Inverted Emulsion Cast Electrically Conducting Polyaniline–Polystyrene Blends

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ABSTRACT: An inverted emulsion method for the synthesis of electrically conductive polyaniline–polystyrene blends of different compositions (10, 30, 50, 70, and 85%, wt/wt) is described. Polymerization of aniline is carried out in chloroform in the dispersed phase by using benzoyl peroxide as a novel oxidant and sulfosalicylic acid as the dopant. The blends synthesized with benzoyl peroxide as the oxidant are of high purity and the excess benzoyl peroxide is readily removed with acetone, which is used to break the emulsion and precipitate the polymer. The absorption spectra, FTIR, FT Raman, and electron paramagnetic resonance spectroscopy confirm the presence of polyaniline in the salt form and polystyrene in the blend. The thermal stability of polyaniline salt decreases with an increase in polystyrene content in the blend. The SEM studies show that the particles of polyaniline–sulfosalicylic acid are dispersed on the polystyrene surface. The blends of polyaniline–polystyrene prepared by the present method were found to display conductivities as high as 0.5–0.1 S cm^{-1}. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1163–1171, 2002

Key words: polyaniline; polystyrene; conductive blends; benzoyl peroxide; inverted emulsion

INTRODUCTION

Polyaniline has emerged as a promising material, as an electrically conducting polymer,[1] because of its unique electrical and optical properties, good environmental stability, and easy chemical and electrochemical synthesis. A major limitation of conducting polyaniline has been its unprocessibility. Numerous studies were carried out for the improvement of its processibility. In this context, conducting polyaniline blends with classical polymers [polystyrene, poly(methyl methacrylate), etc.] have attracted much attention[2] because these blends may exhibit good mechanical properties, so also, the desirable electrical properties. The blends of polyaniline with conventional polymers were prepared chemically by *in situ* polymerization,[3] solution blending,[4] colloidal dispersion[5] and melt processing,[6] and also electrochemically.[7]

In recent years, emulsion polymerization of aniline has come to the forefront.[8,9] The emulsion method for the synthesis of polyaniline–polystyrene blends was reported by Ruckenstein and Yang,[10] who employed benzene–water emulsion by using HCl as the dopant and ammonium persulfate as the oxidant. We recently reported the synthesis of conducting polyaniline by

inverted emulsion method consisting of an emulsion of water with chloroform as a nonpolar organic solvent.[11] Emulsion polymerization is essentially a compartmentalized polymerization reaction taking place in a large number of reaction loci dispersed in a continuous external phase. The reaction is carried out in a heterogeneous system. Inverse emulsion polymerization, on the other hand, consists of an aqueous solution of the monomer that is emulsified in a nonpolar organic solvent, for example, chloroform, as in the present study, and the polymerization is initiated with an oil-soluble initiator, for example, benzoyl peroxide, as in the present case.

There have been some reports on the synthesis of polyaniline–polystyrene blends. As mentioned above, Ruckenstein and Yang[10] have synthesized polyaniline–polystyrene blends by using the emulsion method with HCl as dopant and ammonium persulfate as oxidant in a solution of polystyrene in benzene and aniline in water. They studied the effect of reaction conditions on the conductivity and morphology of the blends synthesized. The blends were also synthesized by the codissolution process by using bis(2-ethyl hexyl)hydrogen phosphate as the dopant species.[12,13] The dependence of electrical conductivity on temperatures of synthesis was investigated. The X-ray photoelectron spectroscopy and morphology of these blends were also examined by Jousseaume et al.[12] Recently, solution cast blends of polyaniline with polystyrene were synthesized under different conditions by Roichman et al.,[14] employing dodecyl benzene sulfonic acid (DBSA) as the dopant and ammo-

TABLE I
The Conductivity and Electronic Absorption Data of Polyaniline–Polystyrene Blends

Polymer/Blend[a]	Yield (g)	Conductivity (S cm^{-1})	Absorption Spectra (λ, nm)							
			Solution				Solid			
Pani–SSA Salt	5.30	5.9×10^{-1}	330	440	630	825				
Pani (90)–PS (10)	5.41	4.2×10^{-1}	314	—	611	—	274	454	680	855
Pani (70)–PS (30)	9.17	1.4×10^{-1}	310	—	611	—	276	450	682	830
Pani (50)–PS (50)	12.71	4.1×10^{-2}	308	—	612	—	276	458	—	835
Pani (30)–PS (70)	20.67	1.9×10^{-3}	345	—	606	—	274	447	—	882
Pani (15)–PS (85)		2.3×10^{-5}	320	—	625	—				

[a] As in Table I.

nium persulfate as the oxidant. They found a correlation between morphology and synthesis conditions.

