

Conducting Blends Obtained from Maleic Acid/Dodecylhydrogensulfate-Doped Polyaniline and Polyvinyl Chloride by Solution Processing

Chellachamy A. Amarnath,¹ Srinivasan Palaniappan,¹ Patrice Rannou,² Adam Pron²

¹Organic Coatings and Polymers Division, Indian Institute of Chemical Technology, Hyderabad 500 007, Andhra Pradesh, India

²DRFMC, UMR 5819 SPrAM (CEA–CNRS–Université J. Fourier Grenoble I), Laboratoire Electronique Moléculaire, Organique et Hybride, CEA Grenoble, Grenoble Cedex 9, France

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ABSTRACT: Solution processible polyaniline, obtained by our newly developed method via emulsion polymerization in the presence of maleic acid and sodium lauryl sulfate with benzoyl peroxide as the oxidizing/polymerizing agent, has been used for the fabrication of conductive blends with poly(vinyl chloride) (PVC), covering the conductivity range from 10^{-5} to 5×10^{-3} S/cm and showing the percolation threshold for the electrical conductivity $f_p = 0.039$. The fabricated blends combine good mechanical properties with enhanced electrical conductivity, since up to conducting phase content $f = 0.231$, their mechanical properties remain essentially the same and characteristic of pure PVC. Differential scanning calorimetry (DSC) measurements show a

single glass-transition temperature (T_g) increasing with growing content of the rigid conductive phase in the blend. This effect can be taken as an evidence of good miscibility of both components of the blend with phase separation at a submicrometric level. The latter has been confirmed by scanning electron microscopy studies showing a necklace-like morphology which assures the continuity of the conductive phase. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1113–1119, 2007

Key words: polyaniline-maleic acid-dodecylhydrogensulfate salt; benzoyl peroxide; emulsion polymerization; polyaniline-poly(vinyl chloride) film

INTRODUCTION

Ever since the successful synthesis of conducting polyacetylene in 1977 by Shirakawa et al.,¹ electrically conducting polymers and their blends with conventional polymers have generated a tremendous interest because of their potential applications in the fabrication of energy storage and transformation devices,^{2–4} electrochromic devices,^{5,6} sensors,^{7–10} and organic electronic devices.^{11–15} Electrically conducting organic polymers, sometimes called “synthetic metals” are materials which show either semiconducting or metallic properties, depending on their electronic state. In particular, they can undergo the semiconductor to metal transition induced by so-called doping reaction which, in chemical terms, is a partial oxidation reaction transforming neutral polymer chains into polycarbocations (*p*-type doping). In some cases the *n*-doping is also possible which, by hole-electron symmetry, consists of transformation of neutral chains into polycarboanions (*n*-type doping). Polymers with basic centers in their main chain, like polyaniline (PANI) and its derivatives, can be *p*-doped in an

acid–base-type reaction involving either Bronsted or Lewis acids.¹⁶ The doping level, y , is usually defined as the number of dopant anions neutralizing the charge of the polymer chain per polymer repeat unit. One of the attractive properties of conducting polymers is the possibility of their conductivity tuning in the wide range from 10^{-8} to 10^5 S/cm by varying the doping level.

However, the major drawback of these polymers is the difficult in processibility, in the doped i.e., conducting state which frequently impedes their blending with industrial polymers. Such blends are of great technological importance because they combine good mechanical properties of the conventional insulating polymers with electrical properties of the conducting ones. “All polymer” conductive materials frequently offer better properties than conductive composites containing nonpolymeric conductive phase like carbon black or metal particles, especially if their percolation threshold is considered.

