

Synthesis and Characterization of Novel Polyfuran/Poly(2-iodoaniline) Conducting Composite

Ayşegül Gök,¹ Bekir Sarı,² Muzaffer Talu²

¹Department of Chemistry, Faculty of Arts and Science, Süleyman Demirel University, 32260 Isparta, Turkey

²Department of Chemistry, Faculty of Arts and Science, Gazi University, 06500 Ankara, Turkey

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ABSTRACT: The electrically conducting polyfuran/poly(2-iodoaniline) (PFu/P2IAN) and P2IAN/PFu composites were prepared by chemical oxidative polymerization using polyfuran and poly(2-iodoaniline) in HCl and CHCl₃ media. The conductivities of composites were determined as a function of the amount of guest polymer. It was found out that the conductivities of P2IAN/PFu composites increased 100-fold, whereas the conductivities of PFu/P2IAN composites did not show a specific increase. The composite compositions were altered by varying guest polymer feed ratios during preparation. Generally, the electrical conductivities of P2IAN/PFu composites increased with increasing the amount of PFu. Homopolymers and composites were further characterized thermally, employing thermogravimetry

(TGA) and morphologically employing scanning electron microscopy (SEM). Further evidences concerning the polymer structures were obtained by FTIR and UV-vis spectroscopies and magnetic susceptibility measurements. TGA results revealed that PFu/P2IAN among the homopolymers (PFu and P2IAN) and P2IAN/PFu composite have the highest thermal stability. The composites synthesized varying the host and the guest polymer order have different conductivities, morphological structures, and thermal properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2823–2830, 2003

Key words: composites; conducting polymers; host–guest systems; morphology; thermal properties

INTRODUCTION

Conducting polymers such as polyaniline, polypyrrole, polythiophene, and polyfuran have received a great deal of attention because of their potential applications in the area of rechargeable batteries,¹ gas-separation membranes,² and electroluminescent diodes.³ However, conducting polymers have disadvantages such as poor mechanical and thermal properties and poor processability.

Several methods have been used to improve the mechanical and thermal properties and processability, including the introduction of substitute groups into the main chain,^{4,5} the synthesis of soluble precursors,⁶ and the preparation of conducting polymer composites by chemical oxidative polymerization.^{7–10}

Recently, the preparation of conductive composites by chemical oxidative polymerization was developed and refined because this method is easier and more effective.^{11–13} According to this procedure, we prepared most composites of polyaniline, polyfuran, and their derivatives for further investigation.^{14,15}

Here we report an analysis of the conductivity, magnetic, spectroscopic, thermal, and morphological properties of a series of PFu/P2IAN and P2IAN/PFu composites. PFu/P2IAN and P2IAN/PFu conducting composites were prepared by varying the synthesis order of the host and the guest polymer. We conjectured whether PFu and P2IAN particles mixed with each other would affect the formation of intermolecular interaction between the two polymers and the structure of the obtained composites.

EXPERIMENTAL

Materials

2-Iodoaniline and furan (Merck, Darmstadt, Germany) were purified by distillation at a reduced pressure before polymerization. Ammonium persulfate [(NH₄)₂S₂O₈], antimony (III) chloride (SbCl₃), chloroform, hydrochloric acid, *N,N*-dimethylformamide (DMF), and diethyl ether were purchased from Merck and used as received.

Polymerization of 2-iodoaniline

Purified 2-iodoaniline (8.76 mmol) was dissolved in 100 mL 1.5M HCl solution. The temperature of solution was maintained at 50°C to dissolve 2-iodoaniline. The required amount (17.5 mmol) of (NH₄)₂S₂O₈ was dissolved in 100 mL 1.5M HCl and then added drop-

Correspondence to: B. Sarı (bsari@gazi.edu.tr).

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TABLE I
Conductivity and Gouy Balance Measurements of PFu/P2IAN Composites

Polymer	Yield of P2IAN in composite (% <i>, m/m</i>)	Conductivity (S/cm)	Magnetic susceptibility (μ_{eff} BM) ^a
PFu/P2IAN	38	4.41×10^{-5}	+210
PFu/P2IAN	52	5.78×10^{-5}	+350
PFu/P2IAN	62	5.98×10^{-5}	+420
PFu/P2IAN	85	6.99×10^{-5}	+510
PFu:P2IAN (1:1) mechanical mixture	—	3.49×10^{-5}	-27
PFu	—	1.44×10^{-5}	-51
P2IAN	—	2.35×10^{-5}	+343

^a μ_{eff} , effective magnetic moment; BM, Bohr magneton.

wise over 60 min to the previous 2-iodoaniline solution and stirred under N₂ atmosphere. The dark-colored precipitate was filtered and washed with 1.5M HCl, distilled water, and diethyl ether. Further, it was dried in a vacuum oven at 70°C.

