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Poly(*o*- and *m*-toluidine)–polystyrene blends: spectral, thermal and electrical properties

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Poly(*o*-toluidine) (POT) and poly(*m*-toluidine) (PMT) blends with polystyrene of five different compositions were prepared by solution blending using THF as the solvent in which both the POT–HNO_3 and PMT–HNO_3 bases are almost completely soluble. The blends have been characterized by spectral, thermal and electrical measurements. The results suggest that blend formation occurs at all compositions presently studied. The thermal stability of the respective blends is higher than that of the POT–HNO_3 and PMT–HNO_3 salts. The maximum conductivity of the blends is 9.2×10^{-4} S cm^{-1}. The results show that POT/PMT can be blended with up to 30% wt/wt of polystyrene without a significant drop in its conductivity. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: polytoluidine; polystyrene; blends)

INTRODUCTION

Within the class of conducting polymers, polyaniline is unique in that its electronic structure and electrical properties can reversibly be controlled both by oxidation and protonation. Because of the wide range of associated electrical and optical properties, coupled with excellent environmental and thermal stability, polyaniline has attracted much attention as a material for potential use in a variety of applications such as optoelectronic devices, batteries, sensors, etc. Recently, conducting polyaniline blends and composites have received greater attention due to their easy synthesis and excellent electrical and optical properties combined with good mechanical strength.

Preparation methods for blends include mechanical mixing[1], casting of a solution containing the components of the blend[2] or polymerization of aniline in the presence of an inert polymer. In the last method, polymerization can be achieved either chemically[3] or electrochemically[4]. The chemical method also includes techniques such as emulsion[5] and dispersion[6]. While polyaniline blends have received greater attention, there seems to be hardly any report on poly(*o*/*m*-toluidine) blends[7]. Solution blending is the most convenient of the above mentioned methods to prepare polytoluidine blends. Generally, the conductive form of polytoluidine is difficult to use for making blends since it is insoluble in common organic solvents. However, we observed that polytoluidine bases are more soluble than their salts in tetrahydrofuran (THF).

The POT base and PMT base prepared from POT–HNO_3 and PMT–HNO_3 salts, respectively, are more soluble in THF when compared to other bases. The polystyrene (PS) is also soluble in THF. We have prepared the POT–PS and PMT–PS blends by solution blending. They were subsequently converted to the salt form by doping with HNO_3. The blends have been characterized using spectral methods such as u.v.–vis., *FT*i.r. and e.p.r., thermal methods such as t.g.a., d.t.a. and d.s.c., electrical methods such as conductivity and dielectric constants and mechanical strength measurements.

EXPERIMENTAL

Five poly(*o*-toluidine) (POT) and poly(*m*-toluidine) (PMT) salts were prepared by chemical oxidative polymerization using protonic acids such as HCl, HNO_3, H_2SO_4, H_3PO_4 and CH_3COOH[8,9]. The salts were converted into bases by dedoping with NH_4OH. The solubility of the polymer base was found as follows: 2 g of the base was dissolved in 100 ml of THF under vigorous stirring for 6 h and the solution was filtered using a pre-weighed G4 sintered funnel. The amount of the polymer base which dissolved in THF, given in parenthesis, are as follows: POT–HNO_3 (1.99 g); POT–HCl (1.95 g); POT–CH_3COOH (0.32 g); POT–H_2SO_4 (0.24 g); POT–H_3PO_4 (0.08 g); PMT–HNO_3 (1.99 g); PMT–HCl(1.97 g); PMT–CH_3COOH (0.39 g); PMT–H_2SO_4 (0.11 g) and PMT–H_3PO_4 (0.07 g). As the solubility of POT–HNO_3 and PMT–HNO_3 bases in THF is very high and the conductivity of the POT–HNO_3 and PMT–HNO_3 salts[8,9] is also the highest, HNO_3 was used for the synthesis (doping) of the salts as well as for doping the blends.

Preparation of POT–HNO_3 base and PMT–HNO_3 base

o-Toluidine (Loba Chemie, India) and *m*-toluidine (Fluka) were double distilled under vacuum. Ammonium persulphate (Ranbaxy, India) and nitric acid (Merck) were analytical reagents. Double distilled water was used.

