

A conducting composite of polypyrrole

I. Synthesis and characterization

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Abstract

A conducting composite of polypyrrole was prepared via electrochemical methods. A polyamide was used as the insulating matrix polymer. The characterization of the composite was done by FT-IR, SEM, TGA, DSC and pyrolysis studies. Conductivity and solubility studies together with spectroscopic methods reveal that H bonding exists between the two polymers and a possible grafting to a certain extent.

Introduction

Electrically conducting polymers have attracted great attention in the past years because of their electronic properties. Many studies have focused on the synthesis of conducting polymers, such as polyacetylene, polypyrrole, polythiophene and their derivatives. Polypyrrole (PPy) can readily be obtained in its conducting form by electrochemical oxidation of pyrrole [1]. Several groups have reported that the electrochemical polymerization of pyrrole can also take place on an electrode which is already coated with an insulating polymer [2–9]. The main purpose is to obtain homogeneous composites which retain the characteristics of both polymers, at least to a certain extent. In these studies low percolation thresholds were achieved with the aid of hydrogen bonding between the host matrix and polypyrrole [9] as well as graft polymers [10, 11]. The films obtained in the latter case showed interesting features, such as differing behaviour in DSC, SEM and FT-IR analyses compared to a simple mechanical mixture of the two polymers. The insolubility of the host matrix in regular solvents after the electrolytic polymerization of the conducting element (e.g. pyrrole, aniline) suggested the generation of a new structure composed of the insulating and conducting polymers. Pyrolysis studies finally revealed that the so-called composite may be a graft copolymer rather than an intimate mixture of the two polymers.

In the above-mentioned technique, polymerization starts around the interface between the electrode surface

and the host polymer film coated on the electrode. The resultant PPy grows inside the matrix forming an electrically conducting polymer alloy film. According to this method we have potentiostatically prepared polypyrrole–polyamide (PA) composites.

Experimental

PPy–PA composites were prepared by the electrochemical polymerization of pyrrole onto a polyamide-coated electrode at a constant potential of +1.5 V versus Ag^0/Ag^+ (10^{-2} M). The polyamide films were dip-coated from a chloroform solution (10 mg l^{-1}) of a commercial polyamide resin (Aldrich Co. 19, 101-9). The amounts of insulating and conducting polymer coatings were determined gravimetrically.

Potentiostatic polymerizations were carried out in a three-compartment cell equipped with Pt foils (1.5 cm^2 each) as the working and counter electrodes and a capillary reference electrode (Ag/Ag^+). The solvent–electrolyte couple was acetonitrile–tetrabutylammonium tetrafluoroborate (TBAFB). Blank runs were also carried out (i.e. in the absence of pyrrole in the electrolytic medium) with PA-coated electrodes to ensure that there were no changes either chemically or by weight in the polymer electrode. Details of the potentiostatic electrolyses have been given elsewhere [12].

Conductivities of samples were measured via a four-probe technique. The composites were characterized by FT-IR (Nicolet 510) and SEM (Cambridge Stereo-

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scan S4-10). Thermal gravimetric analysis and DSC were recorded on a Du Pont 2100 instrument.

Results and discussion

The electrooxidation of pyrrole using a PA-coated Pt anode gave rise to black films which could be peeled off from the electrode surface. Almost equal conductivities on both sides of the films suggest that a homogeneity was achieved, at least in terms of conductivity (Table 1). It is also interesting to note that conductivity was not greatly affected by the percolation composition. There exists only a sixfold decrease between 24% pyrrole (by weight) and the pure polypyrrole obtained under the same conditions. Several percolation threshold values have been cited elsewhere [9, 13–15].

When the films were washed with chloroform (solvent of polyamide) no marked changes were measured in conductivity. The washing procedure was repeated for several weeks in order to see whether there was a loss in weight, since polyamide should easily be removed by chloroform. No weight loss could be detected. The surface appearance of the washed and unwashed films remained the same (Fig. 1). This behaviour can be

TABLE 1. Conductivities of PA-PPy films

%PPy	Electrode side (S cm ⁻¹)	Solution side (S cm ⁻¹)
24	4	4
36	10	10
47	12	15
62	14	19
100	22	25

attributed to a chemical interaction between the two polymers rather than to a simple physical adhesion. FT-IR spectra of the two pure polymers and their mechanical mixture yield different features compared to the electrolytic film (Fig. 2).