Among a rather large number of conducting polymers developed in the last three decades, PANI has attracted a significant attention because of the possibility of its processibility improvement via appropriate selection of the dopant species^{17,18} and the environmental stability of its doped form.¹⁹ Processible PANI of high electrical conductivity has been obtained using functionalized sulfonic acids as proto-

Correspondence to: S. Palaniappan (palaniappan@iict.res.in or palani74@rediffmail.com).

nating (doping) agents^{20–22} and then applied to the fabrication of blend with various technologically important polymers. A significant number of studies have been devoted to PANI protonated with dodecyl benzene sulfonic acid (DBSA) whose amphiphilic nature improves the processibility of the doped PANI (termed as PANI-DBSA) from common solvents such as toluene, xylene, decaline, etc. Moreover its long alkyl substituents induce some compatibility in blends with polymers of similar chemical constitution.²³

PANI-DBSA has been used in melt blends because of its relatively high thermal stability.^{24–26} Solution-cast blends, with PANI-DBSA as the conductive phase, have been investigated with few polymer matrices, such as styrene-butadiene-styrene triblock copolymers (SBS),²⁷ polystyrene,^{28,29} sulfonated polycarbonate,³⁰ ethylene vinyl acetate (EVA) copolymers,^{31–34} and polyacrylonitrile.³⁵ PANI protonated with other sulfonic acids has also been used for blending with industrial polymers. Recently, the preparations of PANI-naphthalene sulfonic acid with polyurethanes and PANI-toluene sulfonic acid with cyanoresins, by solution blending, have been described.^{36,37}

Although blends with a very low percolation threshold for electrical conductivity (< 1%) have been reported,^{38,39} their fabrication methods, in the overwhelming majority of cases, suffer from the necessity of the preparation of specially designed dopant acids, which are not available commercially or the necessity of the use of solvents difficult to be accepted by industry (*m*-cresol (MC), dichloroacetic acid, hexafluoropropanol).^{36,40–42} For this reason, as the conductive component of the blend, we have used PANI doped with maleic acid (MA) and laureate anions which has been prepared using our newly developed method with benzoyl peroxide (BP) as the oxidizing/polymerizing agent.⁴³ As the insulating polymer matrix we have selected poly(vinyl chloride) (PVC). Our interest in PANI blend with PVC was stimulated by the fact that the matrix polymer shows large versatility of mechanical properties. It can be fabricated either in nonplasticized or plasticized forms, mechanical properties of the latter being easily tuned by the selection of the type of the plasticizer and its content.^{44,45} Potential applications of these blends involve electrostatic dissipation materials, electromagnetic interference shields, packaging materials for sensitive electronic equipment, electrochromic devices, and others. Recently, PANI-PVC blends have been used in electroanalytical chemistry as components of solid state ion selective electrodes.⁴⁶

EXPERIMENTAL

Materials

Aniline (Merck) was vacuum-distilled prior to use. Reagent-grade sodium dodecyl sulfate and MA (BDH,

India) were used without further purification. Reagent-grade BP (BDH, India) was recrystallized from chloroform/methanol system. Solvents were purified by the reported procedure.

Synthesis of soluble PANI powder

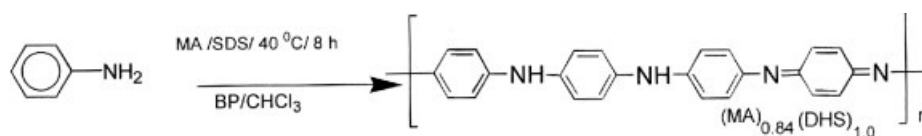
In a typical experiment, 3.0 g BP was dissolved in 30 mL of chloroform taken in a 250-mL round-bottomed flask. To this solution, 20 mL of aqueous solution containing 1.0 g of sodium lauryl sulfate (SLS) was slowly added with stirring, which gave an emulsion. To this emulsion, 50 mL of aqueous solution containing 2.9 g MA acid and 1.0 mL of aniline was added drop wise (15–20 min interval). The reaction mixture was then stirred constantly at 40°C for a period of 8 h. After 8 h, the entire organic phase was filled homogeneously with dark-green PANI, while the aqueous layer appeared colorless. The chloroform phase containing PANI was then separated to give a solution of protonated (doped) PANI, termed subsequently PANI-SOL. Powders of conductive PANI (PANI-POW) were prepared from PANI-SOL by precipitation in acetone followed by consecutive washing with water and acetone and drying at 60°C for 12 h.

Preparation of PANI-PVC films using PANI-POW

PVC (0.5 g) was dissolved in 15 mL tetrahydrofuran (THF). An appropriate amount of PANI-POW or PANI-SOL to give the desired blend composition was then dissolved in a mixed solvent consisting of 2 mL of DMF and 2 mL MC. Both solutions were mixed with constant stirring at 35°C for 24 h. Free-standing films were prepared by casting the solution on an 11 cm diameter Petri dish followed by drying in vacuum at 60°C for 24 h.