Polymerization of furan

Furan (13.3 mmol) was polymerized using SbCl₃ as oxidant in anhydrous medium (CHCl₃) at 20°C under N₂ atmosphere. The ratio of oxidant to monomer was taken as 1.30. Polyfuran (PFu) was washed with CHCl₃ and dried in a vacuum oven at 70°C.

Synthesis of PFu/P2IAN conducting composite

A certain amount of PFu was dispersed in 1.5M HCl medium with stirring at 50°C. Then, (NH₄)₂S₂O₈ was added to the medium and stirred under N₂ atmosphere. A solution of 2-IAn in 1.5M HCl was added dropwise to the dispersed PFu solution. After polymerization was maintained for 24 h, the resultant composite was filtered; washed with 1.5M HCl, distilled water, diethyl ether; and dried. The yield of P2IAN in the composite was calculated gravimetrically.

Synthesis of P2IAN/PFu conducting composite

P2IAN/PFu composite was prepared in a similar way to PFu/P2IAN composite. A certain amount of P2IAN powder was dispersed in CHCl₃. SbCl₃ was then added to the medium and stirred under N₂ atmosphere at 20°C. Furan was added dropwise to this dispersed P2IAN solution. Polymerization was maintained for 24 h; the resultant composite was filtered and washed with CHCl₃. The quantity of PFu was calculated from the total mass of composite.

PFu/P2IAN and P2IAN/PFu composites including P2IAN and PFu at different percentages were prepared with maintenance of constant salt/monomer ratios. The PFu : P2IAN (1 : 1) mechanical mixture of both homopolymers was prepared and its properties were compared with those of PFu/P2IAN and P2IAN/PFu conducting composites.

Characterization

The dc electrical conductivities of dry samples of homopolymers, composites, and (1 : 1) mechanical mixture were measured by use of a four-probe technique. The polymer samples were made into pellets and their conductivity levels were measured using Nippon NP-900 multimeter (Nippon, Osaka, Japan).

Magnetic susceptibility measurements of samples were carried out by use of a Sherwood Scientific Model MKI Gouy Scale (Sherwood, St. Louis, MO), corresponding to the procedure reported elsewhere.¹⁵

FTIR spectra of PFu, P2IAN, PFu/P2IAN, P2IAN/PFu, and PFu : P2IAN (1 : 1) mechanical mixture were recorded using a Mattson-1000 Model spectrophotometer (Ati Unicam Ltd., Cambridge, UK) by use of the KBr disc technique.

UV-vis spectra of P2IAN, PFu/P2IAN, P2IAN/PFu, and PFu : P2IAN (1 : 1) mechanical mixture in DMF were recorded separately using a Unicam UV-2 Model spectrophotometer (Ati Unicam Ltd., Cambridge, UK), using DMF in the reference cell.

Thermogravimetric analyses (TGA) of PFu, P2IAN, PFu/P2IAN, P2IAN/PFu, and a (1 : 1) mechanical mixture of PFu and P2IAN were carried out on a Dupont 951 Model equipment (Dupont, Boston, MA) at a temperature range of 0–900°C. A heating rate of 10°C/min under nitrogen atmosphere was maintained for TGA analyses.

Scanning electron microscopy of homopolymers, composites, and PFu : P2IAN (1 : 1) mechanical mixture was done by use of a JEOL JEM 100 CX II electron microscope (JEOL, Peabody, MA).

RESULTS AND DISCUSSION

Assessments of electrical conductivity and magnetic susceptibility

The conductivities and magnetic susceptibility values of PFu/P2IAN composites including different percentages of P2IAN are given in Table I. As seen in Table I, the conductivities of P2IAN and PFu are determined as 2.35×10^{-5} and 1.44×10^{-5} S/cm, respectively. It may