In Fig. 3(b) the H-bonded carbonyl bond can be seen together with the free carbonyl group stretching. Yet such a chemical interaction cannot only be explained by a rather weak hydrogen bonding phenomenon. This matter was further elucidated by pyrolysis experiments. Figure 4 reveals the gas phase FT-IR of pure compounds, and the electrolytic film after pyrolysis. CO, CO₂ and CH₄ evolutions were clearly observed for the pristine polymers (Figs. 4(A) and (B)). It is remarkable that the spectrum of the film is not a simple addition of the previous two under the same conditions (300 °C, 10⁻³ Torr) (Fig. 4(C)). The pyrolysis FT-IR of the film at *T* = 350 °C reveals different features in accordance with DSC studies (Fig. 4(D)). This temperature has significant meaning in terms of thermal characteristics.

The glass transition temperature of PA lies around 82 °C, and DSC studies yield a different thermal behaviour for the PA-PPy film (Fig. 5). The region 344–368 °C indicates a new thermal behaviour. A simple mechanical mixture of the two polymers, on the other hand, shows the polyamide thermal characteristics as if only one phase existed. This is quite normal since under the given conditions we did not expect any thermal behaviour for polypyrrole.

Thermal gravimetric analysis of the potentiostatically obtained film reveals a single weight loss pattern suggesting a homogeneous single phase system (Fig. 6).

The reproducible response of the electrochemical film compared to pure PPy for several gases also suggests the generation of a new material. This will be the topic of an forthcoming article.

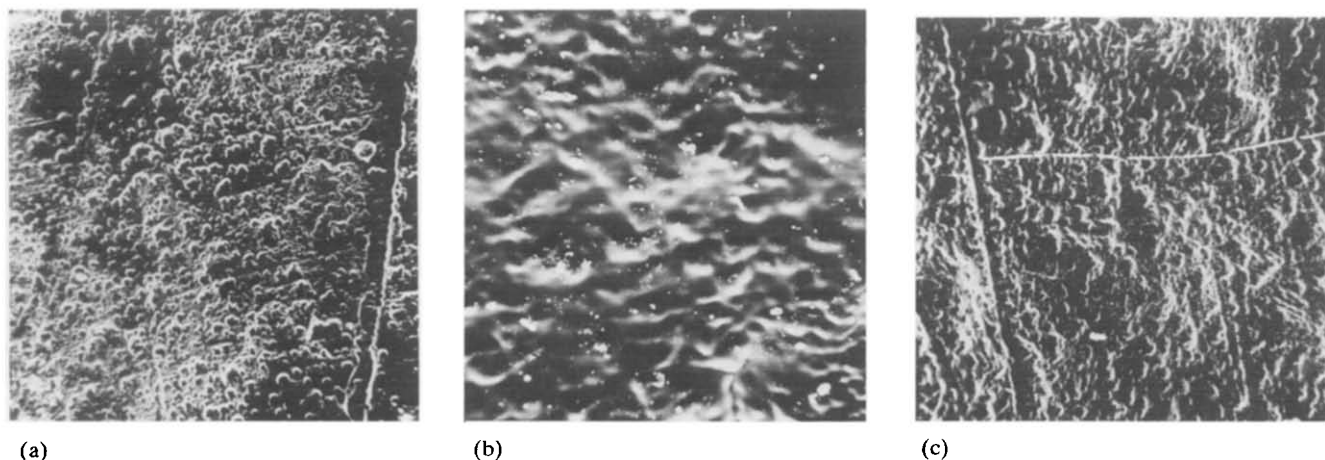


Fig. 1. SEM micrographs of the electrolytic film: (a) electrode side; (b) solution side; (c) film washed with CHCl₃ for several weeks.