Polymer characterization

Resistance measurement of polymer samples was carried out on a two probe connected to a Keithley digital multimeter (MODEL-2010). Fourier transform infrared spectra were recorded using Perkin-Elmer Paragon 500 spectrometer. Thermal analysis of the polymer sample was carried out using Mettler Toledo Star system in the presence of nitrogen atmosphere up to 900°C and at a heating rate of 10°C/min. Morphology studies of the polymer sample was carried out using Hitachi S520 scanning electron microscope instrument operating at 10 kV. The differential scanning calorimetry (DSC) spectra of the polymer samples were recorded on Mettler Toledo DSC 821^e instrument at the heating rate of 10°C/min under nitrogen atmosphere. The tensile strength and elongation (%) of the PANI films were measured using Universal Testing Machine (AGS-10KNG) (Shimadzu,



MA = maleic acid, DHS = dodecylhydrogensulfate

Scheme 1 Structure of polyaniline-maleic acid-dodecyl hydrogen sulfate salt.

Japan). The test specimens were in the form of dumbbells according to ASTM D-638. The films of thickness ~ 0.2 mm, gauge length 50 mm, and width 10 mm were stretched at a crosshead speed of 20 mm/min. The data reported are the average of five measurements.

RESULTS AND DISCUSSION

Emulsion polymerization carried out in the presence of MA/SLS leads to a solution-processible powder (PANI-POW) of the electrical conductivity, $\sigma = 0.11$ S/cm.⁴³ The simplicity of its preparation should be underlined together with the fact that in the developed emulsion polymerization only reagents widely used in chemical and polymer industry are employed. NMR investigations combined with elemental analysis and gravimetric determination of the PANI deprotonation products show that the resulting polymer can be considered as mixed doped PANI of the formula shown in Scheme 1.

This polymer has constituted the basis for the preparation of PANI-PVC conductive blends using the blend-

ing procedure described in detail in the Experimental part. For comparative reasons we have first prepared blends of identical mass fraction of the conductive phase ($f = 0.091$) using two differently prepared forms of PANI, namely PANI-POW and PANI-SOL.

The obtained RT conductivity data were 5.0×10^{-4} and 1.0×10^{-5} for PANI-POW-PVC and PANI-SOL-PVC, respectively. Taking into account the simplicity of its preparation and the higher conductivity measured for the same conductive phase mass fraction (f), the PANI-POW-PVC system was selected for further detailed investigations. In particular, we have verified the protonation and the oxidation state of the conductive phase in the blend by IR spectroscopy, its morphology by scanning electron microscopy, and we have followed the evolution of the conductivity, the tensile strength, and the glass transition (T_g) of the blend with increasing PANI-POW content and finally we have determined the thermal stability of the blend by thermogravimetry.

Figure 1(a,b) shows IR spectra of pure PVC film and PANI-POW-PVC blend ($f = 0.167$), respectively.

