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Solution blending of poly(*o*- and *m*-toluidine) with PMMA in formic acid medium: spectroscopic, thermal and electrical behaviour

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Abstract

Poly(*o*-toluidine) (POT) and poly(*m*-toluidine) (PMT) blends containing 10, 30, 50, 70 and 90 wt% of polymethylmethacrylate (PMMA) were prepared by solution blending using formic acid (HCOOH), which serves both as a dopant and as a solvent in which PMMA, POT–HCOOH base and PMT–HCOOH base are soluble. The blends have been characterized by spectral, thermal and electrical measurements. The infrared spectra suggest that blend formation occurs at all the compositions presently studied. The thermal stability of the blends is higher than that of POT–HCOOH and PMT–HCOOH salts. The conductivity of POT (70)–PMMA (30) and POT (90)–PMMA (10) blends is close to that of POT–HCOOH salt, indicating that POT can be blended with up to 30 wt% of PMMA without significance drop in its conductivity. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Conductive polymeric materials with π-conjugated bonds have been finding a tremendous number of applications in optoelectronic devices, batteries and sensors. Among the conducting polymers, polyaniline is unique due to its special doping mechanism, excellent conductivity and chemical stability. One of the critical factors in processing conducting polyaniline for technological applications is its poor solubility in a majority of solvents. In this context, several substituted polyanilines soluble in organic solvents have been prepared [1–3]. Another approach to the preparation of soluble conducting polyaniline is copolymerization of aniline with a suitable substituted aniline. For example, Chen and Hwang [4] synthesized very recently the first water soluble self-acid-doped polyaniline, poly(aniline-co-*N*-propanesulphonicacid aniline). Functionalized sulphonic acids have been used by Heeger [5] to protonate polyaniline and to induce solubility in the conducting form.

Conducting polyaniline blends and composites have received greater attention in recent years as these possess the desirable mechanical properties of the insulating host matrix together with the electrical and optical properties of the conducting polyaniline guest. Conducting polyaniline blends and composites can be prepared by melt processing [6], or by casting the solution containing the components of the blend [7] or by polymerization of aniline in the presence of an inert polymer either chemically [8] or electrochemically [9]. The chemical method also includes techniques such as emulsion [10] and dispersion [11]. Of all these methods, the solution blending appears to be the most con-

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venient one. Compared to polyaniline blends and composites, the polytoluidine blends and composites have received scant attention. Recently, Yang et al. [12] have reported the synthesis of POT–polypropylene composite films by chemical *in situ* polymerization.

In the solution blending method, the emeraldine base and the host polymer are dissolved in a common solvent and cast as a film. Subsequently, the film of the blend is made conducting by treatment with a suitable acid dopant. On the other hand, the acid dopant if soluble, can be co-dissolved with the emeraldine base and the host polymer in a common solvent and the blend can be obtained as a film in the conducting form by solution casting. In the present study, a slightly different technique has been employed to prepare POT–polymethylmethacrylate (PMMA) and poly(*m*-toluidine) (PMT)–PMMA blends in the powder form. The POT/PMT base is added to a formic acid (HCOOH) solution of PMMA in different proportions. The blend was precipitated by adding formic acid solution to water (non-solvent). The advantage of the present method is that homogeneous doping is achieved since formic acid serves both as a solvent and as a dopant. The POT–PMMA and PMT–PMMA blends were characterized by: (1) spectral techniques such as UV–vis, FTIR and electron paramagnetic resonance (EPR); (2) electrical conductivity measurements; and (3) thermal methods such as thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG).

2. Experimental

2.1. Materials

o-Toluidine (Loba Chemie, India) and *m*-toluidine (Fluka) were double distilled under reduced pressure prior to use. Ammonium persulphate, ammonium hydroxide, nitric acid and formic acid (Merck) were analytical grade reagents and used as received. Polymethylmethacrylate procured from Spectrol, India was used as such.

2.2. Preparation of POT–HNO_3 base and PMT–HNO_3 base

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 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. 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 using 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 PMT–HNO_3 base was also obtained using the above procedure.