TABLE II
Conductivity and Gouy Balance Measurements of P2IAN/PFu Composites

Polymer	Yield of PFu in composite (%, m/m)	Conductivity (S/cm)	Magnetic susceptibility (μ_e , BM) ^a
P2IAN/PFu	8.0	7.48×10^{-5}	-18
P2IAN/PFu	21	6.57×10^{-5}	+27
P2IAN/PFu	35	2.79×10^{-4}	+530
P2IAN/PFu	49	2.77×10^{-3}	+565
P2IAN/PFu	60	1.32×10^{-3}	+570
P2IAN/PFu	71	1.02×10^{-3}	+590
PFu:P2IAN (1:1) mechanical mixture	—	3.49×10^{-5}	-27
PFu	—	1.44×10^{-5}	-51
P2IAN	—	2.35×10^{-5}	+343

^a μ_e ; effective magnetic moment, BM, Bohr magneton.

be seen that the conductivity of the PFu/P2IAN composite is nearly identical to that of PFu, P2IAN, and their (1 : 1) mixture. The conductivities of PFu/P2IAN composites prepared at different percentages were not significantly different.

As seen in Table I, the magnetic susceptibilities of PFu, PFu : P2IAN (1 : 1) mixture, P2IAN, and PFu/P2IAN composites have diamagnetic and paramagnetic properties. Consequently, whereas the conducting mechanisms of PFu and the 1 : 1 mixture are of a "bipolaron" nature, the others demonstrate a "polaron" nature.¹⁶ It may also be seen that the magnetic susceptibility values of composites increased with increasing amounts of P2IAN.

Table II shows the conductivity and magnetic susceptibility values of P2IAN/PFu composites prepared by varying the order of synthesis of the guest polymer. The conductivity values of P2IAN/PFu composites increased with varying the amount of PFu. As seen in Table II, although the order of conductivity values of homopolymers and their (1 : 1) mixture was -5 (i.e., 10^{-5}), the order of conductivity values of P2IAN/PFu composites increased to -3 (i.e., 10^{-3}). As seen from the results, increasing amounts of PFu in the composite structure induce electrical conductivity because of the increase of physical interactions between PFu and P2IAN. With further increases in the amount of PFu in the composite including 49% of PFu, the conductivity did not change, and then remained nearly constant. As a result, it was determined that the conductivities of composites change according to the order of synthesis.

Magnetic susceptibility data of the composites shifted to positive values with increasing amounts of PFu that were different from those of the (1 : 1) mixture; that is, they have a "polaron" nature.¹⁷

FTIR spectroscopy

Figures 1 and 2 show FTIR spectra of PFu/P2IAN (a), PFu (b), P2IAN (c), PFu : P2IAN (1 : 1) mixture (d), and

P2IAN/PFu [Fig. 2(a)]. When the spectra of composites are studied, the characteristic peaks corresponding to both homopolymers (PFu, P2IAN) are seen and the shifts in wavenumbers of these peaks are determined. Although there are some changes in the spectra, it is not possible to propose any suggestions about the possible chemical interactions between PFu and P2IAN by use of the IR data.¹⁸

UV-vis spectroscopy

The UV-vis spectra of P2IAN, PFu/P2IAN, P2IAN/PFu, and the PFu : P2IAN mixture are shown in Figure 3. The UV-vis spectrum of PFu could not be taken because of its insolubility in common solvents. The UV-vis spectrum of P2IAN shows two peaks at 267 and 290 nm; the 267 nm peak corresponds to excitation of the amine nitrogen of the benzenoid segments of P2IAN and the peak at 290 nm corresponds to the polaron/bipolaron transition of doped PANI.^{19,20} We did not see $n \rightarrow \pi^*$ transitions of the quinoid segments, which are all in conformity with the characteristics of doped PANI and their derivatives,^{21,22} for P2IAN and its composites.

The maximum absorbance wavelengths of PFu/P2IAN and the (1 : 1) mixture are the same as those of P2IAN, except the peak at 290 nm and these results agree with conductivity measurements (Table I). However, in the P2IAN/PFu composite the band corresponding to $\pi \rightarrow \pi^*$ transitions shifted to somewhat red. This implies that the P2IAN/PFu composite enhances the conjugation length of P2IAN chains. These results also agree with increases in conductivity (Table II).

