Polymer Vol. 37 No. 23, pp. 5295-5299, 1996
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0032-3861/96/$15.00+0.00

S0032-3861(96)00419-3

ELSEVIER

polymer communications

Highly conducting polymer blend films of polyaniline and nylon 6 by cosolvation in an organic acid

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(Received 21 March 1996)

Polymer blend films of polyaniline and nylon 6 were prepared from homogeneous solutions in formic acid at various weight ratios of polyaniline and nylon 6. Free standing, lustrous and flexible films were obtained by casting. The maximum conductivity of the film was about 0.2 S cm^{-1}, corresponding to a weight ratio of 0.5 wt/wt polyaniline (PAni) and nylon 6. The film exhibits semiconducting behaviour in the range of temperatures between 300 K and 10 K and the data fits in with the VRH model for transport in the range of 150 K to 50 K. Optical absorption spectra reveal absorption bands typical of polyaniline salt. I.r. spectra show a characteristic band at 1145 cm^{-1} which is associated with electrical conductivity in polyaniline. A simultaneous t.g.a.–d.t.a. scan reveals that the melting temperature of PAni/nylon 6 is slightly reduced. The X-ray diffraction pattern indicates that the crystal structure of nylon 6 in the blend film is retained on modification. The films also exhibit good environmental stability and mechanical strength.

(Keywords: polyaniline; nylon 6; solution processing)

Introduction

Conducting polymers have been the subject of much interest, not only from fundamental scientific interest but also from a practical viewpoint, for various functional applications[1,2]. Within the class of conducting polymers polyaniline (PAni) occupies an important place. PAni is unique in that it is soluble and hence processible in the conducting form[3]. It is thermally stable (to temperatures up to approximately 200°C) and stable in air. PAni has been investigated extensively since the beginning of this century[4]. Recently, this conjugated polymer has attracted considerable interest as a conducting material, for the following reasons[5]:

1. the monomer is inexpensive;
2. the conversion of monomer to polymer is straightforward;
3. the polymerization reaction proceeds with high yield;
4. the resulting salt is quite stable and shows a relatively high level of conductivity;
5. when treated with base ($pH > 7.0$) the conducting PAni salt converts to the base form.

Thus PAni is a low-cost conducting polymer that is both stable and processible. Processing of PAni into various forms such as thin films, sheets, transparent films etc. remained an unsolved problem for many years. PAni could not be processed in the melt, since the polymer decomposes at temperatures below a softening or melting point. Nevertheless, in a short communication[6], Wessling reported a patented procedure in which PAni salt was modified to become purer and more homogeneous. The resulting powder was processed using temperatures between 100°C and 250°C.

PAni could also be processed in solution without changing the molecular structure of the polymer. Three solvent-based methods have been reported to dissolve and process PAni:

1. in N-methyl-2-pyrrolidone (NMP)[7];
2. in pyrrolidine or tropylamine[8]; or
3. in concentrated sulfuric and other acids[8,9].

Solution processing of PAni enables the synthesis of conducting blends with insulating polymers that are cosoluble. For example, PAni–aramid blends have been processed from sulfuric acid[9]. The key to processing PAni in solution is to identify a solvent in which both the conducting polymer and the host polymer are soluble. In this study we have used formic acid as a cosolvent for PAni (emeraldine base) and nylon 6. The organic acid also dopes the base form of PAni upon cosolvation.

Materials

The monomer aniline was distilled before use. All reagents were of analytical grade and used without purification. Nylon 6 beads were supplied by IPCL Baroda, India.

Experimental

Synthesis of emeraldine base. PAni was prepared by chemical oxidative polymerization[10] of aniline in 1 M aqueous HCl acid solution using ammonium persulfate as oxidant followed by deprotonation in aqueous alkali. An equimolar ratio of persulfate and aniline was used. The approximate solubility of emeraldine base in formic acid was evaluated using the procedure reported in the literature[7].