2.3. Synthesis of POT–PMMA and PMT–PMMA blends using formic acid

In a typical experiment, 1 g of PMMA was dissolved in 50 ml of concentrated formic acid and to this solution 1 g of polytoluidine base was added. The solution was kept under vigorous stirring for 5 min and it was then filtered to remove any undissolved polytoluidine salt. The filtrate was added to 1 l of double distilled water to precipitate the blend in the powder form. The salt form of the blend obtained was dried in vacuum for 48 h. The blends are denoted using the initial weight percentage of polytoluidine base and PMMA. For example, the blend POT (10)–PMMA (90) indicates that 10% of POT base was taken initially for the preparation of the blend.

2.4. Measurements

The FTIR spectra of the polymer sample were recorded using a Bruker FTIR Multiscan 15 Sf II instrument employing the KBr pellet technique. The UV–vis absorption spectra were recorded using a Hitachi U3400 spectrophotometer. The samples were dissolved in dimethylsulphoxide (DMSO) and then filtered. The filtrate was used for recording the UV–vis spectrum. For each of the samples, the spectra were recorded for two different portions for consistency. The EPR spectra were recorded for the solid samples using a Varian E109 spectrometer operating in the X-band. The samples were evacuated before recording the spectra to remove moisture. The g value, line width and spin concentration for the samples were determined using charred dextrose as the standard [13]. The TGA and DTA thermograms were recorded using an STA-1500 thermal analysis system (Polymer Laboratories, USA) at a heating rate of 10°C min^{-1} in air atmosphere up to 900°C. The DSC measurements were carried out in oxygen atmosphere at a heating rate of 10°C min^{-1} from 25 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 condition using a Keithley Model 220 programmable current source and a Keithley Model 195A digital voltammeter is expected to be less than 2%. The reproducibility of the results was checked by measuring (i) the resistance for two pellets for each sample and (ii) twice for each pellet. The yield

Table 1
Characteristic IR bands and absorption spectral data of POT–PMMA and PMT–PMMA blends

System	IR bands (cm^{-1})				λ_{max} (nm)	
PMMA	1731 *vs*	–	–	754 *s*	–	–
POT–HCOOH salt	–	1590 *m*	1490 *s*	–	315	610
POT–HCOOH base	–	–	–	–	312	605
POT (10)–PMMA (90)	1732 *vs*	1590 *w*	1490 *w*	750 *w*	315	605
POT (30)–PMMA (70)	–	–	–	–	315	605
POT (50)–PMMA (50)	1727 *vs*	1588 *m*	1485 *m*	751 *w*	315	605
POT (70)–PMMA (30)	–	–	–	–	315	610
POT (90)–PMMA (10)	1721 *vs*	1588 *vs*	1486 *vs*	–	315	610
PMT–HCOOH salt	–	1588 *m*	1487 *s*	–	312	610
PMT–HCOOH base	–	–	–	–	312	610
PMT (10)–PMMA (90)	1732 *vs*	1590 *w*	1490 *w*	752 *m*	310	605
PMT (30)–PMMA (70)	–	–	–	–	310	605
PMT (50)–PMMA (50)	1731 *vs*	1591 *m*	1488 *w*	751 *m*	310	610
PMT (70)–PMMA (30)	–	–	–	–	310	610
PMT (90)–PMMA(10)	1718 *vs*	1588 *m*	1487 *m*	–	310	610

of the polymer blends and density of the polymer pellets were also determined.