In this article, a method is described for the synthesis of polyaniline–polystyrene blends by using chemical oxidative polymerization by the inverted emulsion pathway. The oxidizing agent presently used is benzoyl peroxide, which is widely used as an initiator in many polymerization reactions. Traditionally, ammonium persulfate was used in the polymerization of aniline. Because ammonium persulfate is a strong oxidizing agent and polymerization of aniline is exothermic, controlling the reaction temperature is rather difficult and, consequently, polymers with a wide distribution of molecular weights result. The removal of inorganic by-product (ammonium sulfate) from the produced polymer is also difficult. This limitation is overcome by using an organic oxidant such as benzoyl peroxide, which is a relatively milder oxidant than ammonium persulfate, and the excess of oxidant can easily be removed from the polymer by using solvents such as acetone, which is used as a nonsolvent in the inverse emulsion process. Thus, polyaniline blends containing 10, 30, 50, 70, and 85 wt/wt of polystyrene were prepared by the inverted emulsion pathway. The blends obtained were characterized by various spectroscopic and other physicochemical methods.

EXPERIMENTAL

Materials

Aniline (Merck) was purified by distillation under reduced pressure prior to use. Polystyrene (M_w = 90,850) was of commercial grade. Polystyrene (Spectral Chemicals, Mumbai, India), sodium lauryl sulfate, sulfosalicylic acid, benzoyl peroxide, sodium sulfate (all S. D. Fine chemicals, Boisar India), chloroform, acetone, and DMSO (all Merck, Mumbai, India) were analytical grade reagents and were used as procured.

Synthesis of polyaniline–polystyrene blends

The blends were prepared by using an inverted emulsion pathway where an aqueous solution of sodium

lauryl sulfate and the dopant sulfosalicylic acid constitutes the continuous phase and a chloroform solution of aniline and polystyrene with the oxidant benzoyl peroxide constitutes the dispersed phase. The initial ratio of polyaniline to polystyrene required to prepare the blend was determined by the inverted emulsion polymerization of aniline under identical conditions but without polystyrene. From the yield of polyaniline–sulfosalicylic acid salt obtained, the amount of aniline monomer required to prepare a given blend was determined.

In a typical experiment, 24.2 g of benzoyl peroxide in 100 mL of chloroform was taken. To this solution, 100 mL chloroform solution containing 2.3 g of polystyrene and 4.5 mL of aniline was added. Added to the above solution with stirring was 4.5 g of the emulsifier (sodium lauryl sulfate) in 50 mL of water. To this milky-white emulsion, 250 mL of aqueous solution of 0.1M sulfosalicylic acid was added dropwise with continuous stirring over a period of half an hour to polymerize aniline and dope the polyaniline formed. During the progress of the reaction, the colorless emulsion turns green in color. The reaction was allowed to proceed for 24 h. The organic phase was separated and washed repeatedly with water. The dark-green chloroform solution of the blend was then treated with anhydrous sodium sulfate to remove the excess water. The viscous organic solution was then added to 1.5 L of acetone to break the emulsion and precipitate the blend. It was filtered, washed with acetone, and dried in vacuum for 36 h to obtain a dark-green powder. Polyaniline–polystyrene blends containing varying ratios (10, 30, 50, 70, and 85 wt/wt) of the two constituent polymers were synthesized. The yield of the blends was between 90 and 95% in each case (Table I).

Measurements

For recording the UV–visible absorption spectra, a Hitachi UV-3400 spectrophotometer was used. The spectra were measured in dimethylsulfoxide (DMSO) at three different concentrations and checked for consistency. Solid-state UV–visible spectra were recorded

in nujol mull on a quartz plate. The FTIR spectra were recorded by using a Bruker FTIR Multiscan 15 Sf II instrument by the KBr pellet technique. The FT Raman spectra were recorded for the powder sample by using a Bruker RFS100/S spectrometer and a Nd^{3+}:YAG laser with 30 mW power at the sample. The electron paramagnetic resonance (EPR) spectra were recorded by using a Varian E109 spectrometer operating in the X-band. The sample tube was evacuated before recording the spectrum to remove the moisture. To obtain the g value and spin concentration, the EPR spectra of the samples and charred dextrose as a standard were measured under identical conditions of microwave frequency (9.05 GHz), microwave power (2 mW), modulation frequency (100 kHz), field set (3280 G), scan range (100 or 200 G), modulation intensity (1 Gpp), modulation time (0.064 s), and scan time (200 s). The spin concentration was determined by comparing the area under the EPR signal of polyaniline with that of charred dextrose. The calculated areas are likely to be within 5% of the true value.[11] The electrical conductivity (dc) of the samples was measured at ambient temperature by using the four-probe method (pressure contact) on pressed pellets obtained by subjecting the powder to a pressure of 50 kN. The error in the resistance measurements under galvanostatic condition using a Keithley model 220 programmable current source and a Kiethley model 195A digital voltammeter is <2%. The consistency in the measurements was checked by measuring the resistance twice for each pellet and for a batch of two pellets for each sample. The SEM measurements were carried out by using a JEOL (Japan) JSM 480A scanning electron microscope. The TGA and DTA were recorded up to 600°C by using a STA 851E thermal analysis system at a heating rate of 20°C min^{-1} in nitrogen atmosphere.