Solutions of emeraldine base and nylon 6 in formic acid. Solutions of PAni and nylon 6 in formic acid with

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Table 1 Conductivity of PAni/nylon 6 at various blend ratios

PAni/nylon 6 (wt/wt)	Conductivity ($S cm^{-1}$)
10/90	0.02
20/80	0.04
30/70	0.06
40/60	0.16
50/50	0.23
60/40	0.21
70/30	0.20

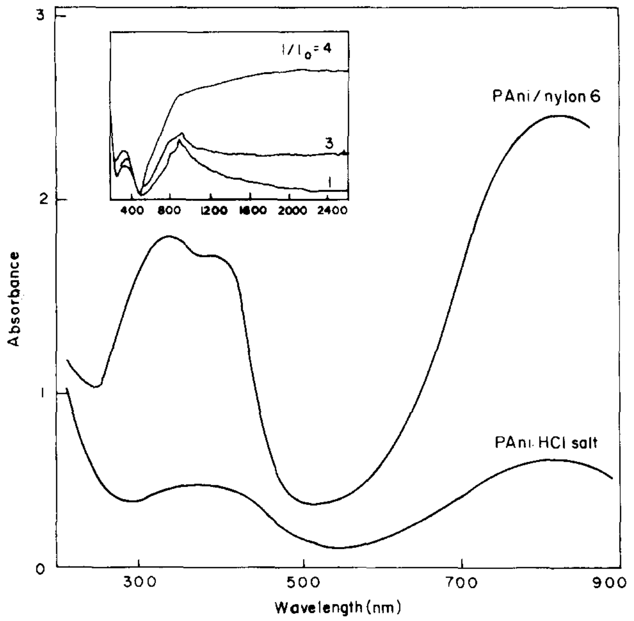

Figure 1 Optical absorption spectrum of PAni/nylon 6 film (PAni weight fraction 0.5) and PAni film (inset showing u.v.-v.i.s. spectrum of PAni/PVC stretch-aligned to varying degrees)

varying weight ratios of PAni to nylon 6, as shown in *Table 1*, were prepared by adding the blue powder (emeraldine base) to nylon 6 solution in formic acid. The mixture was stirred for about 4 h at room temperature to dissolve PAni. The resulting homogeneous solution was cast in a petri dish to obtain an even coating and dried in a dessicator under dynamic vacuum for about 12 h. The films were flexible and lustrous. The side of the film exposed to air had a distinct dark blue tint. The films were about 30–50 μm thick.

Characterization. Electrical conductivity of the films was measured using the four-probe method[11] with a Keithley 195A DMM, a Keithley 220 programmable current source and colloidal silver for electrical contacts. Conductivities below room temperature were measured by attaching the film to a four-probe apparatus (dipstick cryostat) which was evacuated to 0.05 torr and subsequently filled with helium exchange gas. A Lakeshore 330 Auto tuning temperature controller was used to monitor the temperature. U.v.-v.i.s. optical absorption spectra was taken using Hitachi 150-20 apparatus, i.r. spectra using a Perkin-Elmer 781 IR spectrophotometer, X-ray diffraction patterns using a Rigaku RAD-C wide angle diffractometer with Ni-filtered CuKα radiation, and t.g.a.–d.t.a. scans using a simultaneous t.g.–d.t.a. thermal analyser (Shimadzu-DT40) at a heating rate of 10°C min^{-1} in an atmosphere of nitrogen.

Results and discussion

Figure 1 shows the optical absorption spectrum of PAni/nylon 6 film (PAni wt. fraction 0.5) and PAni film cast on a quartz substrate, along with an inset showing the spectra[15] of PAni/PVC stretch-aligned to varying degrees. Absorption bands appear in the range 450–550 nm, which is the characteristic absorption spectrum