To a 1 M HNO_3 solution containing *o*-toluidine (0.1 M) maintained at 0°C, an aqueous solution of ammonium persulphate (0.1 M) was added dropwise. During the

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addition of persulphate, the temperature of the reaction mixture was maintained within ± 1°C of that of the ice bath and then kept at 10°C for 24 h. The total volume of the reaction mixture was 2 l. Poly(*o*-toluidine)–HNO_3 (POT–HNO_3) salt was then washed with 2 l distilled water and then with 1 l methanol. The POT–HNO_3 salt was dedoped in 2 l of 0.5 M NH_4OH and kept overnight with stirring. The POT–HNO_3 base obtained was filtered, washed with 250 ml of 0.5 M NH_4OH and dried in vacuum. The poly(*m*-toluidine)–HNO_3 (PMT–HNO_3) base was also obtained using the above procedure.

Preparation of the POT–PS and PMT–PS blends

In a typical experiment, 1 g of the polymer base was dissolved in 50 ml of THF under vigorous stirring. This solution was added to 50 ml of THF containing 1 g of PS. The mixture was stirred for 1 h and it was then added to 1 l petroleum ether (non-solvent) and kept aside for 2 h. The blend that precipitated was filtered and dried under vacuum for 24 h. By this method, PS blends containing 10, 30, 50, 70 and 90% wt/wt of POT/PMT base were prepared. The yield for the blends was calculated from the amounts of the polymer base and PS used. The blend was doped by treatment with 250 ml of 1.5 M HNO_3 for 4 h under stirring. The salt form of the blend was dried in vacuum and they are distinguished using the initial percentage wt/wt of the polymer base and PS employed. For example, the blend POT(10)–PS(90) indicates that 10% of the POT base was taken initially for the preparation of the blend.

Measurements

The *FT*i.r. spectra of the samples were recorded using a Bruker *FT*i.r. Multiscan 15 Sf II instrument employing a KBr pellet technique. The u.v.–vis. absorption spectra of the samples were measured using an Hitachi U3400 spectrophotometer. The samples were dissolved in dimethylsulphoxide (DMSO) and then filtered. The filtrate was used for recording the spectra. For each sample, the spectra were recorded for two different portions for consistency. The e.p.r. spectra were obtained for the solid samples using Varian E109 spectrometer operating in the X-band. The samples were evacuated before recording the spectra to remove moisture. The *g* values, line widths and spin concentrations of the samples were determined using charred dextrose as the standard[8,9]. The t.g.a. and d.t.a. thermograms were recorded using an STA-1500 thermal analysis system (Polymer Laboratories, USA) in air atmosphere up to 900°C and at a heating rate of 10°C min^{-1}. The d.s.c. measurements were carried out in oxygen atmosphere at a heating rate of 10°C min^{-1} from ambient temperature to 300°C using a DuPont 9900 TA system. The electrical conductivity of the samples was measured at ambient temperature 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 conditions using a Keithley Model 220 programmable current source and a Keithley Model 195A digital voltammeter is estimated to be less than 2%. The reproducibility of the results was checked by measuring (i) the resistance twice for each pellet, and (ii) the resistance for a batch of two pellets for each sample. The dielectric data for the samples were obtained using a Keithley Model 3330 LCZ meter at ambient temperature at four frequencies: 120 Hz, 1, 10 and 100 kHz. The densities of the blends were estimated for the pressed pellets obtained by subjecting the powder to a pressure of 50 kN. The mechanical strength of the pellets was determined using a Shore-D hardness tester (C.V. Instruments, UK). The pellets were of equal weight and pressed at a pressure of 50 kN.

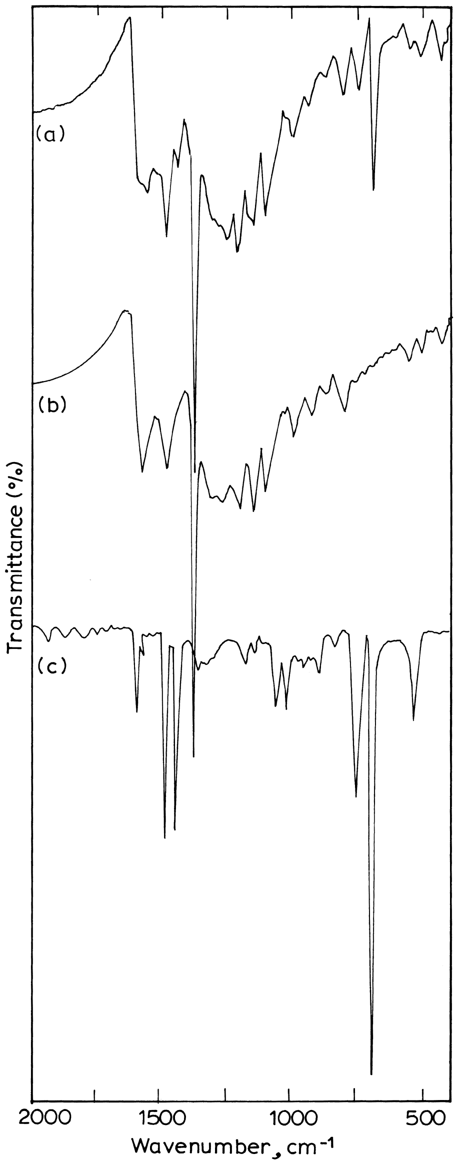

Figure 1 *FT*i.r. spectra of (a) POT(50)–PS(50) blend, (b) POT–HNO_3 salt and (c) PS