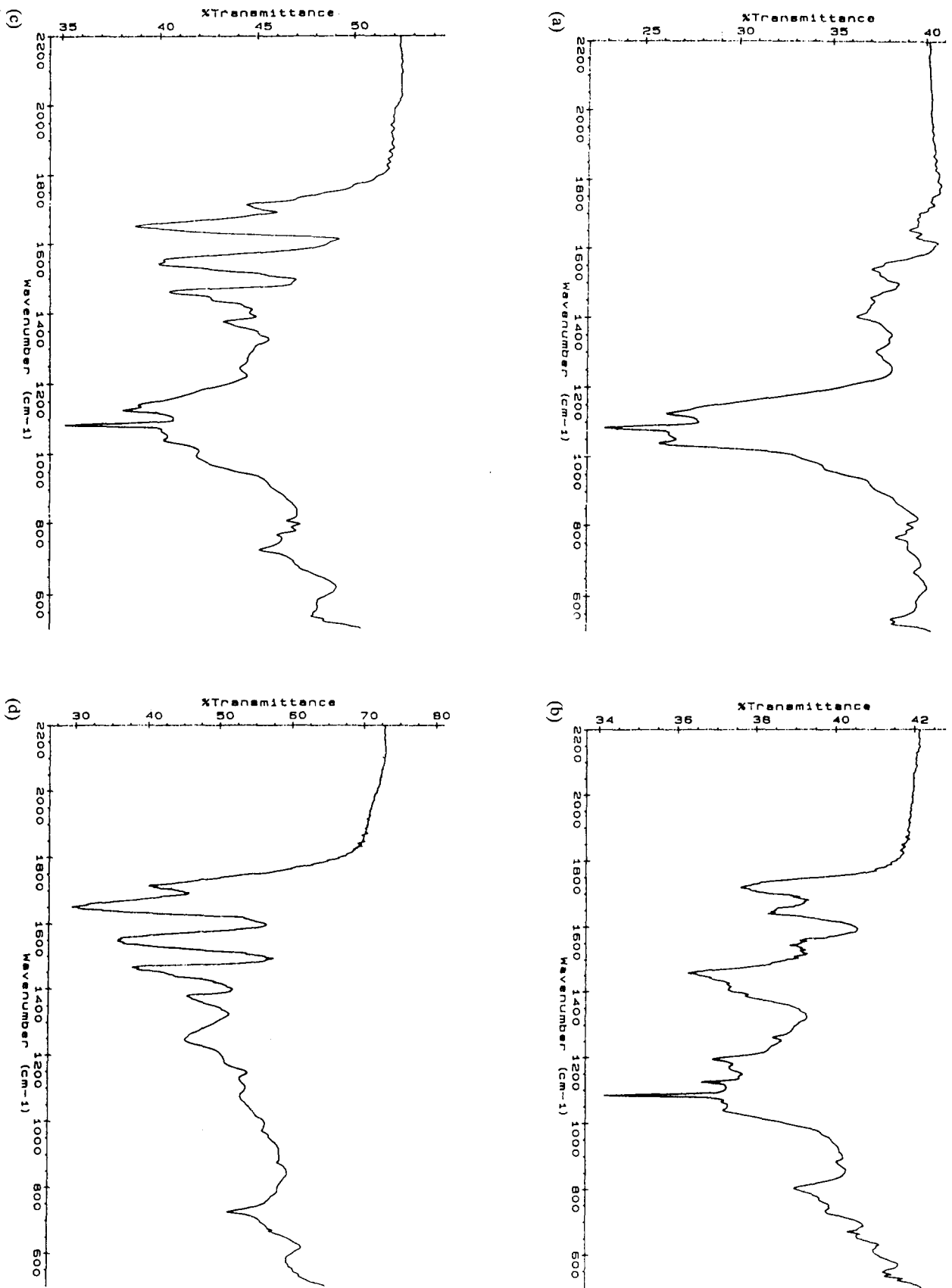
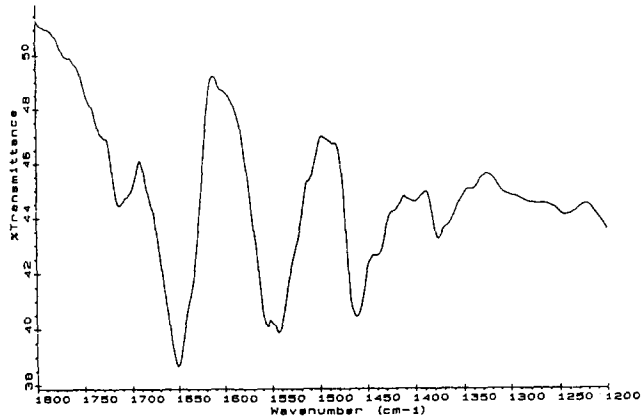
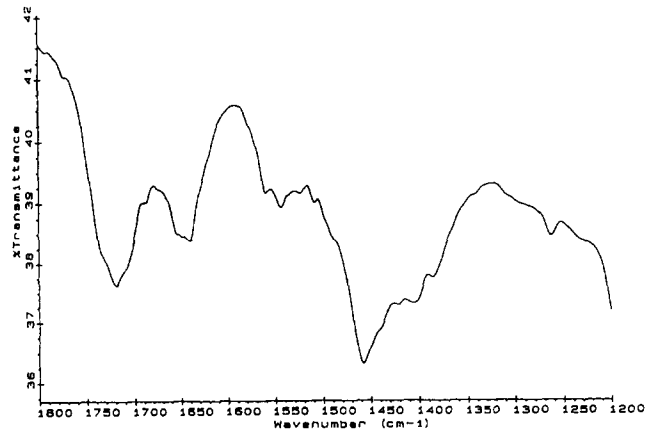