Thermogravimetric analysis

The TGA thermograms of PFu and P2IAN homopolymers are seen in Figures 4 and 5, respectively. The TGA curve of PFu (Fig. 4) shows a significant loss of mass at low temperature according to P2IAN. TGA thermograms of PFu/P2IAN, P2IAN/PFu, and the (1 :

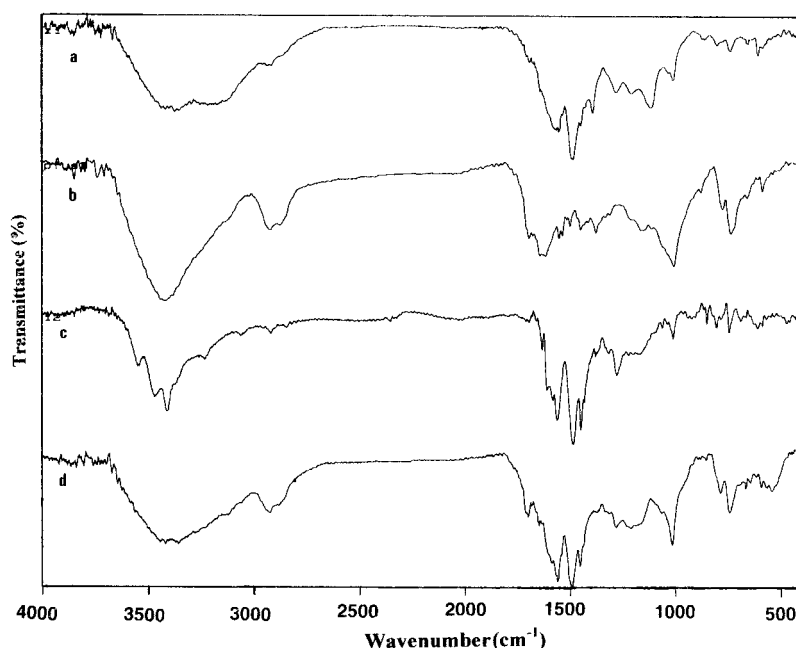


Figure 1 FTIR spectra of polymers: (a) PFu/P2IAN; (b) PFu; (c) P2IAN; (d) PFu : P2IAN (1 : 1) mechanical mixture.

1) mixture are given in Figure 6. As seen in the TGA curves, whereas the PFu : P2IAN (1 : 1) mixture nearly decomposes (such as PFu) at 900°C, 34% of the composites remain undecomposed.

PFu, which is completely insoluble in most common organic solvents, also remained black after repeated washings with anhydrous chloroform, thus suggesting that it was obtained in the oxidized form. Indeed, SbCl_3 is able not only to promote (by a redox process) the oxidative coupling of furan rings, but also to ex-

tract electrons from the polymer backbone, to yield a polymer complex in which inorganic species, such as Cl^- and SbCl_4^- , are present as counter-ions. Moreover, the excess of SbCl_3 and its reduction products (such as Sb and having oligomeric and ketone groups) probably remain embedded in the polymer during its precipitation. This hypothesis is confirmed by TGA of PFu, which shows (Fig. 4) a progressive weight loss attributed to evaporation of nonchemically bonded SbCl_3 and reduction products with low molecular

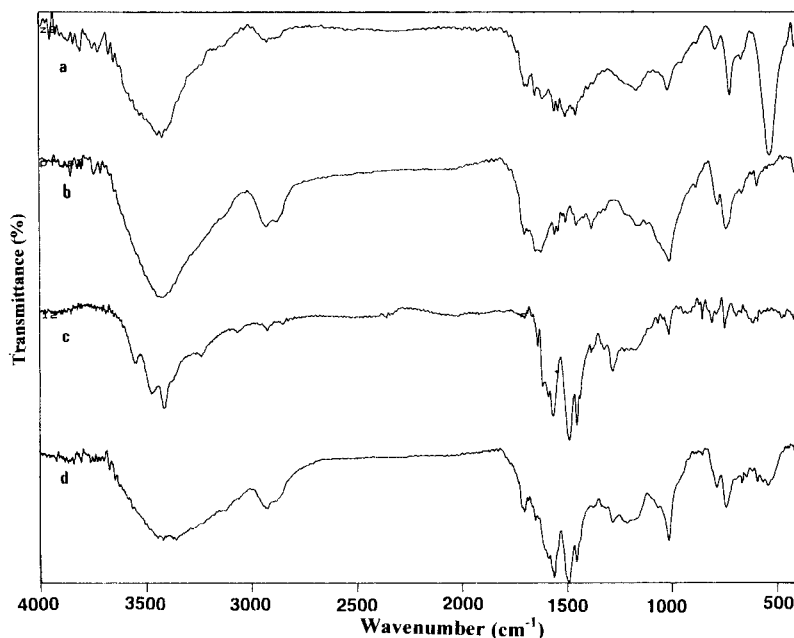


Figure 2 FTIR spectra of polymers: (a) P2IAN/PFu; (b) PFu; (c) P2IAN; (d) PFu : P2IAN (1 : 1) mechanical mixture.