RESULTS AND DISCUSSION

Spectroscopy

***FT*i.r. spectra.** The characteristic i.r. peaks of polystyrene (PS), POT–HNO_3 , PMT–HNO_3 salts and their blends are presented in *Table 1*. The i.r. spectra of the POT(50)–PS(50) blend, POT–HNO_3 salt and PS are shown in *Figure 1*. The i.r. spectrum of POT–HNO_3 salt (redoped) exhibits six principal absorptions at 1585, 1490, 1385, 1212, 1153 and 807 cm^{-1} as observed for polyaniline–HCl salt[10]. The high frequency bands at 1585 and 1490 cm^{-1}, which are of nearly equal intensity, correspond to the C–C (or C–N) stretching and in plane C–H bending modes, respectively. The 807 cm^{-1} band is assigned to the out of plane C–H bending mode. In addition, there is a weak broad band around 1300 cm^{-1} assignable to the N–H bending. The i.r.

Table 1 The i.r. peaks and absorption maxima of POT–PS and PMT–PS blends

System	λ_{max} (nm)		IR peaks (cm^{-1})		
Polystyrene (PS)	—	—	—	750 s	690 m
POT–HNO$_3$ salt	313	620	1384 vs	—	—
POT–HNO$_3$ base	313	610	—	—	—
POT(10)–PS(90)	311	605	1385 w	758 s	696 vs
POT(30)–PS(70)	310	620	—	—	—
POT(50)–PS(50)	313	625	1384 vs	748 w	696 m
POT(70)–PS(30)	310	625	—	—	—
POT(90)–PS(10)	314	620	1384 vs	—	698 w
PMT–HNO$_3$ salt	314	615	1384 vs	—	—
PMT–HNO$_3$ base	314	610	—	—	—
PMT(10)–PS(90)	310	610	1385 w	755 s	696 vs
PMT(30)–PS(70)	310	610	—	—	—
PMT(50)–PS(50)	314	615	1384 s	744 w	694 s
PMT(70)–PS(30)	315	620	—	—	—
PMT(90)–PS(10)	315	615	1384 vs	—	694 w

spectrum of polystyrene exhibits characteristic bands at 1600, 1493, 757 and 698 cm^{-1}.

The i.r. spectra of POT–PS and PMT–PS blends of different compositions have been analysed by monitoring the relative intensities of the peaks at 757 and 698 cm^{-1} which are characteristic of polystyrene and the 1385 cm^{-1} band characteristic of POT–HNO$_3$ and PMT–HNO$_3$ salts. The i.r. spectrum of the POT(10)–PS(90) blend almost resembles that of polystyrene. The 1385 cm^{-1} absorption characteristic of POT–HNO$_3$ is observed as a very weak band. With an increase in the amount of POT in the blend, the intensities of the bands due to polystyrene decrease. For example, the spectrum of the POT(50)–PS(50) blend shows the 1384 cm^{-1} absorption as a very strong band while the 748 and 696 cm^{-1} bands appear as weak and medium intensity, respectively. For the POT(90)–PS(10) blend, the characteristic bands due to POT are observed as in the case of POT–HNO$_3$ and the bands due to polystyrene are greatly decreased in intensity. The i.r. spectrum of PMT–HNO$_3$ salt is similar to that of POT–HNO$_3$ salt. The i.r. spectral features of POT–PS and PMT–PS blends are quite similar (*Table 1*). As the i.r. spectra of the POT–PS and PMT–PS blends exhibit bands characteristic of both polystyrene and POT/PMT, it can be concluded that formation of blend occurs at all compositions employed in the present study.