3. Results and discussion

3.1. Spectroscopy

3.1.1. FTIR spectra

The IR spectra of POT–HCOOH salt and PMMA are discussed first. The IR spectrum of POT–HCOOH (redoped) salt exhibits six principal absorptions at 1590, 1490, 1385, 1212, 1150 and 800 cm^{-1} as observed for the polyaniline-HCl salt [14]. The 1590 and 1490 cm^{-1} bands correspond to the C—C ring stretching vibrations of the benzenoid ring. The band at 1385 cm^{-1} corresponds to C—H bending mode. The bands at 1212 and 1150 cm^{-1} could be assigned as due to the C—C (or C—N) stretching and in plane C—H bending modes, respectively. The 800 cm^{-1} band is assigned to the out-of-plane C—H bending mode. The IR spectrum of PMMA exhibits bands at 1731 (*vs*), 1386 (*m*), 1150 (*m*) and 754 cm^{-1} (*s*). The 1731 cm^{-1} band is characteristic of the C=O stretching mode while the 754 cm^{-1} band is due to C=O bending. The IR spectra of POT–PMMA blends of different compositions have been analyzed by monitoring the intensities of the bands at 1590 and 1490 cm^{-1} characteristic of POT–HCOOH salt and the bands at 1731 and 754 cm^{-1} characteristic of PMMA (Table 1). The bands at 1386 and 1150 cm^{-1} were not considered as these are displayed by both POT–HCOOH salt and PMMA.

The IR spectrum of POT (10)–PMMA (90) blend

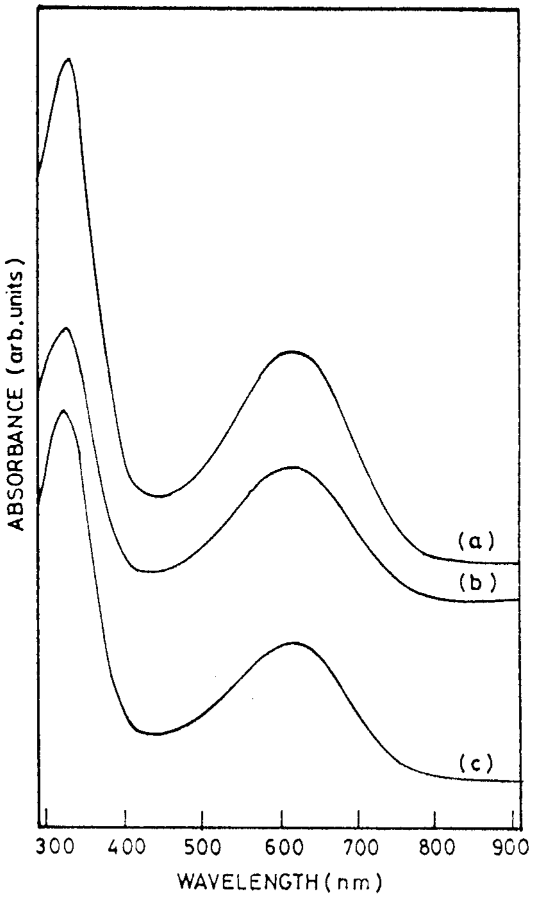

Fig. 1. UV–visible spectra of (a) POT–HCOOH salt, (b) POT–HCOOH base, and (c) POT (50)–PMMA (50) blend.

Table 2
The *g* value, line width and spin concentration of POT–PMMA and PMT–PMMA blends

System	*g*-value	Linewidth	Spins g^{-1}	A/B ratio
POT–HCOOH salt	2.0026	1.7	5.79×10^{20}	1.0
POT–HCOOH base	2.0040	7.9	8.53×10^{17}	1.0
POT (10)–PMMA (90)	2.0041	8.0	4.86×10^{18}	0.9
POT (30)–PMMA (70)	2.0029	2.4	3.34×10^{19}	1.0
POT (50)–PMMA (50)	2.0026	2.2	4.60×10^{19}	1.0
POT (70)–PMMA (30)	2.0025	2.0	3.22×10^{20}	1.1
POT (90)–PMMA (10)	2.0026	2.0	4.24×10^{20}	1.0
PMT–HCOOH salt	2.0025	1.8	8.29×10^{20}	1.0
PMT–HCOOH base	2.0040	8.0	4.82×10^{17}	1.0
PMT (10)–PMMA (90)	2.0039	4.2	5.57×10^{17}	1.0
PMT (30)–PMMA (70)	2.0027	2.2	3.10×10^{19}	1.0
PMT (50)–PMMA (50)	2.0026	2.0	4.69×10^{19}	1.0
PMT (70)–PMMA (30)	2.0026	2.0	5.02×10^{20}	1.0
PMT (90)–PMMA (10)	2.0027	2.0	6.08×10^{20}	1.0