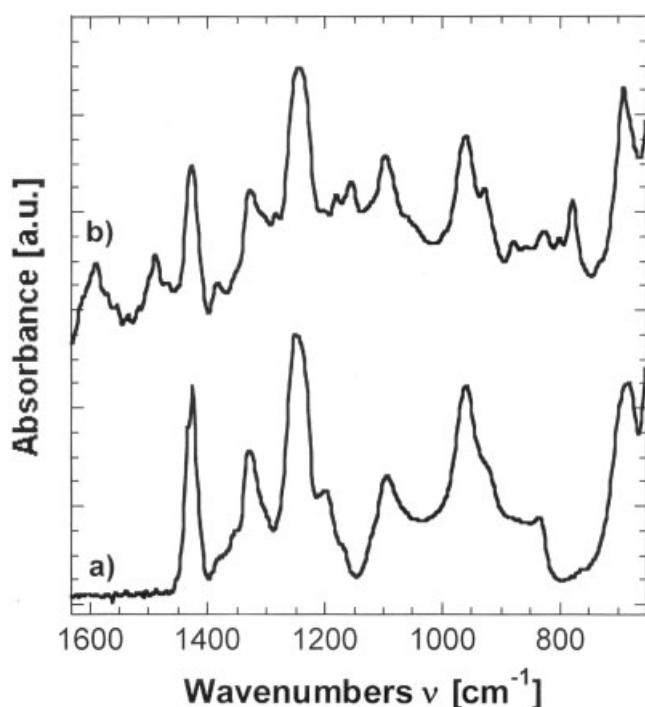


Figure 1 Infrared spectra of (a) PVC film and (b) PANI-POW-PVC ($f = 0.167$) film processed in identical conditions.

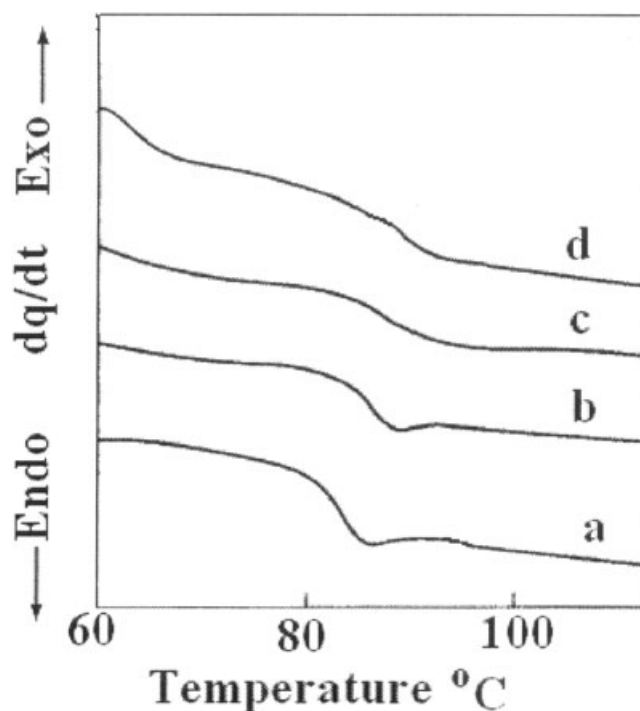


Figure 2 DSC curves of (a) PVC, (b) PANI-POW-PVC ($f = 0.091$), (c) PANI-POW-PVC ($f = 0.167$), and (d) PANI-POW-PVC ($f = 0.231$).

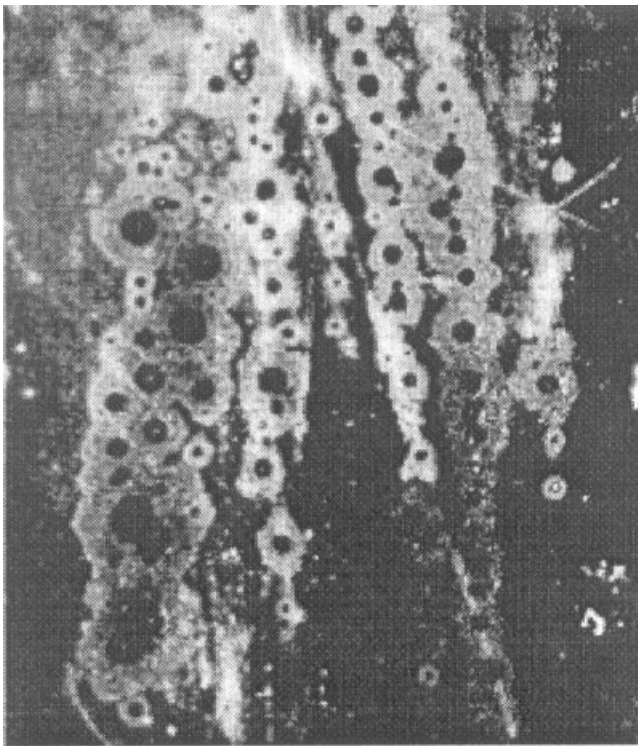
60 μm

Figure 3 Scanning electron micrograph of PANI-POW-PVC ($f = 0.167$).