RESULTS AND DISCUSSION

Polyaniline blends synthesized by the inverse emulsion polymerization are soluble in organic solvents such as DMSO and dimethylformamide. Also, the blends obtained are of high purity. The excess benzoyl peroxide is readily removed with acetone, which is used to break the emulsion. The infrared spectra show qualitatively that the polyaniline content increases with increase in the aniline/polystyrene ratio.

Spectroscopy

FTIR spectroscopy

The spectra of polyaniline sulfosalicylic acid salt and the blends of compositions polyaniline (70)–polystyrene (30) and polyaniline (30)–polystyrene (70) are presented in Figure 1. The spectra of the blends were analyzed by monitoring the relative intensities of the bands around 3450, 3200, and 1120 cm^{-1} characteristic of polyaniline salt, 1675 cm^{-1} band characteristic of the dopant sulfosalicylic acid, and the bands near 759 and 699 cm^{-1} due to polystyrene. The intense band at 1490 cm^{-1} was not taken into consideration as it appears in the spectrum of both polyaniline salt and polystyrene. An increase in the amount of polystyrene in the feed is reflected by an increase in the intensity of the peaks near 690 and 750 cm^{-1} and also a decrease in the intensity of the bands at 3400 and 3200 cm^{-1}. The spectrum of the blend with 85% polystyrene is similar to that of polystyrene.

The broad band in the polyaniline–sulfosalicylic acid salt spectrum at 1573 cm^{-1} is assigned to the C=C ring-stretching vibration of the benzenoid form. The band at 1466 cm^{-1} is assigned to C—N stretching of the quinoid ring, which is caused by the protonation of the polyaniline matrix by the dopant. The band at 1219 cm^{-1} in the salt spectrum corresponds to the symmetric component of the C=C (or C—N of the benzenoid ring) stretching mode. The doping of polyaniline leads to the formation of —Q=N$^+$H— groups. The positive charge on the polymer chain may lead to an increase in the dipole moment of the molecule and consequently result in the increased intensity of the IR bands.[15] In the IR spectrum of the salt, a fairly intense band appears at 945 cm^{-1}, which is absent in the spectrum of the base. It may be assigned to the ring-breathing mode of the benzenoid group, which becomes infrared active on protonation. A shift is observed for the above bands in the spectra of the blends. The bands at 1573, 1219, 1123, and 789 cm^{-1} in the polyaniline salt spectra shift by 10–20 cm^{-1} to higher frequencies in the blends. However, the band at 945 cm^{-1} shifts to a lower wavenumber by about 10 cm^{-1}. These shifts suggest some chemical interaction taking place between polystyrene and polyaniline chains. In addition to the above bands, the spectrum of the polyaniline salt also exhibits two new bands in the IR spectrum of the salt, as mentioned above, an intense band near 3450 cm^{-1} and a medium intensity band at 3230 cm^{-1}, assignable to asymmetric and symmetric stretching modes of —NH$_2^+$, respectively. The —NH$^+$ stretching band may overlap with the asymmetric NH$_2$ stretching, thus accounting for the broadness of the band. The —NH$_2^+$ group may also be involved in hydrogen bonding. The band at 1693 cm^{-1} is due to the carboxylic group characteristic of the dopant sulfosalicylic acid. The presence of SO$_3^-$ group is supported by the appearance of a band around 590 cm^{-1} in the spectrum of the polyaniline–sulfosalicylic acid salt attributed to the degenerate bending mode of SO$_3^-$ group. The IR spectrum of polystyrene shows characteristic peaks at 1598, 1495, 1452, 759, and 699 cm^{-1}.
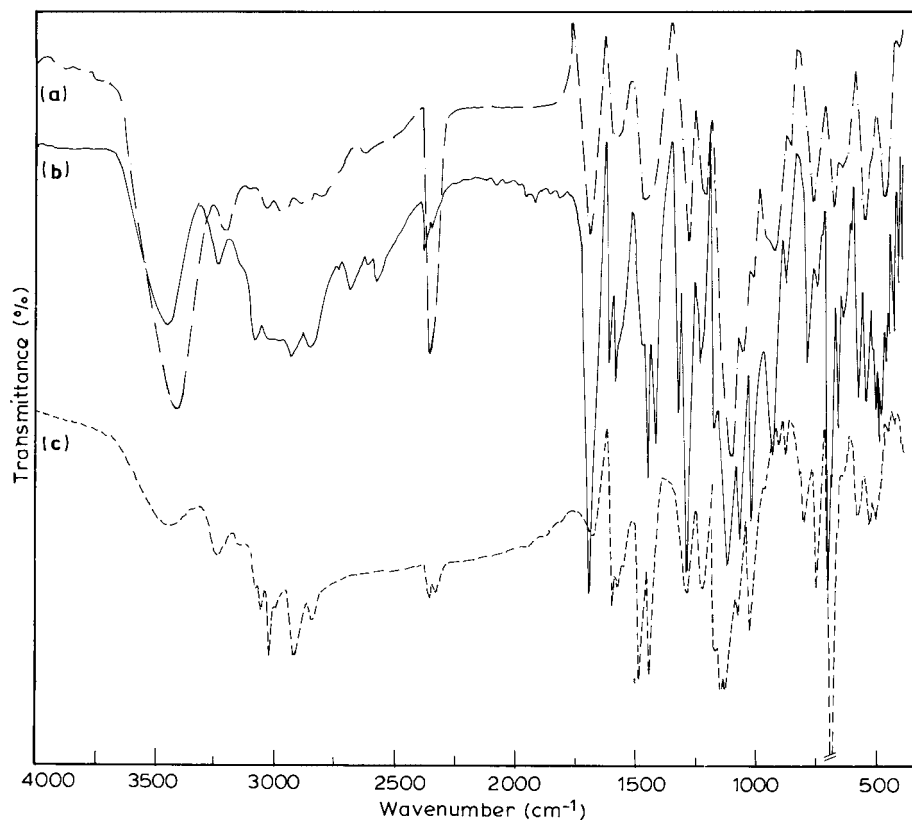
Figure 1 The FTIR spectra of (a) polyaniline–sulfosalicylic acid salt; (b) polyaniline (70)–polystyrene (30); and (c) polyaniline (30)–polystyrene (70) blends.