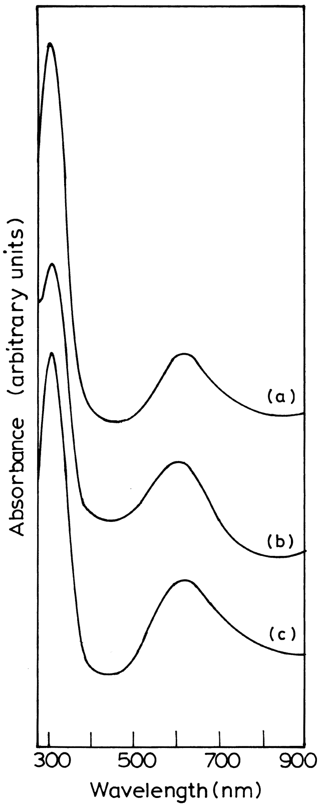

Figure 2 U.V.–vis. spectra of (a) POT–HNO$_3$ salt, (b) POT–HNO$_3$ base and (c) POT(50)–PS(50) blend

U.V.–visible spectra. The POT–HNO$_3$, PMT–HNO$_3$ salts and their bases as well as the blend samples were dissolved in DMSO. The absorption spectra were recorded for the DMSO solutions and the absorption maxima are given in *Table 1*. As representative systems, the absorption spectra of the POT–HNO$_3$ salt, POT–HNO$_3$ base and POT(50)–PS(50) blend are shown in *Figure 2*. The absorption spectrum of POT–HNO$_3$ base exhibits two bands at 313 and 610 nm. The POT–HNO$_3$ salt also exhibits only two bands at 312 and 620 nm. The u.v.–vis. spectrum of the POT–HNO$_3$ base in DMSO acidified with HNO$_3$ shows three bands around 325, 420 and 830 nm. Since POT–HNO$_3$ salt shows only two bands, it indicates that some

Table 2 The e.p.r. parameters of POT–PS and PMT–PS blends

System	*g* value	Line width (G)	Spin conc. (spins g^{-1})	*A*/*B* ratio
POT–HNO$_3$ salt	2.0021	1.6	5.53×10^{20}	1.0
POT–HNO$_3$ base	2.0033	8.0	2.78×10^{17}	1.0
POT(10)–PS(90)	2.0031	2.8	1.80×10^{19}	1.0
POT(30)–PS(70)	2.0026	1.3	1.49×10^{20}	1.0
POT(50)–PS(50)	2.0022	1.7	1.63×10^{20}	1.0
POT(70)–PS(30)	2.0027	1.5	2.76×10^{20}	1.0
POT(90)–PS(10)	2.0027	1.0	4.90×10^{20}	0.9
PMT–HNO$_3$ salt	2.0019	2.0	9.14×10^{20}	1.0
PMT–HNO$_3$ base	2.0039	8.0	3.61×10^{17}	1.0
PMT(10)–PS(90)	2.0035	2.5	5.18×10^{19}	1.0
PMT(30)–PS(70)	2.0029	1.5	9.65×10^{19}	1.0
PMT(50)–PS(50)	2.0024	1.5	1.29×10^{20}	1.0
PMT(70)–PS(30)	2.0029	1.7	3.20×10^{20}	1.0
PMT(90)–PS(10)	2.0026	1.0	8.41×10^{20}	1.0

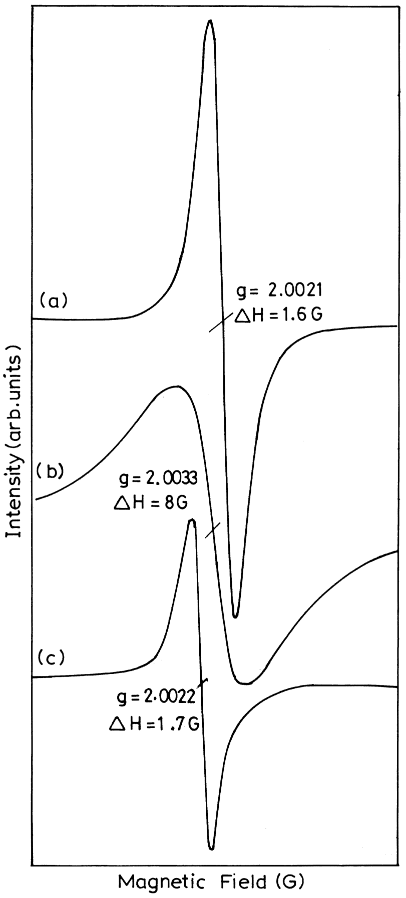

Figure 3 E.p.r. spectra of (a) POT–HNO_3 salt, (b) POT–HNO_3 base and (c) POT(50)–PS(50) blend

amount of base is present along with the salt. The POT–PS blends exhibit two bands around 310–314 and 605–625 nm confirming the presence of POT base in the blends. The u.v.–vis. absorption spectra of the PMT–PS blends are similar to those of POT–PS blends (*Table 1*).