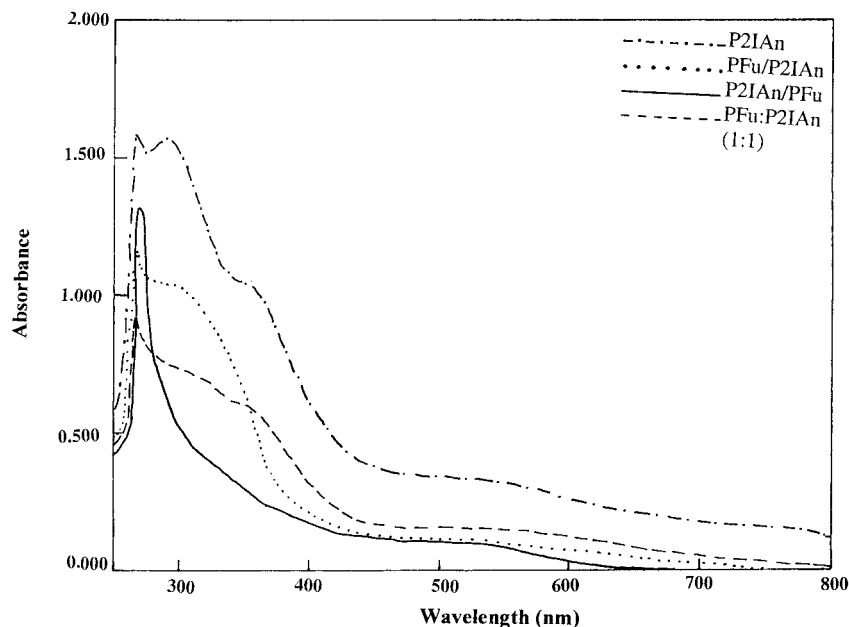


Figure 3 UV-vis spectra of polymers.

weight below 500°C, the temperature at which the degradation of the polymer starts to occur.

The results obtained from thermograms are tabulated in Table III. As seen in Table III, the three decomposition temperatures (T_i , T_m , T_f) of the samples are different from each other. From TGA thermograms of polymers, it can be concluded that the initial mass loss between 50 and 120°C is attributed

mainly to release of moisture, solvent, and dopant from the surface of samples.²³ At the second decomposition temperature (150–225°C), polymer chain structures decompose after the elimination of dopant acids from polymer chains.^{19,24} According to the initial decomposition temperature (T_i), PFu/P2IAN has the highest decomposition temperature (225°C), whereas that of PFu has the lowest (114°C).

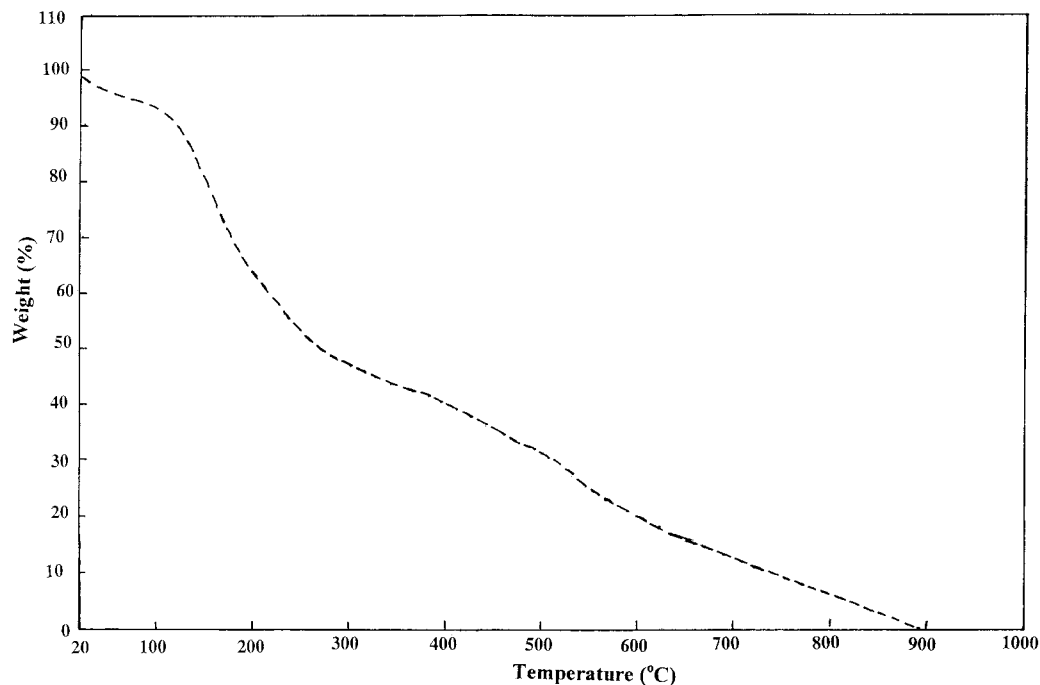


Figure 4 TGA thermogram of PFu.