FT Raman spectra

The FT Raman spectra were recorded for polyaniline–sulfosalicylic acid salt, polystyrene, and their blends and the data are given in Table I. The band at 1617 cm^{-1} is due to a Raman active —C≡C— ring stretching vibration of the quinoid structure.[16] It appears as a weak- to medium-intensity band in the spectrum of the salt. The Raman bands at 1594 and 1504 cm^{-1} are assigned to C—C ring stretching vibrations of quinoid and benzenoid rings, respectively; the 1352 and 1268 cm^{-1} bands correspond to the N—H and the C—H bending modes, respectively. The polyaniline salt undergoes protonation of the amine nitrogen on doping leading to the formation of Q=N$^+$H species. The 1332 cm^{-1} band may be assigned to C (ring)—N stretching mode.

The polyaniline–polystyrene blends show Raman spectra similar to that of polyaniline–sulfosalicylic acid salt. Polystyrene shows very intense Raman bands at 3058, 2907, 1602, 1033, and 1002 cm^{-1}. Interestingly, the most intense band at 1002 cm^{-1} found in the spectrum of polystyrene is absent in the spectra of the blends even in the case of the blend polyaniline (15)–polystyrene (85). It is observed that with an increase in the polystyrene content, the relatively broad band around 1585 cm^{-1} in the blend becomes narrower, whereas the band at 1170 cm^{-1} becomes broad

and unsymmetrical. The less intense peak observed at 1445 cm^{-1} in the spectrum of the salt decreases further in intensity as the amount of polyaniline in the blend decreases, and in the blend polyaniline (30)–polystyrene (70), it vanishes nearly completely. A similar kind of behavior is noticed for the peak at 1617 cm^{-1}, observed as a shoulder in the spectrum of polyaniline–sulfosalicylic acid salt. An increase in the amount of polyaniline in the blend causes a decrease in the intensity and narrowing of the peak at 1585 cm^{-1}. A similar narrowing of the 1350 cm^{-1} band in the spectra of the blends occurs when the polystyrene content increases.