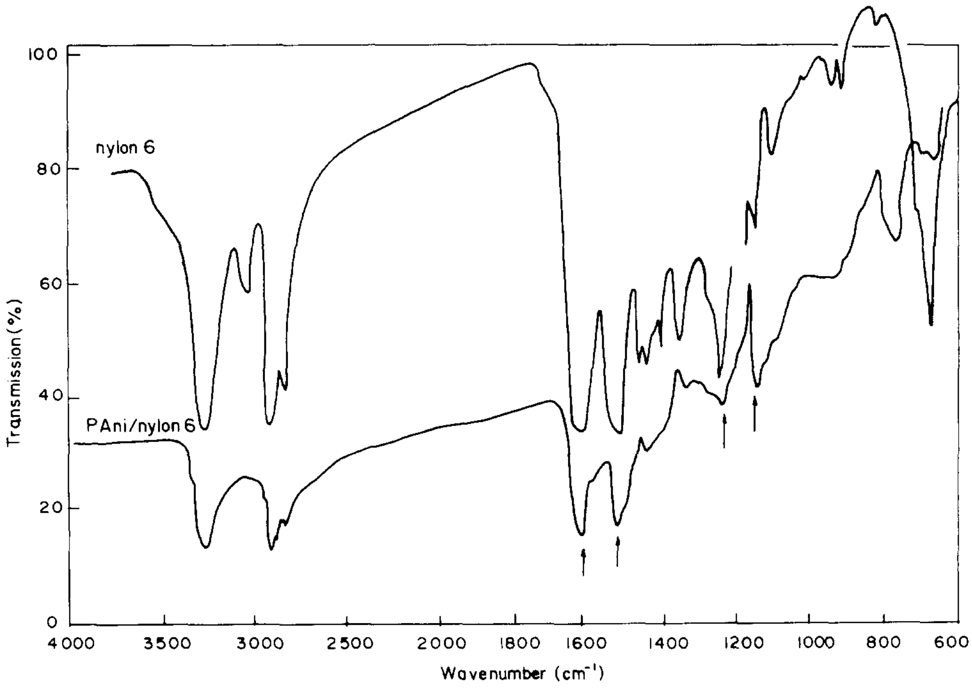

Figure 2 I.r. spectra of pristine nylon 6 film and PAni/nylon 6 film (PAni weight fraction 0.5)

of the salt form of PAni[12–14]. Min and MacDiarmid, in a recent report[15] on the concept of secondary doping of PAni, emphasized the importance of polymer chain conformation as a major factor in determining the conductivity of an intrinsically conducting polymer, which in turn depends on the method of processing. For instance, films of PAni complexed with CSA were amorphous (coil-like structure) when cast from chloroform solution and partially crystalline (rod-like structure) when cast from *m*-cresol. They also found that conformational changes from coil to rod can be effected by mechanical stretching of the PAni films (see inset in *Figure 1*), leading to an increase in electrical conductivity. It is interesting to note that the absorption spectra of PAni/nylon 6 film corresponding to 0.5 weight fraction of PAni, which was cast from solutions in formic acid, are comparable to the spectra of stretched ($l/l_0 = 4$) PAni/PVC film. The high conductivity of PAni/nylon 6 film may be attributed to the ordering of chains on evaporation of solvent. Thus the absorption spectra gives an indication of the type of conformation in polymer films and hence the conductivity.

Figure 2 shows the i.r. spectra of pristine nylon 6 film and PAni/nylon 6 film (PAni weight fraction 0.5). The absorption bands near 1600 cm^{-1} have been associated with C=C stretching in quinonoid ring and C=C stretching in benzenoid ring respectively[16,17]. Furthermore, it has been reported in the literature[16,18] that the absorption band at 1145 cm^{-1} is associated with electrical conductivity in polyaniline.

Figure 3a shows the X-ray diffraction pattern of pristine nylon 6 film and *Figure 3b* the pattern of PAni/nylon 6 film (PAni weight fraction 0.5). The X-ray diffraction pattern of PAni complexed with sulfuric acid is also shown in the inset[19] for comparison. The X-ray diffraction pattern of PAni/nylon 6 film is comparable to