E.p.r. spectra. The *g* value, line width, spin concentration and *A*/*B* ratios of POT–PS and PMT–PS blends are given in *Table 2*. The ambient temperature e.p.r. spectra of POT–PS and PMT–PS blends exhibit a single signal without hyperfine structure as observed for POT–HNO_3, PMT–HNO_3 salts and their bases. As representative examples, the e.p.r. spectra of POT–HNO_3 salt, POT–HNO_3 base and the POT(50)–PS(50) blend are shown in *Figure 3*. As noted from *Table 2*, the *g* values of the POT salt and its base are close and therefore the *g* values can not be used to determine whether POT is present in the blend in the salt form or base form. The *g* values for the POT–PS blends lie in the range from 2.0022 to 2.0031 and the *A*/*B* peak ratios are close to unity indicating that the spins are of free electron type. The line widths (1.0–2.8 G) are close to that of pure POT–HNO_3 salt indicating the presence of POT salt in the blend. The spin concentration of the POT(10)–PS(90) blend (1.80×10^{19} spins g^{-1}) lies in-between that of the POT–HNO_3 salt and its base. The spin concentration increases with an increase in the amount of POT in the blend and then becomes nearly constant ($\approx 10^{20}$ spins g^{-1}). The e.p.r. characteristics of PMT–PS blends are similar to those of POT–PS blends (*Table 2*).

Thermal stability

T.g.a. and d.t.a. thermograms. The t.g.a. and d.t.a. thermograms for POT–HNO_3, PMT–HNO_3 salts, their bases, polystyrene, POT–PS and PMT–PS blends were recorded in air atmosphere and the percentage weight loss and corresponding temperature are given in *Table 3*. As representative systems, the t.g.a. and d.t.a. thermograms of POT–HNO_3 salt and POT(50)–PS(50) blend are shown in *Figure 4*. For POT–HNO_3 salt, the t.g.a. thermogram exhibits a three-step weight loss in the range 30–300°C. In the first step, loss of moisture occurs[11]. The second step is due to the elimination of acid dopant and correspondingly a weak exotherm is found around 165°C. The third step ends at 300°C and the corresponding exotherm appears in the d.t.a. near 270°C. During the third step, the elimination of oligomers is expected. The degradation of POT–HNO_3 salt commences at 300°C, complete weight loss occurs at 650°C and the d.t.a. exhibits a very broad exotherm around 480°C. The t.g.a. of the POT–HNO_3 base reveals that it is stable upto 310°C. Complete weight loss occurs around

Table 3 The t.g.a. and d.s.c. data for POT–PS and PMT–PS blends

System	Temp (°C) and % weight loss			Exo	
	1st Step	2nd Step	3rd Step	Peak temp (°C)	Enthalpy (J g^{-1})
POT–HNO_3 salt	30–145	145–185	185–300	160	2930
	8.5	7.0	4.5		
POT(10)–PS(90)	30–140	140–325	—	170	300
	5.0	2.5	—		
POT(50)–PS(50)	30–140	140–180	180–310	170	455
	4.0	4.5	6.0		
POT(90)–PS(10)	30–140	140–185	185–285	170	470
	7.5	7.4	3.3		
PMT–HNO_3 salt	30–145	145–170	170–300	160	2890
	20.0	6.5	7.0		
PMT(10)–PS(90)	30–130	130–340	—	175	290
	4.5	3.0	—		
PMT(50)–PS(50)	30–135	135–190	190–325	175	385
	3.0	3.0	4.0		
PMT(90)–PS(10)	30–115	115–190	190–290	175	520
	5.5	8.3	3.0		