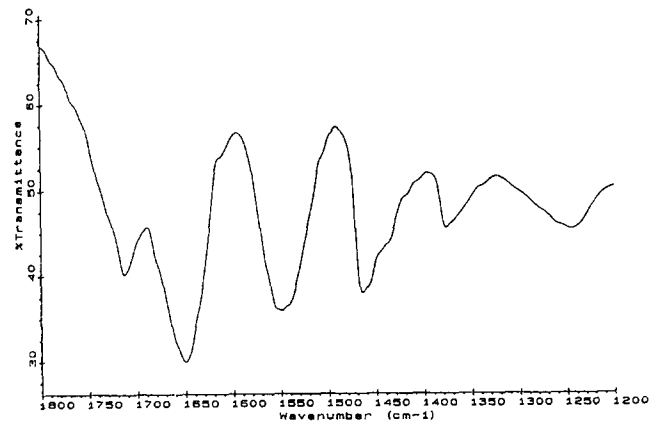
Fig. 2. FT-IR spectra of (a) pure PPV, (b) electrolytic film, (c) mechanical mixture of the two pure polymers and (d) pure polyamide.



(a)



(b)



(c)

Fig. 3. FT-IR spectra of (a) mechanical mixture, (b) film and (c) pure PA.

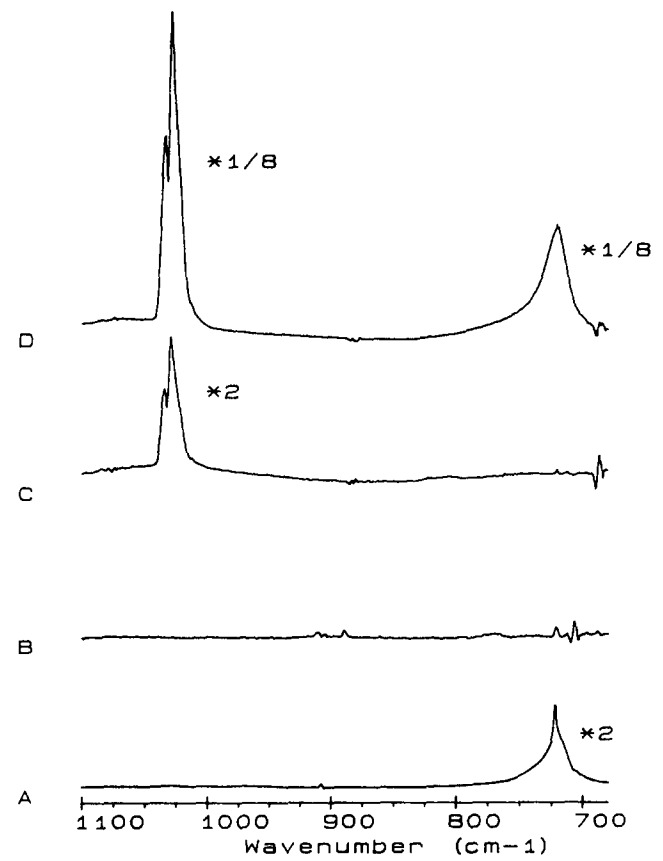
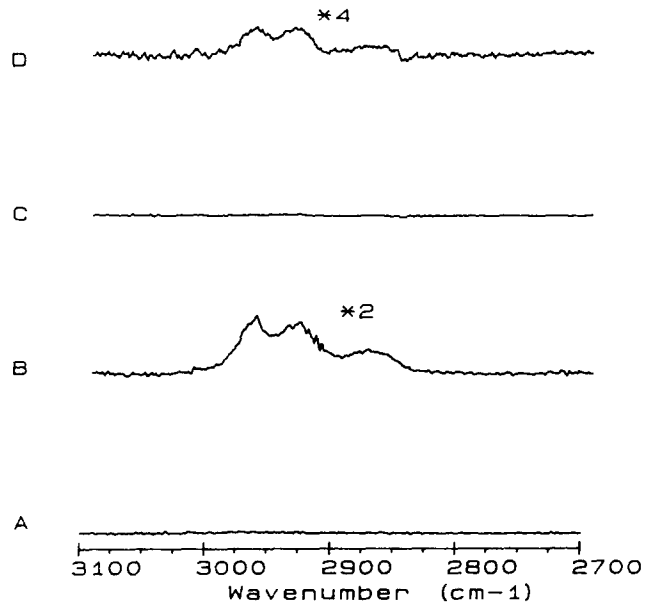


Fig. 4. Gas phase FT-IR spectra (300 °C, 10⁻³ Torr) of (A) polypyrrole, (B) polyamide, (C) electrolytic film and (D) electrolytic film at 350 °C, 10⁻³ Torr.