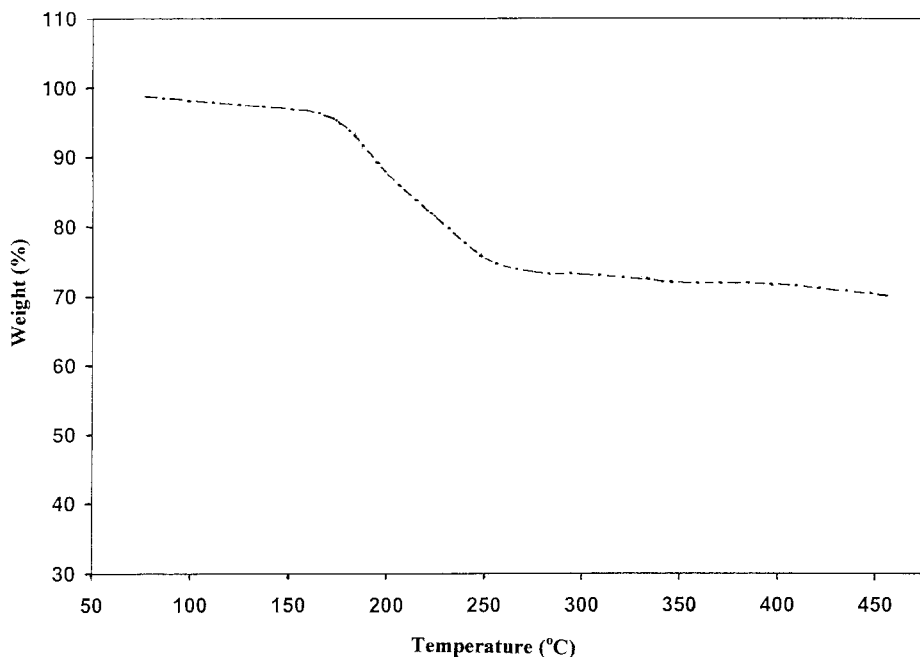


Figure 5 TGA thermogram of P2IAn.

The PFu/P2IAn composite system prepared by varying the synthesis order is thermally more stable than P2IAn/PFu. Although P2IAn/PFu has the highest conductivity, it has the lowest thermal stability. Similar results were observed for the PFu/P2ClAn composite in our previous study.²⁵ High doping is one factor responsible for the high con-

ductivity. Consequently, doping dramatically reduces the stability of polymer. The undoped emeraldine base state of polyaniline and its alkyl derivatives is thermally more stable than the doped emeraldine salt state.²⁶ Moreover, the thermal stability of PFu and P2IAn increased with preparing the PFu/P2IAn composite.