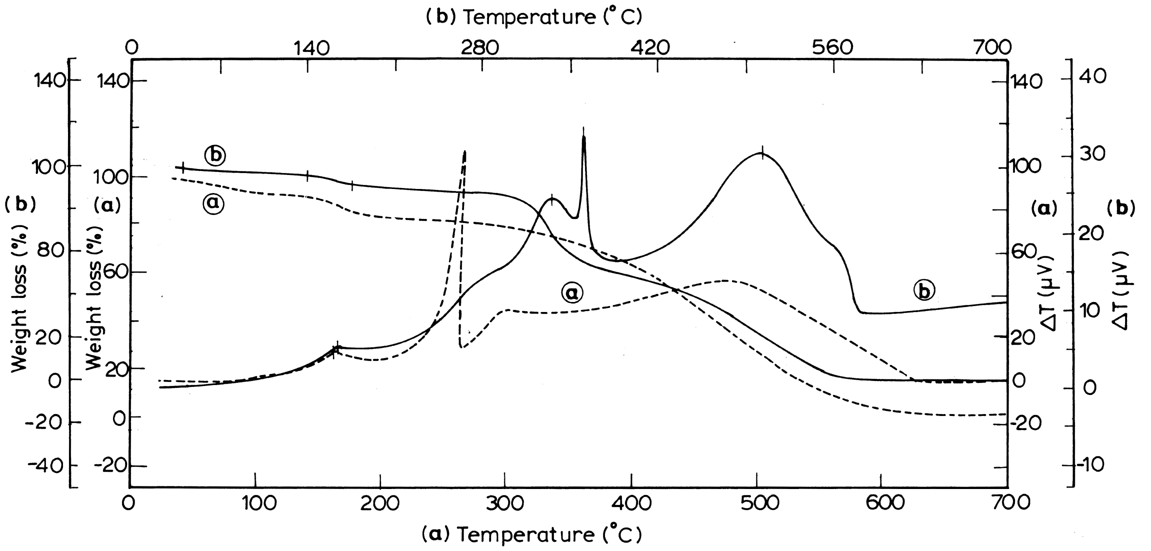

Figure 4 T.g.a. and d.t.a. thermograms of (a) POT–HNO$_3$ salt and (b) POT(50)–PS(50) blend

590°C and the d.t.a. exhibits an exotherm around 490°C. The t.g.a. of PS reveals that it is stable upto 275°C and the degradation is complete near 450°C.

A two-step weight loss is found for the POT(10)–PS(90) blend. The first step is due to loss of moisture, while the second step could be attributed to the loss of acid dopant from the POT. The d.t.a. shows a weak exotherm around 330°C. The decomposition begins at 325°C and goes to completion around 530°C. The d.t.a. shows a sharp endotherm near 405°C and a broad exotherm at 515°C. On the other hand, a three-step weight loss is noted for POT(50)–PS(50) and POT(90)–PS(10) blends. The d.t.a. for these two blends shows a sharp exotherm around 350°C and a broad one near 500°C and the position of the peak maxima seems to depend on the blend composition. For example, for the POT(50)–PS(50) blend the d.t.a. exhibits exotherms around 360 and 500°C and for the POT(90)–PS(10) blend, around 325 and 580°C. For the POT(50)–PS(50) blend, in the third step, the loss of oligomers is expected. The onset of degradation takes place near 310°C for the POT(50)–PS(50) blend and around 285°C for the POT(90)–PS(10) blend and goes to completion around 650°C. Thus the temperature for the onset of degradation decreases with an increase in the POT content in the blend indicating that the thermal stability of the POT–PS blends increases with the amount of PS. The thermal behaviour of PMT–PS blends is similar to that of POT–PS blends (*Table 3*).

D.s.c. thermograms. The d.s.c. thermograms of the POT–PS and PMT–PS blends were recorded from ambient temperature to 250°C under oxygen atmosphere. The d.s.c. thermograms of POT–HNO$_3$ salt and the POT(50)–PS(50) blend are shown in *Figure 5* as representative systems. The d.s.c. thermogram of POT–HNO$_3$ salt shows a weak endothermic peak around 60°C due to dehydration and a sharp exothermic peak around 160°C with an enthalpy value of 2930 J g^{-1} corresponding to the oxidative degradation. The d.s.c. thermograms of POT–PS and PMT–PS blends also show a weak endothermic peak around 50–70°C and a sharp exothermic peak near 170°C. The exothermic peak temperatures and the corresponding enthalpy

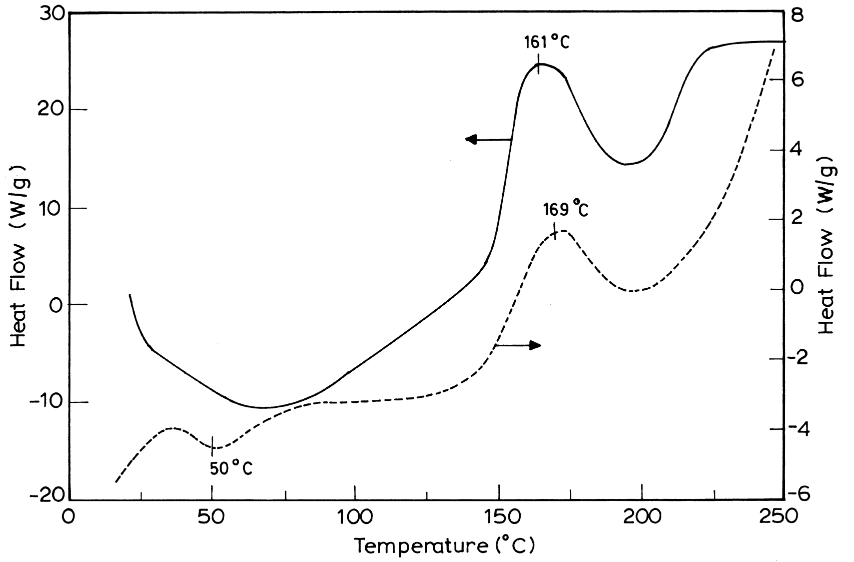

Figure 5 D.s.c. thermograms of POT–HNO$_3$ salt (—) and POT(50)–PS(50) blend (- - -)