almost resembles that of PMMA and the bands characteristic of POT salt observed at 1590 and 1490 cm^{-1} are weak (Table 1). With increase in the amount of POT in the blend, the bands due to PMMA decrease in intensity and also become slightly broader while the intensity of the bands due to POT increases. For example, for POT (50)–PMMA (50) blend, the intensity of both the 1590 and 1490 cm^{-1} bands increases. The 1590 cm^{-1} band becomes more intense than that of the 1490 cm^{-1} band. For POT (90)–PMMA (10) blend, the bands characteristic of POT salt become very intense while those due to PMMA are reduced in intensity or disappear. The 1732 cm^{-1} band in the spectra of POT–PMMA blends shifts gradually to lower wavenumbers with increase in the amount of POT in the blend (Table 1).

The IR spectrum of PMT–HCOOH (redoped) salt is similar to that of POT–HCOOH salt. The spectral changes observed for PMT–PMMA blends are similar to those of the corresponding POT–PMMA blends (Table 1). From the presence of bands characteristic of both PMMA and POT/PMT in the IR spectra, it can be concluded that the formation of blend occurs at all the compositions under study.

3.1.2. UV–visible spectra

The absorption spectra of POT–HCOOH, PMT–HCOOH salts, bases and their blends were recorded in DMSO. The absorption maxima are listed in Table 1. As representative systems, the absorption spectra of POT–HCOOH salt, its base, and POT (50)–PMMA (50) blend are shown in Fig. 1. The absorption spectrum of POT–HCOOH base shows two bands at 312 and 605 nm. The absorption spectrum of POT–HCOOH base in DMSO acidified with HNO_3 shows three bands around 325, 420 and 830 nm. Since POT–HCOOH salt shows only two bands and not three bands, it indicates that the POT salt is insoluble in

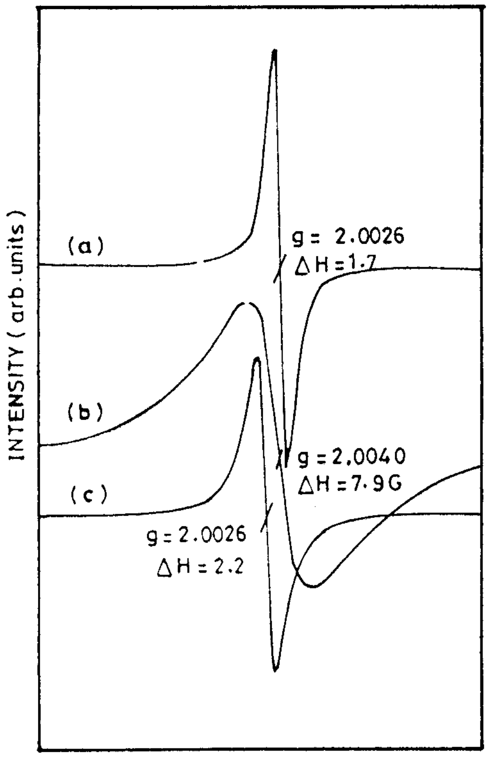

Fig. 2. EPR spectra of (a) POT–HCOOH salt, (b) POT–HCOOH base, and (c) POT (50)–PMMA (50) blend.