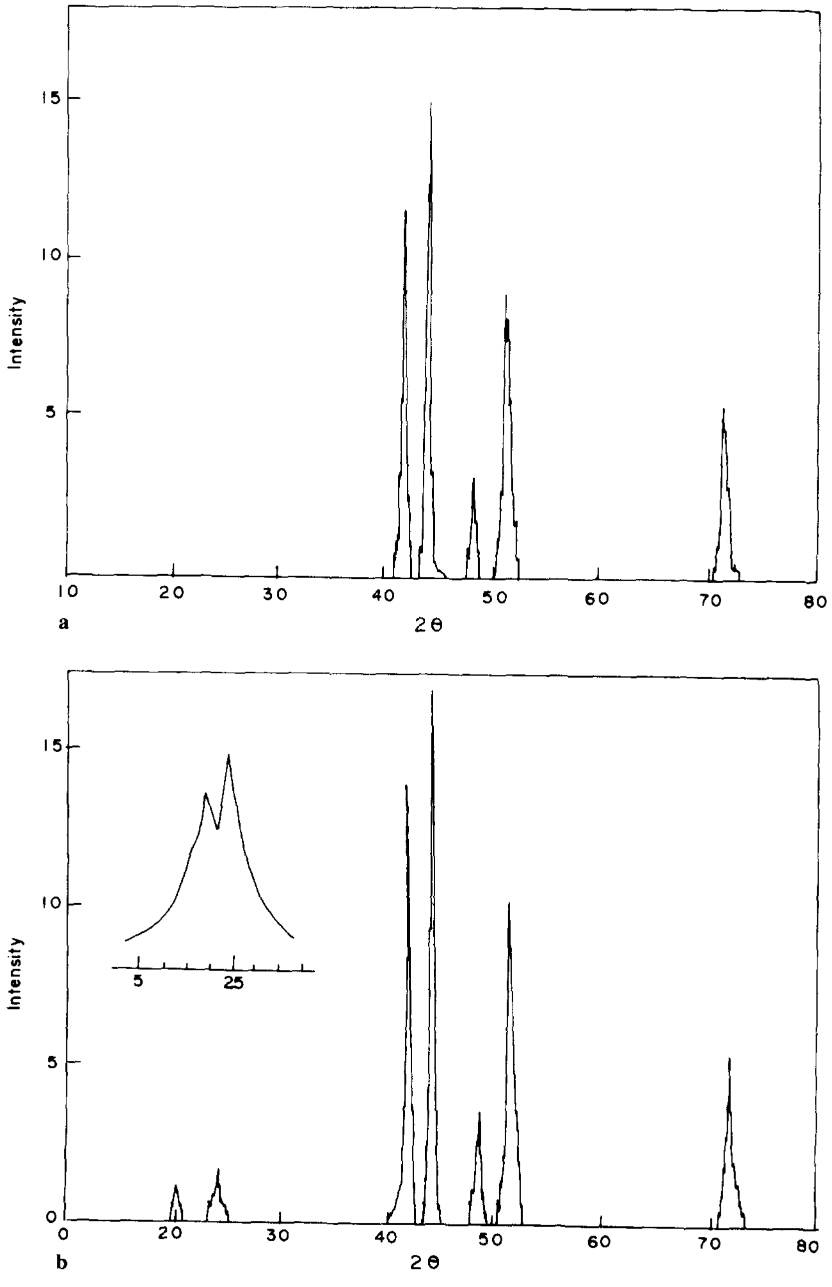

Figure 3 X-Ray diffraction pattern of (a) pristine nylon 6 film; (b) PAni/nylon 6 film (PAni weight fraction 0.5) (inset shows X-ray diffraction pattern of PAni complexed with H_2SO_4)

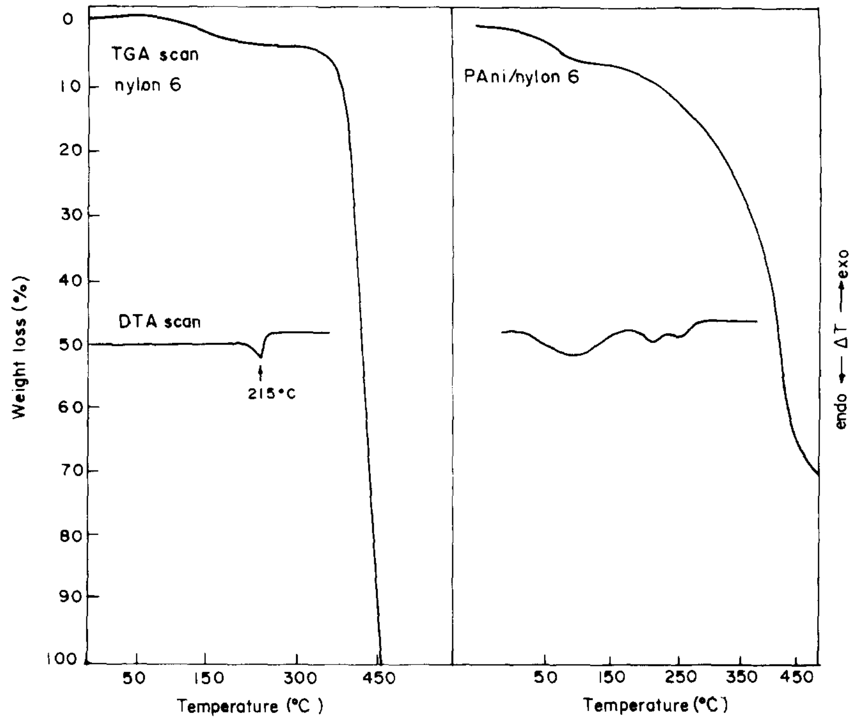

Figure 4 T.g.a.–d.t.a. scans of pristine nylon 6 film and PAni/nylon 6 film (PAni weight fraction 0.5)