Absorption spectra

The absorption spectra of polyaniline–polystyrene blends dissolved in DMSO were recorded. The absorption maxima are listed in Table II. The spectra of polyaniline–sulfosalicylic acid salt, the polyaniline (90)–polystyrene (10) blend recorded in DMSO and in the solid state, are given in Figure 2. The absorption spectrum helps to detect the presence or otherwise of the polyaniline salt and its base. The solution spectrum of the polyaniline base taken in DMSO exhibits two bands near 325 and 625 nm. On the other hand,

TABLE II
FT Raman Data (wavenumber in cm^{-1}) of Polyaniline Sulphosalicylic Acid Salt, Polystyrene, and Their Blends

Polystyrene	Pani–SSA Salt	Pani (90)–PS (10)[a]	Pani (70)–PS (30)	Pani (50)–PS (50)	Pani (30)–PS (70)	Pani (15)–PS (85)
—	1651	—	—	—	—	—
1602	—	1618	1614	—	—	—
1583	1594	1585	1585	1589	1587	1591
—	1533	—	—	—	—	1532
—	1504	1500	1501	1502	1503	1501
1450	1445	1449	1448	1446	—	—
—	1416	1426	1426	—	—	1412
—	—	—	1414	—	1351	1354
—	1352	1345	1352	1353	—	—
1328	1332	—	—	—	—	—
—	1268	—	1260	1261	1262	1274
—	1244	1244	1240	1244	1237	1234
1200	—	—	—	—	—	—
1156	1171	1171	1171	1172	1172	1170
1032	—	—	1075	—	—	—
1002	—	—	—	—	—	—

[a] Pani, polyaniline; PS, polystyrene.

the polyaniline salt in DMSO shows four peaks at 330, 440, 630, and 825 nm. Although there is general agreement regarding the assignment of the 325 nm absorption band of the base as arising from the $\pi–\pi^*$ transition, there has been no unambiguous identification of the origin of the 620 nm absorption band.[17–19] The absorption at 620 nm in the emeraldine base is assigned as due to the $n–\pi^*$ transition from the nonbonding nitrogen lone pair to the conduction (π^*) band,[18] while Wan et al.[19] assigned it to the excitation of the imine segment of the polyemeraldine chain. The bands near 430 and 830 nm in the salt were assigned as due to polaron transitions.[20] The blends exhibit two peaks around 620 and 310 nm, confirming the presence of polyaniline in the blend. The absence of the other two peaks at 430 and 820 nm indicates that the salt is poorly soluble in DMSO and that there is some amount of base always present.
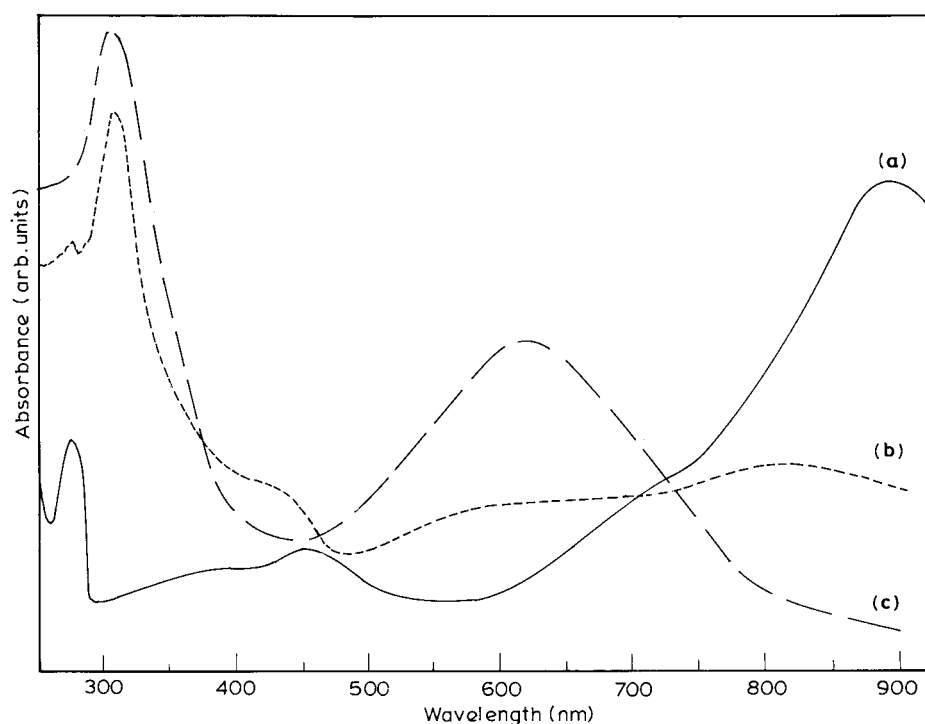

Figure 2 The electronic absorption spectra of (a) polyaniline–sulfosalicylic acid salt in DMSO; polyaniline (90)–polystyrene (10) blend in (b) DMSO; and (c) solid state.