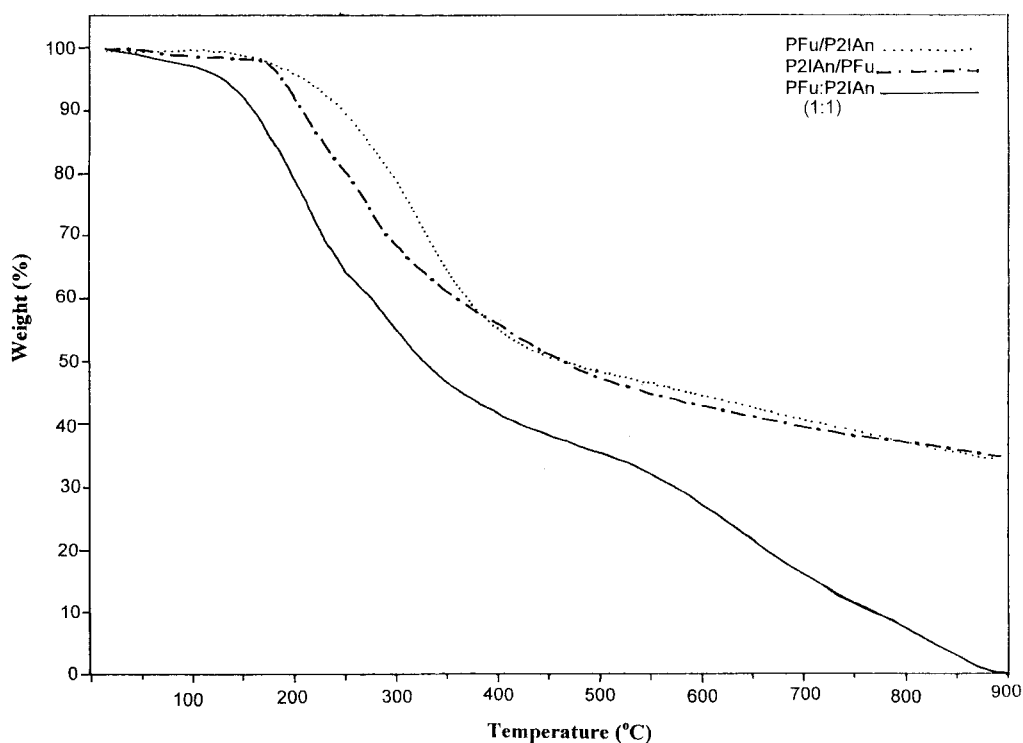


Figure 6 TGA thermogram of composites and (1 : 1) mechanical mixture.

TABLE III
Decomposition Temperatures of Polymers^a

Polymer	T_i (°C)	T_m (°C)	T_f (°C)
PFu/P2IAn	225	326	400
P2IAn/PFu	172	278	359
PFu:P2IAn (1:1)	150	260	370
mechanical mixture	530	635	732
P2IAn	191	217	257
PFu	114	181	273
	273	341	409
	518	541	568

^a T_i , initial temperature; T_m , maximum decomposition temperature; T_f , final temperature.

Scanning electron microscopy

Scanning electron micrographs of homopolymers and composites are shown in Figure 7(a)–(d). The micrograph for P2IAn [Fig. 7(a)] shows a vessel form and fibrillar structure. The surface morphology of PFu reveals two different structures [Fig. 7(b)]. The SEM micrograph of PFu shows a nonporous and uniform structure on the under layer, whereas it shows a granular and spongelike structure on the upper surface. Micrographs of PFu/P2IAn and P2IAn/PFu composites are different from those of their homopolymers and each other. The SEM micrograph of PFu/P2IAn [Fig. 7(c)] reveals a thin granular and porous structure,