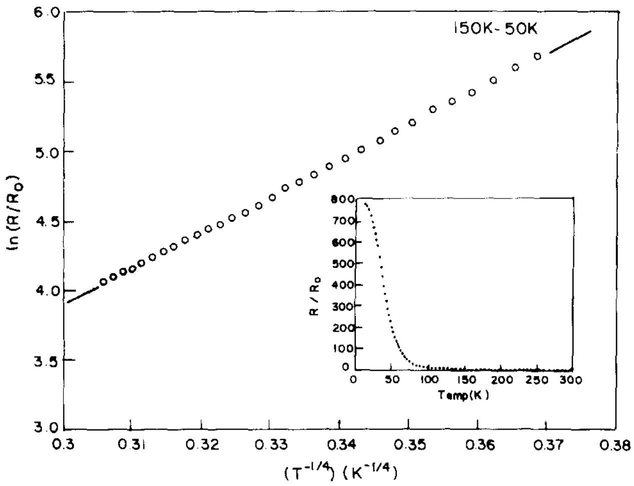

Figure 5 Plot of ln resistance vs $T^{1/4}$ of PAni/nylon 6 (PAni weight fraction 0.5). The normalized resistance–temperature plot is shown in the inset

that of pristine nylon 6 film but for a difference in the relative intensities of the peaks. This suggests that chemical modification does not affect the crystal structure of nylon 6. In addition to the five peaks characteristic of pristine nylon 6, PAni/nylon 6 film shows two more reflections between $2\theta = 20°$ and $25°$, corresponding to the crystalline peaks of PAni complexed with formic acid.

Figure 4 shows the t.g.a.–d.t.a. scans, using a simultaneous t.g.a.–d.t.a. analyser, of pristine nylon 6 film and PAni/nylon 6 film (PAni weight fraction 0.5). The t.g.a.–d.t.a. scan of PAni/nylon 6 film shows an earlier onset of weight loss and a broad d.t.a. peak from 30 to 150°C, both indicative of poor thermal stability when compared to pristine nylon 6 film. The d.t.a. scan also indicates that the melting temperature of nylon 6 is slightly reduced on modification. PAni/nylon 6 (PAni weight fraction 0.5) retains 30% of its original weight at 500°C whereas the pristine nylon 6 decomposes completely below 500°C.

Normalized resistance of PAni/nylon 6 film (PAni weight fraction 0.5) measured in the temperature range 300–10 K is shown in the inset in *Figure 5*. The data are analysed in the Mott's variable range hopping conduction in three dimensions in the temperature range 150–50 K.

The dependence of resistance on temperature for three-dimensional hopping is given by the Mott[20] equation as

$$\rho \propto \exp\left[(T_0/T)^{1/4}\right]$$

where T_0 is the Mott characteristic temperature.

Figure 5 is a plot of ln resistance vs $T^{-1/4}$ for PAni/nylon 6 (PAni weight fraction 0.5) and shows ln resistance proportional to $T^{-1/4}$ in the temperature range 150–50 K, indicative of three-dimensional variable range hopping.

Conclusions

1. Free-standing, lustrous and flexible PAni/nylon 6 films have been successfully prepared by casting.
2. The maximum conductivity of the film was about $0.2\,\mathrm{S\,cm^{-1}}$, corresponding to a weight ratio of 0.5 wt/wt PAni and nylon 6.
3. The film is semiconducting in nature.
4. The melting temperature of PAni/nylon 6 film is slightly lower than that of pristine nylon 6.
5. The crystal structure of nylon 6 is retained on modification.
6. The films exhibit good environmental stability and mechanical strength.
7. Since the films are stable and retain the mechanical

properties of the host polymer (nylon 6), films, fibres and coatings can be fabricated from solution for use in antistatic applications, electromagnetic shielding, transparent conducting films and for the fabrication of novel electrodes for use in electronic devices.

Acknowledgement

The authors acknowledge the support of the Department of Science and Technology (SVS/DST/237).

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