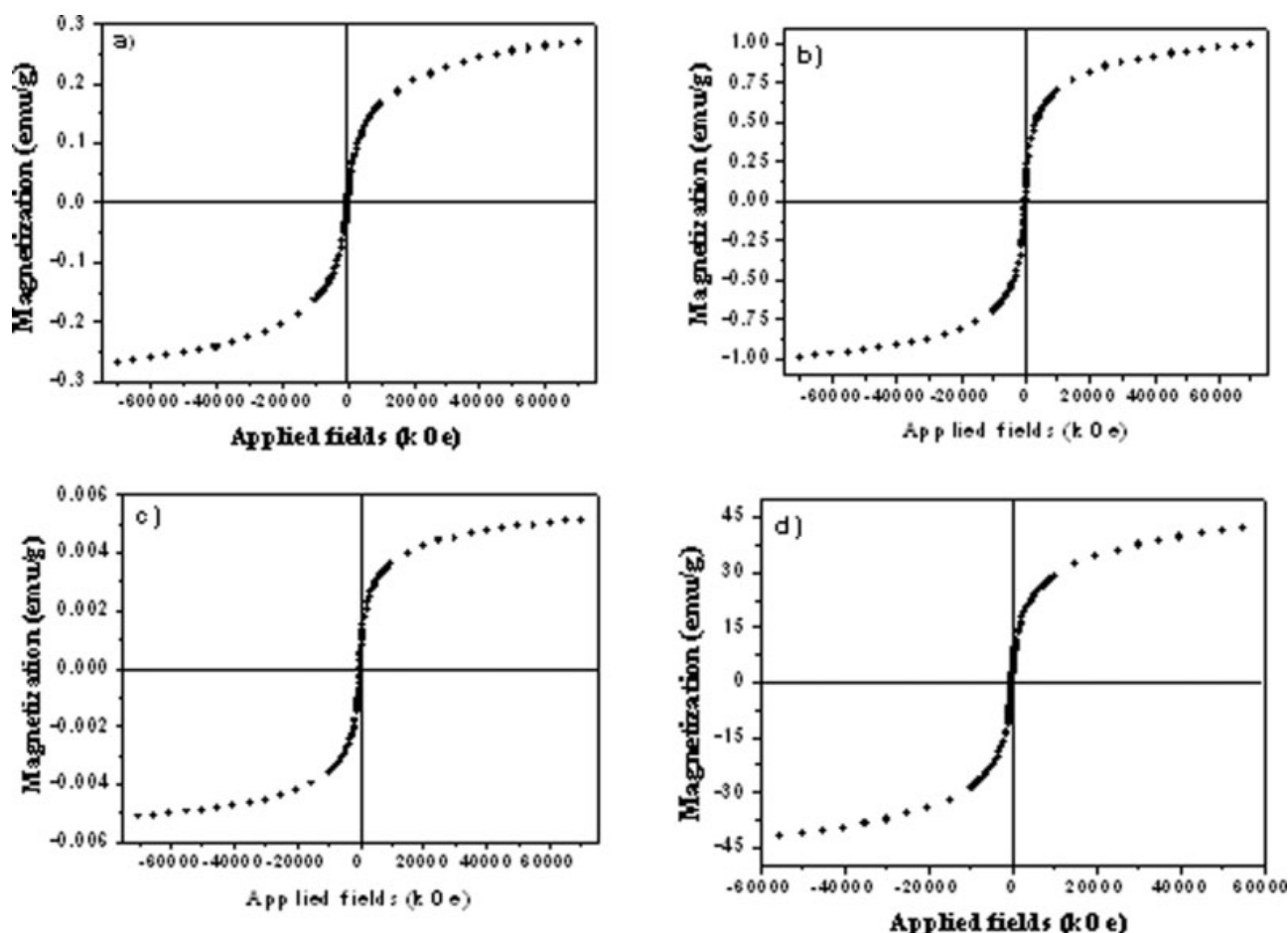


Figure 7 Magnetic curves of (a) SPAN-D/ Fe_3O_4 -NC, (b) SPAN-A/ Fe_3O_4 -NC, (c) SPAN-D, and (d) Fe_3O_4 nanoparticles.

TABLE I
Magnetic Properties of Nanocomposites and Polymers

Sample	M_s (emu/g)	M_r (emu/g)
Fe ₃ O ₄	41.8	11.4
SPAN-D/Fe ₃ O ₄ -NC	0.29	0.06
SPAN-A/Fe ₃ O ₄ -NC	0.98	0.37
SPAN-D	0.005	0.001
SPAN-A	0.007	0.002

thermal stability due to quite strong interactions of sulfonic and amino groups in SPANs with surface changes of Fe₃O₄ nanoparticles.

Magnetic properties

Figure 7 shows the room temperature magnetic curve of (a) SPAN-D/Fe₃O₄-NC, (b) SPAN-A/Fe₃O₄-NC, (c) SPAN-D, and (d) Fe₃O₄ nanoparticles, respectively. The values of magnetic saturation (M_s), remnant magnetization (M_r) of composites and pristine polymers are presented in Table I. As shown in Table I, Fe₃O₄ nanoparticles shows superparamagnetic behavior ($M_s = 41.8$ emu/g). On the other hand, pristine polymers SPAN-D and SPAN-A are antimagnetic. The magnetic behavior observed in the composites is due to encapsulation of magnetic Fe₃O₄ nanoparticles into conducting polymer matrix.

Conducting properties

The room temperature conductivity of SPAN-D/Fe₃O₄-NC (6.4×10^{-2} S cm⁻¹), SPAN-A/Fe₃O₄-NC (6.92×10^{-2} S cm⁻¹) was higher than that of pristine PANI (5.12×10^{-4} S cm⁻¹), SPAN-D (2.85×10^{-3} S cm⁻¹) and SPAN-A (2.01×10^{-3} S cm⁻¹), respectively. The increase in conductivity of SPAN-D or SPAN-A is over pristine PANI, possibly because of self-doping by the —SO₃H moiety. The higher conductivity of the composites is due to (i) encapsulated Fe₃O₄ nanoparticles in polymer matrix are favoring the conductance of electrons, and (ii) diffraction peaks of nanocomposites from XRD results shows that molecular chains in the composites are in more ordered state and are more crystalline than pristine polymers. This observation is consistent with previous report in which conductivity of polymer is increased when polymer chains are more ordered.⁵¹

To study the effect of agglomeration, conductivity and magnetic saturation of composites were measured in certain time intervals. The magnetic saturation and conductivity of the composites almost retained same even after one and two months, which indicates that little agglomeration observed in the morphology of the composites (TEM images) was do

not significantly affect on their conducting and magnetic properties.

CONCLUSIONS

The positive and negative surface charges on the surface of Fe₃O₄ nanoparticles can be effectively utilized to bind a conducting polymer having suitable complementary charges in the backbone structure. SPAN meets this requirement and composites of SPAN with Fe₃O₄ nanoparticles are prepared using such interactions. As a result of molecular level interactions between Fe₃O₄ particles and SPAN, the nanocomposites show different thermal, electrical and magnetic properties than their pristine polymers. Conductivity of composites is 1 order of magnitude higher than that of SPANs. SPANs/Fe₃O₄ nanocomposites show magnetic behavior.

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