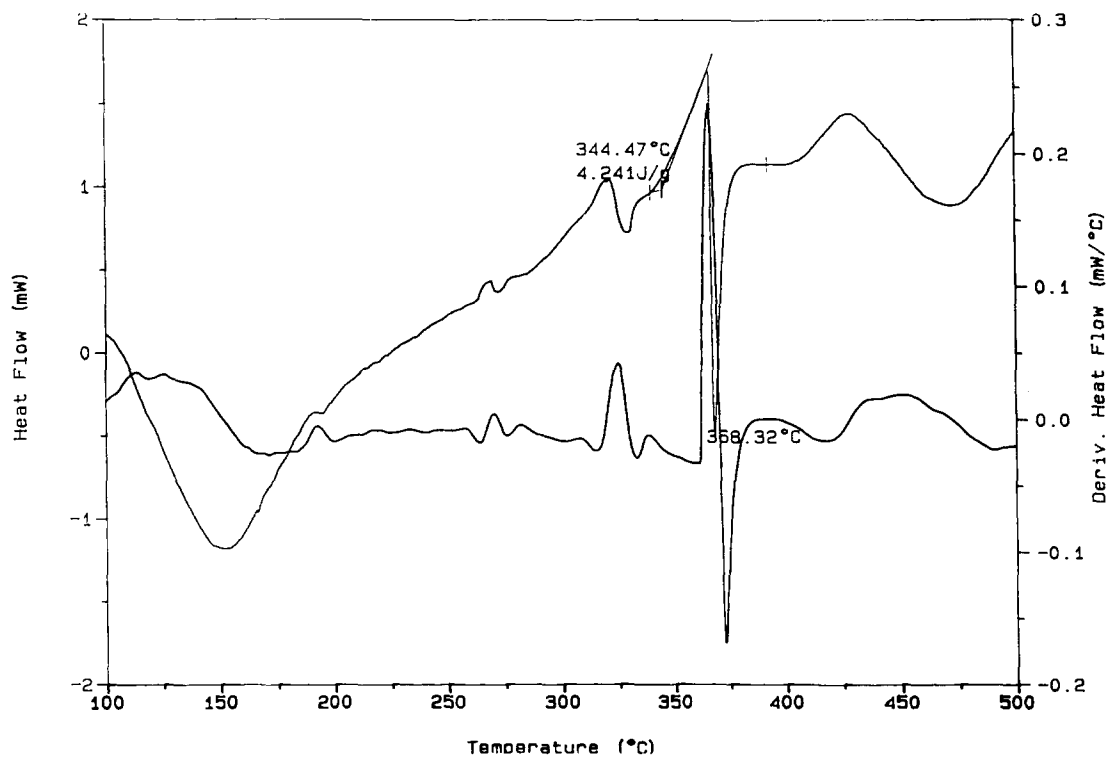


Fig. 5. Differential scanning calorimetry results for the PA-PPy electrolytic film.

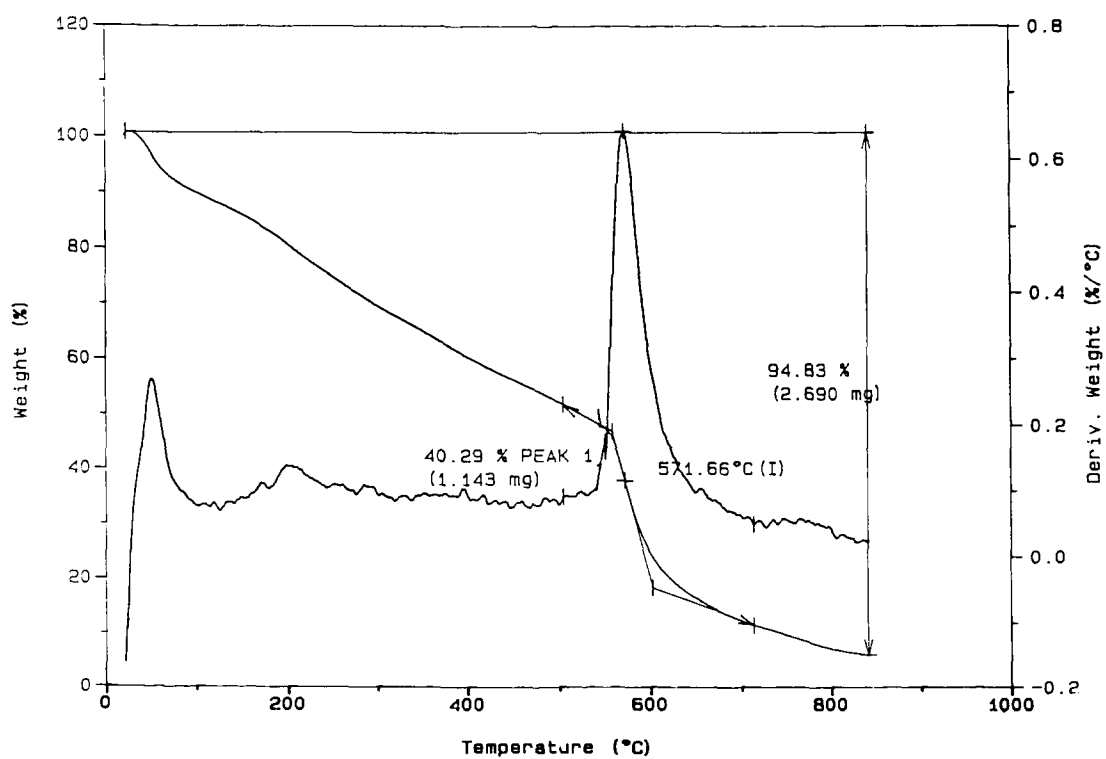


Fig. 6. Thermal gravimetric analysis of the PA-PPy electrolytic film.

Conclusions

We have enough evidence to believe that the PA-PPy polymer alloy film contains copolymers of the two elements (PA and PPy) to a certain extent. H bonding is also evident, but it cannot explain the pyrolysis results alone.

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