Table 4 The conductivity, yield (%) and density of POT–PS and PMT–PS blends

System	Conductivity ($S\ cm^{-1}$)	Yield (%)	Density ($g\ cm^{-3}$)
POT–HNO_3 salt	1.7×10^{-3}	98.6	1.14
POT(10)–PS(90)	$<10^{-8}$	94.0	1.01
POT(30)–PS(70)	2.2×10^{-5}	85.9	1.02
POT(50)–PS(50)	7.0×10^{-4}	92.8	1.08
POT(70)–PS(30)	9.0×10^{-4}	83.5	1.10
POT(90)–PS(10)	9.2×10^{-4}	88.9	1.13
PMT–HNO_3 salt	1.5×10^{-3}	99.3	1.16
PMT(10)–PS(90)	$<10^{-8}$	96.2	1.01
PMT(30)–PS(70)	$<10^{-8}$	80.3	1.04
PMT(50)–PS(50)	2.6×10^{-5}	84.3	1.07
PMT(70)–PS(30)	1.8×10^{-4}	80.7	1.14
PMT(90)–PS(10)	4.7×10^{-4}	86.9	1.15

values for POT–PS blends are listed in *Table 3*. The peak temperatures for the POT–PS blends are higher than those of the POT–HNO_3 salt indicating that the blends are more stable than the POT salt. The heat released by POT blends increases with the amount of POT in the blend. The d.s.c. thermograms of PMT–PS blends are similar to those of POT–PS blends (*Table 3*). The energy released by POT blends is lower than that of the corresponding PMT blends.

Electrical properties

Conductivity. The conductivity values of POT–HNO_3 and PMT–HNO_3 salts and their blends containing PS are presented in *Table 4*. For the POT(10)–PS(90) blend, the conductivity is less than $10^{-8}\ S\ cm^{-1}$ and therefore this composition is not suitable for applications. The onset of conductivity occurs for the POT(30)–PS(70) blend ($2.2 \times 10^{-5}\ S\ cm^{-1}$). With an increase in the amount of POT in the blend, the conductivity increases and then remains almost constant. For example, the conductivities of POT(70)–PS(30) and POT(90)–PS(10) blends are 9.0×10^{-4} and $9.2 \times 10^{-4}\ S\ cm^{-1}$, respectively, and these values are close to that of the pure POT–HNO_3 salt. Thus the POT–HNO_3 salt can be blended up to 30% with polystyrene without affecting its conductivity significantly to improve its mechanical strength. The conductivity of PMT–HNO_3 salt is close to that of POT–HNO_3 salt. The PMT(10)–PS(90) and PMT(30)–PS(70) blends are insulators (*Table 4*). The conductivities of the PMT–PS blends are lower than those of the corresponding POT–PS blends suggesting that POT is a better system than PMT to make blends by this method.

Dielectric measurements. The dielectric constant (ε_r') measurements can be used to identify the mechanism of charge transport. For band transport, ε_r' is negative. This corresponds to retardation of the current response due to inertial mass of the carriers. The value of negative ε_r' is limited by the rates of relaxation processes or by the frequency used for measurement. In the hopping regime, electrons remain in a localized states: at low frequency and they follow the variation of the external field. For this situation, ε_r' is positive and proportional to the square of the size of the localized state. In the critical regime for the states near the mobility edge anomalous diffusion takes place and ε_r' has a large positive value (referred to as 'the dielectric catastrophe')[12].

The dielectric constant ε_r' and dissipation factor (tan δ) of the POT–PS and PMT–PS blends are given in *Table 5*. The values given are for PS blends containing 10, 50 and 90% initial wt/wt of the conducting polymer base as only these values show significant variation. The ε_r' and tan δ values of POT(10)–PS(90), POT(50)–PS(50) and POT(90)–PS(10) blends decrease with an increase in frequency similar to those of POT–HNO_3 salt. For example, the ε_r' values for the POT(10)–PS(90) blend at 120 Hz, 1, 10 and 100 kHz are 2.59×10^4, 1.52×10^4, 1.13×10^4 and 9.61×10^3, respectively, and the corresponding tan δ values are 9.51, 2.19, 0.43 and 0.29.