This comparison is facilitated by the fact that two principal peaks of the protonated form of PANI appear in the spectral region where no band originating from PVC vibrations are expected. In the spectrum of the PANI-POW-PVC blend these two peaks at 1585 (quinoid ring stretching) and 1490 cm^{-1} (benzenoid ring stretching), respectively, are accompanied by two other bands characteristic of PANI at 1155 cm^{-1} (electronic like absorption of $\text{N}=\text{Q}=\text{N}$, where Q = quinoid ring) and 825 cm^{-1} ($\text{C}-\text{H}$ out of plane deformation of 1,4-disubstituted benzene). Thus, as expected PANI salt used for blending remains in its protonated state which assures its conductivity. The bands at 1425 ($\text{C}-\text{H}$ bond), 1330 ($\text{C}-\text{H}$ bond), 1250 ($\text{C}-\text{Cl}$ str), 1100 ($\text{C}-\text{C}$ str), 960 ($\text{C}-\text{H}$ bond), and 690 ($\text{C}-\text{Cl}$ bond) cm^{-1} originate from the PVC matrix as can be clearly concluded from the comparison of Figure 1(a,b).

Films of $f < 0.13$ are transparent and homogeneous by visual observation. This optical clarity, confirmed also by optical microscopy, is a good indication of miscibility of both blend components and suggests that the phase separation, necessary for the macroscopic conductivity, takes place at a submicrometric level.

The miscibility of particular components in a given polymer blend can commonly be ascertained through T_g measurements.^{40,47} A continuous increase of T_g with growing content of the more rigid phase can be taken as a manifestation of intimate miscibility. As

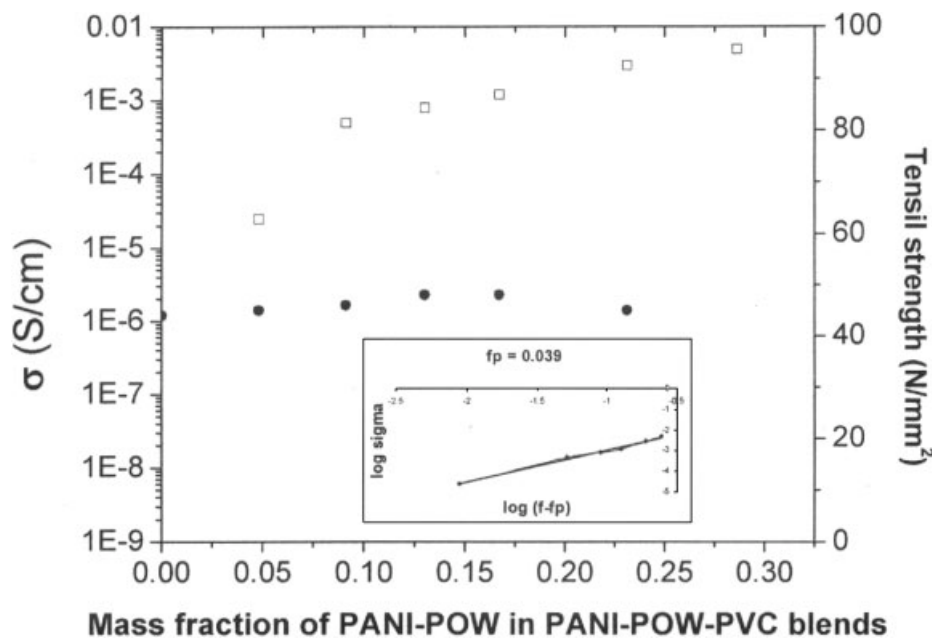


Figure 4 Electrical conductivity and tensile strength versus the conductive phase mass fraction measured for PANI-POW-PVC blends. (●) denotes the tensile strength versus mass fraction of PANI-POW-PVC and (□) denotes electrical conductivity versus mass fraction of PANI-POW-PVC. The inset shows the fitting of the experimental data to the scaling law of percolation. The determined percolation threshold is $f_p = 0.039$.

can be seen from Figure 2 this trend is observed for PANI-POW-PVC blends. T_g of pure PVC is 85°C , and it clearly increases upon addition of PANI-POW (Fig. 2). For $f > 0.23$ no T_g ascribed to the PVC component can be detected indicating that we are in the mass fraction (f) range exceeding the mechanical percolation threshold for the more rigid phase, i.e., PANI-POW. Thus, submicrometric-scale homogeneity of the blend evidenced by optical microscopy is confirmed by DSC measurements.