TABLE III
EPR Data of Polyaniline–Polystyrene Blends

Polymer/Blend[a]	Spin Concentration (spins g^{-1})	Line Width, ΔH (G)	g Value	A/B Ratio
Pani–SSA salt	2.2287×10^{20}	1.40	2.0037	0.97
Pani–SSA base	2.9245×10^{18}	8.50	2.0025	1.03
Pani (90)–PS (10)	2.1637×10^{20}	2.25	2.0038	0.97
Pani (70)–PS (30)	1.2959×10^{20}	3.00	2.0034	1.08
Pani (50)–PS (50)	7.6492×10^{19}	1.97	2.0046	0.99
Pani (30)–PS (70)	6.5954×10^{19}	2.50	2.0044	0.95
Pani (15)–PS (85)	6.3163×10^{19}	2.00	2.0035	0.98

[a] As in Table I.

The spectra in the solid state exhibit four peaks for the blends, polyaniline (90)–polystyrene (10), and polyaniline (70)–polystyrene (30) in the region 270, 450, 680, and 850 nm. The blends of composition polyaniline (50)–polystyrene (50) and polyaniline (30)–polystyrene (70) do not display the 680 nm absorption. As the amount of polyaniline in the blend decreases, the number of peaks in the solid-state spectra reduces from four to three. Thus, the spectra confirm the presence of polyaniline salt in the blend. The salt being poorly soluble as stated above, the absorption spectra of the blends taken in solution (DMSO) show only two bands. Thus, the UV spectra reveal the presence of both the salt and the base forms of polyaniline in the blend. The bands in the solid-state spectra of the polyaniline–polystyrene blends show a large shift in comparison to those observed in the spectra taken in DMSO. This shift is attributable to the increased intermolecular forces present in the solid state and the absence of solute–solvent interactions (Table II). The bands tend to be broad in the solid-state spectra. Blending of polyaniline with polystyrene does not seem to involve important modifications in the electronic structure of the polyaniline polymer, as noted earlier.[12]

EPR spectra

The spin concentration, line width, g value, and A/B peak ratio (that is, the ratio of the area of the positive to the negative peak) of polyaniline–polystyrene blends are presented in Table III. The EPR spectra of the polyaniline–sulfosalicylic acid salt and the polyaniline (30)–polystyrene (70) blend are shown in Figure 3. The ambient temperature EPR spectra of the blends show a single signal without hyperfine structure similar to those observed for polyaniline–sulfosalicylic acid salt and its base. The g value for polyaniline blended with polystyrene lies in the range of 2.0025 to 2.0046. The A/B ratio is close to unity, thereby indicating that the spins are a free-electron type. The line widths (1.97–3.00 G) are nearer to that of pure polyaniline–sulfosalicylic acid salt, indicating the presence of polyaniline salt in the blend. The spin concentration

of the blends polyaniline (90)–polystyrene (10) (2.1637 $\times 10^{20}$ spins g^{-1}) and polyaniline (70)–polystyrene (30) (1.2959 $\times 10^{20}$ spins g^{-1}) is nearer to that of the polyaniline–sulfosalicylic acid salt (2.2287 $\times 10^{20}$ spins g^{-1}). As the amount of polystyrene in the blend increases, the spin concentration decreases and becomes nearly constant ($\approx 10^{19}$ spins g^{-1}) and lies in between that of the polyaniline–sulfosalicylic acid salt and its base. From the line width and the spin concentration, it can be concluded that polyaniline is present in the salt form in the blends.

Electrical properties

Conductivity

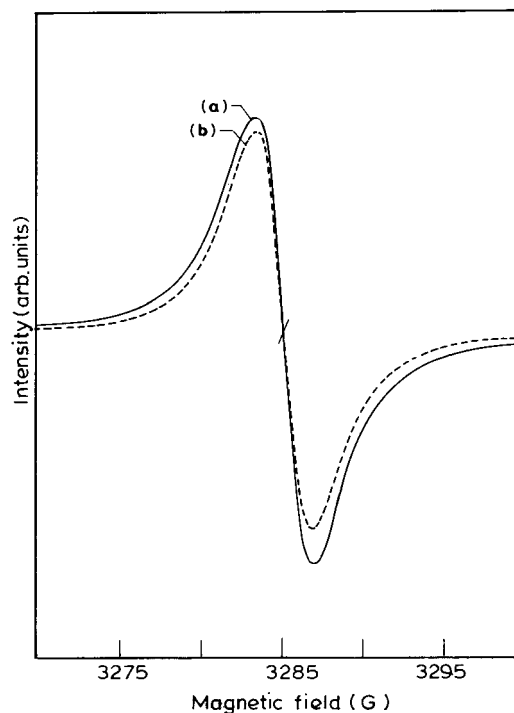The conductivity measurements on polyaniline–sulfosalicylic acid salt and its blends with polystyrene

Figure 3 The EPR spectra of (a) polyaniline–sulfosalicylic acid salt and (b) polyaniline (30)–polystyrene (70) blend.