Blending with POT results in the drastic enhancement of ε_r' and tan δ for PS. For example, the ε_r' and tan δ values for PS[13] at 10 kHz are 2.56 and 5×10^{-5} while the corresponding values for the POT(10)–PS(90) blend are 4.15 and 4.0×10^{-2}. The ε_r' and tan δ values of the POT–PS blends increase with the amount of POT in the blends. For example, the ε_r' values for POT(10)–PS(90), POT(50)–PS(50) and POT(90)–PS(10) blends at 10 kHz are 4.15, 7.77×10^3 and 8.10×10^3, respectively. The corresponding tan δ values are 4.0×10^{-2}, 7.36 and 8.42. The dielectric constant and tan δ for the POT(50)–PS(50) and POT(90)–PS(10) blends could be measured at higher

Table 5 The dielectric constant (ε_r') and dissipation factor (tan δ) of POT–PS and PMT–PS blends

		ε_r' and tan δ		
System	120 Hz	1 kHz	10 kHz	100 kHz
POT–HNO_3 salt	2.59×10^4	1.52×10^4	1.13×10^4	9.61×10^3
	9.51	2.19	0.43	0.29
POT(10)–PS(90)	5.25	4.52	4.15	4.00
	0.12	0.06	0.04	0.03
POT(50)–PS(50)	—	—	7.77×10^3	4.80×10^3
	—	—	7.36	0.86
POT(90)–PS(10)	—	—	8.10×10^3	5.30×10^3
	—	—	8.42	2.11
PMT–HNO_3 salt	—	—	7.99×10^5	2.45×10^4
	—	—	7.43	1.04
PMT(10)–PS(90)	1.46×10^1	1.44×10^1	9.49	8.20
	0.76	0.26	0.13	0.10
PMT(50)–PS(50)	2.94×10^2	1.97×10^2	1.09×10^2	4.07×10^1
	3.50	2.96	2.37	0.86
PMT(90)–PS(10)	—	—	1.86×10^5	1.09×10^4
	—	—	6.54	1.01

frequencies (10 and 100 kHz). The dielectric constant and tan δ values of the POT–PS blends lie in-between those of POT–HNO_3 salt and PS showing that formation of blends occurs at these compositions. The very high positive dielectric constant obtained in the present study could be attributed to the localization of charge carriers. For PMT–HNO_3 salt, the values of ε_r' and tan δ could be measured only at higher frequencies (10 and 100 kHz) and these values are higher than those of POT–HNO_3 salt. The dielectric behaviour of PMT–PS blends is similar to that of POT–PS blends (*Table 5*).

Hardness measurements. The mechanical strengths of the films were estimated by hardness measurements. The hardness of polystyrene is 87 while that of pure POT–HNO_3 salt is 70. The hardness of the POT(10)–PS(90), POT(50)–PS(50) and POT(90)–PS(10) blends are 83, 78 and 73, respectively. The mechanical strength of the blends is higher than that of pure conducting POT–HNO_3 salt and it increases with an increase in the amount of polystyrene. Thus, the mechanical strength of the POT–HNO_3 salt is improved by blending with polystyrene. A similar behaviour was noted for PMT–PS blends.

Yield and density. The percentage yields of the POT–PS and PMT–PS blends (prepared in the undoped form) lie in the range 83.5–94.0 while those of PMT–PS blends lie in the range 80.3–96.2 (*Table 4*). The present method is thus suitable to prepare conducting polymer blends in the powder form in reasonably good yield. The densities of the POT(10)–PS(90) and POT(30)–PS(70) blends (1.01 and 1.02 g cm^{-3}, respectively) are close to that of polystyrene (1.04 g cm^{-3}) (*Table 4*). The density of the blends increases with the amount of POT and reaches a maximum for POT(90)–PS(10) (1.13 g cm^{-3}) which is close to that of pure POT–HNO_3 salt. A similar behaviour was noted for PMT–PS blends (*Table 4*).

CONCLUSIONS

The IR spectra confirm that blend formation occurs at all the compositions studied presently. The thermal stability of POT–PS and PMT–PS blends is higher than that of the pure POT and PMT salts, respectively. The dielectric constant and tan δ values of the blends lie in-between those of PS and pure POT/PMT salt. Using the present method, the POT/PMT can be blended with up to 30% (by weight) of PS to improve its mechanical strength without significant loss in its conductivity.

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