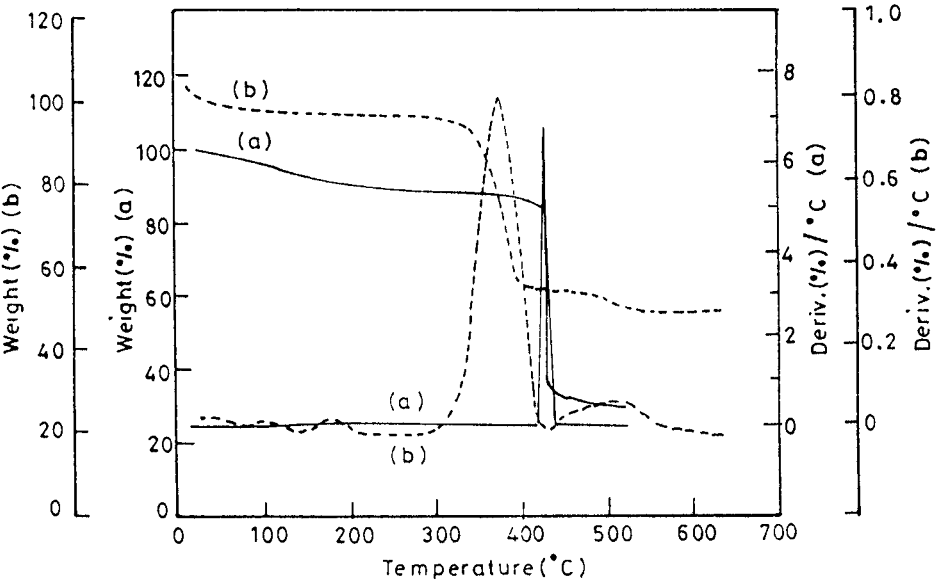

Fig. 3. TGA and DTG thermograms of (a) POT–HCOOH salt, and (b) POT (50)–PMMA (50) blend.

DMSO and some base is also present along with the salt in solution. The POT–PMMA blends also exhibit two bands around 315 and 610 nm, confirming that some amount of POT base is always present in the blend. The absorption characteristics of PMT–PMMA blends are similar to those of POT–PMMA blends.

3.1.3. EPR spectra

The *g* value, line width, spin concentration and A/B peak ratio of POT–PMMA and PMT–PMMA blends are presented in Table 2. The ambient temperature EPR spectra of POT–PMMA blends show a single signal without hyperfine structure, as observed for the POT–HCOOH salt and its base. As representative systems, the EPR spectra of POT–HCOOH salt, its base and POT (50)–PMMA (50) blend are given in Fig. 2. As noted from Table 2, the *g* values of the POT salt and its base are close to each other and therefore cannot be utilized to determine whether POT is present in the salt form or the base form in the blend. For the POT–PMMA blends, the *g* value lies in the range 2.0025–2.0040 and the A/B peak ratio is close to unity indicating that the spins are free electron type. The line widths of POT–PMMA blends lie in the range 2.0–3.0 G. The spin concentration of POT (10)–PMMA (90) blend is nearer to that of the POT base indicating that POT is present in the base form. The spin concentration of POT–PMMA blend increases with the amount of POT and becomes almost constant ($\sim 10^{20}$ spins g^{-1}). From the line width and spin concentration, it can be concluded that POT is present in the salt form in POT–PMMA blends, except for POT (10)–PMMA (90) blend. The EPR characteristics of PMT–PMMA blends are similar to those of POT–PMMA blends.

3.2. Thermal analysis

3.2.1. TGA and DTG thermograms

The thermogravimetric (TGA) and derivative thermogravimetric (DTG) analyses of POT–HCOOH, PMT–HCOOH salts and POT–PMMA and PMT–PMMA blends were carried out under air atmosphere. As representative systems, the TGA and DTG thermograms of POT–HCOOH salt and POT (50)–PMMA (50) blend are shown in Fig. 3. For POT–HCOOH salt, the degradation starts near 400°C and a 30% residue is found around 500°C. Correspondingly, the DTG shows a peak at 430°C. The TGA of PMMA revealed that the degradation commences around 275°C and goes to completion near 375°C. For POT (10)–PMMA (90) blend, the degradation starts around 295°C and a 35% residue is found around 625°C. The DTG record shows a peak at 370°C. On the other hand, the degradation starts near 295°C for POT (50)–PMMA (50) blend also and a higher amount, 50% of the residue remains at 625°C. The DTG exhibits in addition to a broad hump near 525°C, an intense peak around 375°C. With a still higher amount of POT, for example for POT (90)–PMMA (10) blend, the degradation begins at a higher temperature around 430°C and goes to completion at 625°C. The DTG shows a