TABLE IV
TGA and DTA Data of Polyaniline–Polystyrene Blends

| Polymer/Blend[a] | Temperature Range, °C and (%) Weight Loss | | | Peak Temperature (°C) | |
	(1st Step)	(2nd Step)	(3rd Step)	Endo	Exo
Pani–SSA salt	100–160 (6%)	260–340 (31%)	480	280	—	475
Pani (90)–PS (10)	60–150 (7%)	235–330 (26%)	420	—	306	428
Pani (70)–PS (30)	65–170 (8%)	240–340 (26%)	410	239	309	419
Pani (50)–PS (50)	85–180 (8%)	240–340 (15%)	410	260	330	412
Pani (30)–PS (70)	60–170 (6%)	260–350 (18%)	405	—	420	455
Pani (15)–PS (85)		250–355	405	—	—	408

[a] As in Table I.

carried out as pellets using the four-probe technique are given in Table II. The conductivity of polyaniline–sulfosalicylic acid salt is 0.59 S cm^{-1} and the higher conductivity obtained by the present method could be attributed to the more homogeneous protonation of the imine nitrogens. The electrical conductivity of the blend does depend on the volume fraction of polyaniline in the blend. On the other hand, the polyaniline–polystyrene blends prepared using bis(2-ethylhexyl)hydrogen phosphate as the dopant species by the codissolution method[13] were reported to exhibit conductivity varying from 0.46 to 2.1×10^{-4} S cm^{-1}. However, the polystyrene–polyaniline–DBSA blends,[14] obtained by codissolution as a function of polyaniline–DBSA content, show higher conductivity, about 1 S cm^{-1}. The conductivity of polyaniline–sulfosalicylic acid salt as expected decreases with increase in the polystyrene content of the blend. The dependence of the conductivity of the blend on the concentration of the dopant and the mole ratio of the oxidant was not investigated. The conductivity of polyaniline–polystyrene blends, of compositions 90, 10 and 70, 30 (4.2×10^{-1} and 1.3×10^{-1} S cm^{-1}, respectively), is nearly of the same order as that of the polyaniline salt (0.59 S cm^{-1}). A drop in the conductivity to 4.1×10^{-2} S cm^{-1} is observed for the polyaniline (50)–polystyrene (50) blend. It drops down further to 10^{-3} and 10^{-5} S cm^{-1} in the case of blends of composition polyaniline (30)–polystyrene (70) and polyaniline (15)–polystyrene (85), respectively. Electrical conductivity can be interpreted on the basis of hopping mechanism between polaronic clusters.[20]

Thermal analysis

TGA and DTA thermograms

The thermogravimetric (TGA) and differential thermal analysis (DTA) studies of polyaniline–polystyrene blends were performed from 25 to 600°C at a heating rate of 20°C min^{-1} under nitrogen atmosphere at a flow rate of 80 mL/min.

The TGA of the polyaniline salt shows a three-step weight loss. The weight loss in the first step up to 100°C due to loss of moisture is about 6%. In the second step, at 260°C, the weight loss is nearly 31%, which is attributed as due to the removal of the dopant sulfosalicylic acid. A slow and somewhat gradual weight loss profile is observed for the polyaniline salt after 480°C, due to the degradation of the salt. The DTA curve of polyaniline–sulfosalicylic acid salt synthesized at room temperature shows an endothermic peak at 305°C and an exothermic peak around 540°C. The exotherm corresponds to the degradation of polyaniline, while the endotherm corresponds to the loss of the dopant. The TGA studies reveal that polystyrene is stable up to 275°C and the polymer degradation commences near 345°C and goes to completion around 450°C.

The polyaniline (90)–polystyrene (10) blend also shows a three-step weight loss in ranges similar to those of polyaniline–sulfosalicylic acid salt (Table IV). The first step is due to the loss of moisture and the second step corresponds to the loss of the dopant. The next step is attributed to the degradation of the polymer. An endotherm is found in the DTA curve near 230°C corresponding to the second step in the TGA curve. A strong exotherm at about 420°C is observed in the DTA curve corresponding to the decomposition of the blend. As the amount of polystyrene in the blend increases, the decomposition temperature is lowered to some extent. The stability of the polyaniline salt apparently decreases with an increase in the polystyrene content of the blend (Table IV).