The submicrometric level of phase separation constitutes the *conditio sine qua non* of the blend macroscopic conductivity; in some cases it can lead to extremely low percolation levels.^{38,39} Any phase separation

involving micrometric-size aggregations or other morphological features would inevitably lead to an increase of the percolation threshold. In our blends we observe some areas of this type. Figure 3 shows the scanning electron micrograph of a film of PANI-POW-PVC ($f = 0.167$). The dark regions correspond to the PVC phase while the bright ones to the conductive PANI phase. A necklace-like morphology is observed in which PVC particles are surrounded by the conductive PANI phase forming a percolating network at the micrometric scale.

The investigations of the percolation behavior are crucial for the determination of the utility of any newly developed blend. In its classical version the

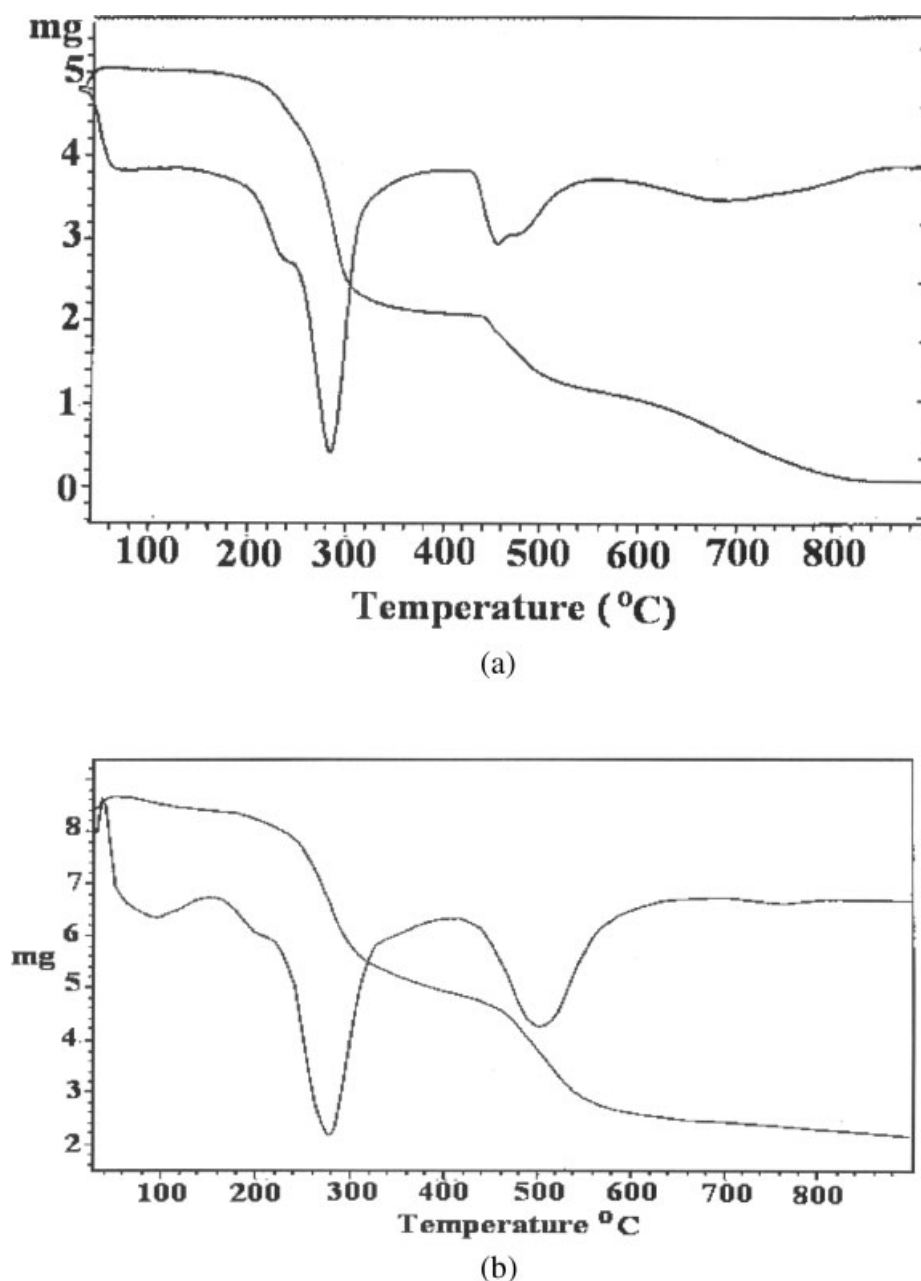


Figure 5 TGA-DTG thermogram of (a) PANI-POW-PVC ($f = 0.167$) film and (b) pure PANI-POW.

electrical percolation curve is constructed from the dependence of the electrical conductivity of the blend on the volume fraction of the conductive phase. Since we have not determined the exact density of PANI-POW, in the performed calculations we have replaced the volume fraction by the mass one. This is a reasonable assumption since the density of PANI doped with similar dopants is close to that of PVC (1.3 g/cm³). The obtained electrical percolation curve is presented in Figure 4.

Fitting of the obtained results to the scaling law of percolation theory⁴⁸

$$\sigma(f) = c(f - f_p)^\alpha \quad (1)$$

leads to the percolation threshold, $f_p = 0.039$ and the critical exponent, $\alpha = 1.43$. This value is smaller than that predicted by the universal law ($\alpha = 2.0$) but very close to the critical exponent obtained by Reghu et al.⁴⁹ for blends of PANI with poly(methyl methacrylate) ($\alpha = 1.43$) who attribute this decrease of the exponent value to thermally induced hopping between disconnected or weakly connected parts of the percolating network.

It should be noted that up to $f = 0.231$ the measured tensile strength of the blend remains essentially unchanged (Fig. 4) and, within the experimental error, identical to that of pure PVC (tensile strength ~ 45 N/mm², elongation $\sim 3\%$). In the same f range, the electrical conductivity increases by several orders of magnitude. Higher value of the mechanical percolation