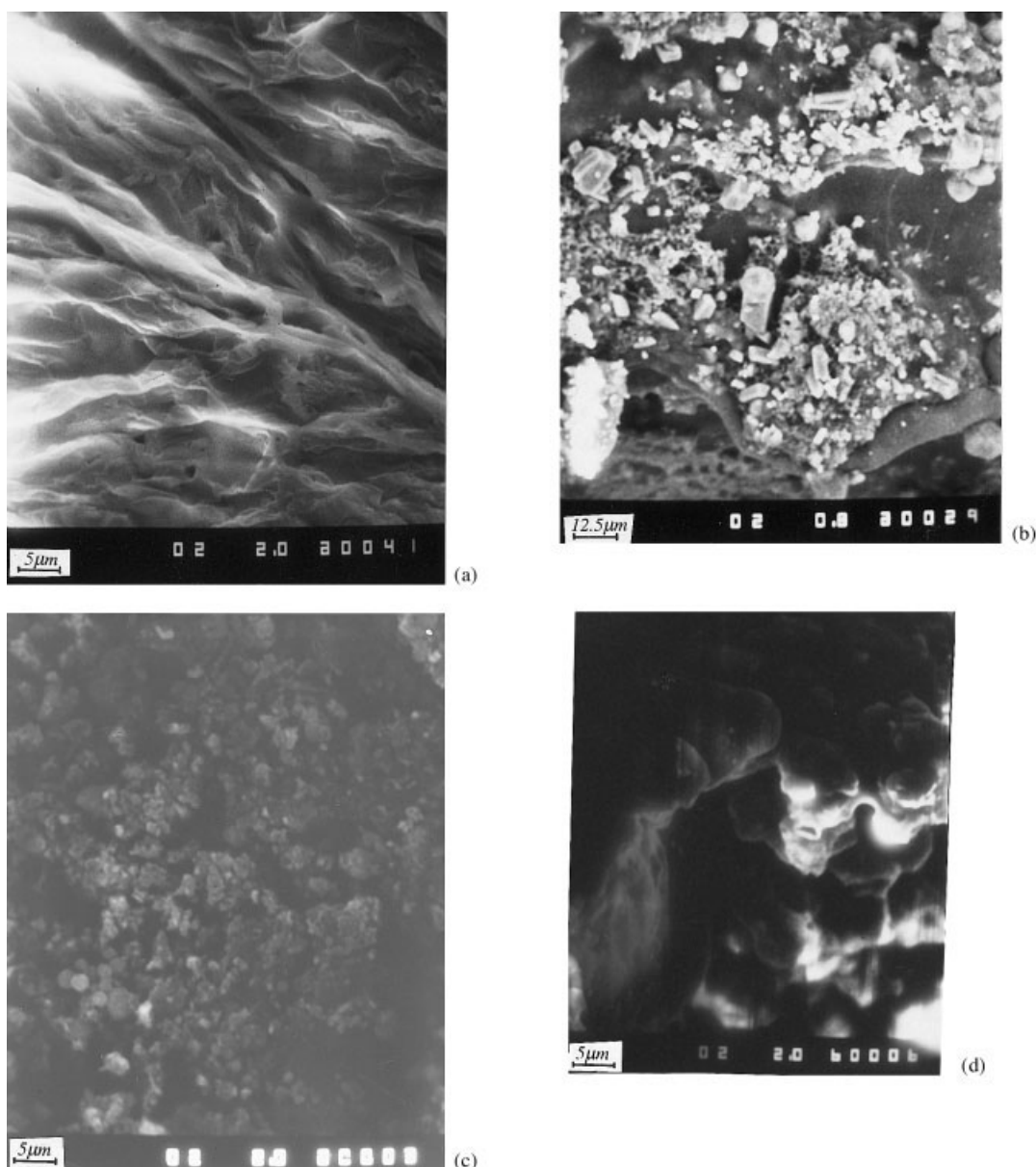


Figure 7 (a) SEM micrograph of P2IAn (magnification $\times 2000$; bar = $5.0 \mu\text{m}$). (b) SEM micrograph of PFu (magnification $\times 800$; bar = $12.5 \mu\text{m}$). (c) SEM micrograph of PFu/P2IAn (magnification $\times 2000$; bar = $5.0 \mu\text{m}$). (d) SEM micrograph of P2IAn/PFu (magnification $\times 2000$; bar = $5.0 \mu\text{m}$).

whereas that for P2IAN/PFu [Fig. 7(d)] shows a large granular structure. Differences in the morphology of homopolymers and composites depend on the monomer and the order of synthesis.^{27,28} From the SEM micrographs it can be concluded that PFu/P2IAN and P2IAN/PFu can be homogeneous composites.

It was found that the conductivity values and electronic, thermal, and morphological properties of composites obtained by different techniques changed according to varying the host and the guest polymer order.

1. In the PFu/P2IAN composite system, the conductivities did not greatly change with increasing guest polymer. However, in the P2IAN/PFu composite the conductivities significantly increased with increasing PFu content. Similar results were also obtained for the polypyrrole-polyimide conducting system.²⁹
2. The shift to long wavelength of maximum absorbance value of P2IAN/PFu composite supported the conductivity increase corresponding to PFu/P2IAN.
3. In TGA thermograms, the mechanical mixture of homopolymers shows a weight loss at lower temperature (150°C), whereas the composites prepared by different techniques reveal greater temperature stabilities (225 and 172°C). Similar results were also obtained for the polypyrrole-polyimide system.³⁰
4. From SEM micrographs, it was found that composites synthesized by different techniques have different surface morphologies. Additionally, it was determined that the guest polymer was homogeneously distributed through the host polymer. In literature studies, similar results were revealed for the polyaniline-polystyrene composite system.³¹

CONCLUSIONS

The electrical conductivity of the 2IAN/PFu composite was higher than that of the PFu/P2IAN composite. This may be explained as being attributed to the introduction of PFu into the P2IAN backbone, which occurs more easily than the introduction of P2IAN into PFu chains. In the P2IAN/PFu conducting composite, the electrical conductivity was increased to 2.77×10^{-3} S/cm with increasing amounts of PFu. The

PFu/P2IAN composite was thermally more stable than the P2IAN/PFu composite and their homopolymers. The thermal and conductivity properties of PFu and P2IAN were modified by preparing PFu/P2IAN and P2IAN/PFu composites. We propose that the synthesized composites could be used in most areas of applications of conducting polymers.

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