Morphology

SEM

The morphology of polyaniline–sulfosalicylic salt and its blends with polystyrene was investigated. The SEM of polyaniline salt and its blends was obtained as such except for the polyaniline (15)–polystyrene (85) blend, which was surface coated with gold prior to the recording of the SEM.

The SEM pictures reveal that the polyaniline–sulfosalicylic acid salt possesses a granular nature [Fig. 4(a)]. The particles are sharp edged with lamellar
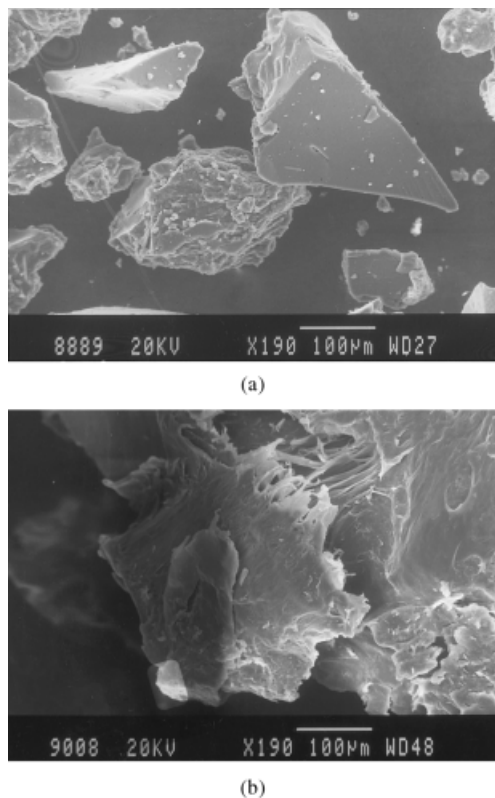
Figure 4 The SEM micrographs of (a) polyaniline–sulfosalicylic acid salt and (b) polyaniline (15)–polystyrene (85) blend.

structure on one side. The polyaniline salt particles show a rough pattern on one side, whereas the other side is comparatively smoother. No distinct feature is seen in the SEM micrographs of the blends. The particles of the polyaniline–sulfosalicylic acid salt were found to be dispersed on the surface of polystyrene in the blends, polyaniline (90)–polystyrene (10), polyaniline (70)–polystyrene (30), and polyaniline (50)–polystyrene (50).

In the case of the polyaniline (15)–polystyrene (85) blend, the morphology was found to be predominantly characteristic of polystyrene. The surface of the particles was noted to be rough with irregular terrain [Fig. 4(b)]. Layered protrusions and smooth edges could also be seen in the micrographs, differing from those observed for the polyaniline salt particles, which are sharp edged.

On the other hand, the morphology of polyaniline–polystyrene blends prepared by the codissolution method using bis(2-ethyl hexyl) hydrogen phosphate as the dopant with ammonium persulfate in HCl solution as the oxidant exhibits a smooth surface.[12] They showed two phases, one of polystyrene characterized by fractured surface and the other of polyaniline–DBSA characterized by the structure of aggregates and agglomerates. A layer of the dopant DBSA was

visible for the blend synthesized by the solution cast method (in xylene) with ammonium persulfate in sulfuric acid as the oxidant.[14] The SEM micrographs of the blends synthesized via the emulsion method show spherical particles that disappear when the polyaniline content in the blend increases.[21] It demonstrates that the morphology of the blend is dependent on the method of synthesis; the solution method gives a smooth surface for the blend while that synthesized by the emulsion pathway exhibits spherical particular morphology. On the other hand, the inverted emulsion procedure gives rise to particles of polyaniline–sulfosalicylic acid dispersed on the polystyrene surface with two distinct phases of polystyrene and polyaniline being evident. Thus, the blend is not a simple mixture of its constituents.

CONCLUSION

New polyaniline–polystyrene blends of varying compositions (wt/wt) were synthesized at room temperature by using the inverted emulsion method with benzoyl peroxide as the new oxidant and sulfosalicylic acid as the dopant in a heterogeneous solution of chloroform and water. This two-step procedure has the advantage of a better distribution of the oxidant among small particles of the dispersed phase of the emulsion obtained in the first step. The polymer blends obtained are of high purity because the excess of benzoyl peroxide is readily removed with acetone, which is used to break the emulsion. The absorption and EPR spectra reveal the presence of polyaniline in the salt form in the blend. The evidence for the presence of polystyrene in the blend was obtained from the FTIR spectra. The SEM studies reveal particles of the polyaniline–sulfosalicylic acid salt dispersed on the surface of polystyrene. The blends are stable up to a temperature of 400°C.

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