Table 3
Conductivity, yield and density of POT–PMMA and PMT–PMMA blends

System	Conductivity (S cm^{-1})	Yield (%)	Density (g cm^{-3})
POT–HCOOH salt	5.2×10^{-3}	80.0	1.32
POT (10)–PMMA (90)	$< 10^{-8}$	88.4	1.20
POT (30)–PMMA (70)	1.3×10^{-6}	88.1	1.21
POT (50)–PMMA (50)	1.8×10^{-4}	86.5	1.25
POT (70)–PMMA (30)	1.7×10^{-3}	83.2	1.27
POT (90)–PMMA (10)	2.0×10^{-3}	82.1	1.30
PMT–HCOOH salt	3.1×10^{-3}	80.1	1.31
PMT (10)–PMMA (90)	$< 10^{-8}$	89.0	1.22
PMT (30)–PMMA (70)	1.1×10^{-6}	88.9	1.24
PMT (50)–PMMA (50)	4.0×10^{-5}	87.2	1.28
PMT (70)–PMMA (30)	1.0×10^{-3}	86.1	1.29
PMT (90)–PMMA (10)	2.5×10^{-3}	85.4	1.30

weak peak at 155°C and a sharp intense peak at 459°C. From the TGA and DTG studies, it appears that the thermal stability of the POT–PMMA blends is higher than that of the pure POT–HNO_3 salt. The thermal behaviour of PMT–PMMA blends is similar to that of POT blends.

3.3. Electrical properties

3.3.1. Conductivity

The conductivities of POT–HCOOH and PMT–HCOOH salts and their blends containing PMMA are given in Table 3. For POT–HCOOH salt, the conductivity is 5.2×10^{-3} S cm^{-1}. For POT (10)–PMMA (90) blend, the conductivity is less than 10^{-8} S cm^{-1} and therefore this composition is not useful for conductive applications. The conductivity observed for POT (30)–PMMA (70) blend is 1.3×10^{-6} S cm^{-1}. With further increase in the amount of POT in the blends, the conductivity increases and then remains nearly constant. For example, the conductivity of POT (70)–PMMA (30) and POT (90)–PMMA (10) blends is 1.7×10^{-3} and 2.0×10^{-3} S cm^{-1}, respectively, and it is close to that of POT–HCOOH salt. The above results demonstrate that the POT–HCOOH salt can be blended up to 30% with PMMA to impart mechanical strength without significantly affecting its conductivity. The conductivities of PMT–HCOOH salt and PMT–PMMA blends are similar to those of the corresponding POT salt and its blends.

3.3.2. Yield and density

The yield of POT–PMMA blends lies in the range 80–88% and that of PMT–PMMA blends in the range 85–89% (Table 3). The yield is lower because some of the salt which precipitates was filtered before adding formic acid solution of the blend to water. The density of POT–HCOOH salt is 1.32 g cm^{-3} and that of PMMA is 1.19 g cm^{-3}. The density of POT–PMMA blends (1.20–1.30 g cm^{-3}) is in between that of POT–HCOOH salt and PMMA (Table 3). The density of the blend increases with the amount of POT in the blend. Similarly, the density of PMT–PMMA blends (1.22–1.30 g cm^{-3}) lies in between those of PMT–HCOOH salt (1.31 g cm^{-3}) and PMMA (1.19 g cm^{-3}).

4. Conclusions

The IR spectra confirm the blend formation at all the compositions investigated. The EPR spectra indicate that POT/PMT is present in the salt form in the blends. The thermal stability of POT–PMMA and PMT–PMMA blends is apparently higher than that of POT and PMT salt, respectively. Using the present method, the POT/PMT can be blended with up to 30% (by weight) of PMMA without significant loss in its conductivity.

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