threshold with respect to the electrical one constitutes *conditio sine qua non* of the preparation of blends, which show enhanced electrical conductivity while retaining good mechanical properties of the host polymer. This is the case of the blends described in this article; the mechanical percolation is manifested only for $f > 0.231$ by brittle nature of the fabricated blends which impedes the correct determination of their mechanical properties.

The next question to be answered is whether the developed blends are sufficiently thermally stable for technological applications. Figure 5(a) shows a typical TGA/DTG thermogram of PANI-POW-PVC blend. Up to $\sim 200^\circ\text{C}$ only little mass loss ($\sim 1\%$) is observed because of the moisture present in the blend and possible removal of residual entrapped solvent. Above 200°C thermal degradation of the blend occurs in three steps as evidenced by a significant mass loss in the temperature range of $200\text{--}310^\circ\text{C}$, followed by two less-pronounced mass losses. It is instructive to compare this behavior with that of pure PANI-POW [Fig. 5(b)].⁵⁰ A fourfold bigger mass loss is observed for pure PANI-POW, in the temperature range from RT to 200°C , as compared with the case of the blend ($f = 0.167$). This is understandable since the hygroscopic component constitutes only a fraction of the blend.

The onset of the second mass loss is, in pure PANI-POW, shifted to higher temperatures by $\sim 20^\circ\text{C}$, as compared with the blend. This may indicate that the second step of the blend decomposition also involves the PVC matrix.

Finally, the retention of the blend conductivity at elevated temperatures is important from the practical point of view. Our preliminary studies show that heating of the blends up to 100°C does not influence their room temperature conductivity. Tests at higher temperatures are in progress.

CONCLUSIONS

To summarize, using cheap reagents, we have prepared conductive blends of PANI and PVC, showing a low percolation threshold for electrical conductivity ($f_p = 0.039$) and exhibiting good mechanical properties of unblended PVC both below and above the electrical percolation threshold. The range of conductivities covered by these blends enables their application not only as electrostatic dissipation (ESD) materials ($\sigma = 10^{-9}$ to 10^{-5} S/cm) but also for purposes requiring higher blends conductivities.

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