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POLYMERIZATION OF PYRROLE ON POLYACRYLAMIDE ELECTRODES

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Key Words: Pyrrole, Polyacrylamide, Electrochemical Polymerization

ABSTRACT

Polymerization of pyrrole on a polyacrylamide (PAA) coated electrode was carried out in acetonitrile. Different compositions of semi-conducting, composite films of PAA/Polypyrrole (PP_y), were prepared by the electrochemical polymerization of pyrrole on PAA electrodes. The polymerization was possible only for a certain thickness of the polyacrylamide on the platinum. Conductivites of PAA/PP_y films at different compositions were obtained. The electrochemical properties of polypyrrole-polyacrylamide (PP_y/PAA) composite films have been investigated by using cyclic voltammetry. The PP_y/PAA composite film is suitable as the electroactive material due to its stable and controllable electrochemical properties. The films were examined by FTIR spectroscopy. The topography of surface films were analyzed by scanning electron microscope (SEM). The response behavior of PP_y/PAA films at different compositions when exposed to Ar, C_3H_8 and H_2 gases indicated that these films were only slightly sensitive to H_2 gas.

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INTRODUCTION

Great effort has been devoted to the electrochemical synthesis and study of conducting polymer films such as polypyrrole, polythiophene, polyaniline and polyfuran [1-8]. The film formation and the electrical and physical properties of the resulting films were found to be strongly affected by the method of preparation [9-13].

The electrochemical polymerization of pyrrole in acetonitrile had been reported on Pt electrodes [14]. The properties of intrinsically conducting polymers make them suitable materials for several applications. Electrochemical polymerization of some compounds on polymer-coated electrodes was yet another concern for realizing electrically conducting composites [15-19]. The main purpose is to obtain homogeneous blends which retain the characteristics of the two components. In the above mentioned technique polymerization starts around the interface between the electrode surface and the host polymer film coated on the electrode. The preparation of such composites by electrochemical polymerization of pyrrole on polymer (matrix) coated working electrodes is one of the best methods used to improve several properties of PP_y [20-25] .

The electropolymerization was proposed to occur through oxidation of a monomer molecule on the electrode. The only contribution of the electrolyte in the film is the doping process during the polymerization process. The aim of this paper is to show that pyrrole can be polymerized in a polymer matrix of conventional insulating polymer by an electrochemical method. The main objective of this study is to obtain a semi-conducting polymer which can be used as a gas sensor [26-29]. Here we report the response of PAA/PPy towards Ar, C_3H_8 and H_2 gases. In this study the composite films were said to be an intimate mixture of the two polymers (PAA and PP_y) having a certain degree of H bonding. Thus, several properties of the film, like different FTIR, DSC and SEM characteristics, as well as the insolubility of the insulating matrix (PAA) in the composite were attributed to that phenomenon [30].

EXPERIMENTAL

Reagents

Polyacrylamide (PAA), acetonitrile, tetrabutylammonium tetra fluoroborate (TBAFB) were all Aldrich reagent grade, at highest purity and therefore, no further purification was done. Pyrrole (Merck) was distilled under vacuum. All solutions were de-aerated by bubbling N_2 through it, at room temperature for 5-10 minutes before polarization has started.

Electrode and Cell

Two Pt foils were used as the working and the counter electrodes. The surface area of the working electrode was 1.5 cm^2 and the counter electrode was 1.0 cm^2. The working and counter electrodes were burned in a reducing flame. Both surfaces of the anode were coated by the polyacrylamide which was dissolved in water and dried until a constant weight was obtained. As the reference electrode, a saturated $Ag/AgBF_4$ (s), electrode was used, and all potentials in this work are related to it.

Preparation of PP_y/PAA Composite

The electrochemical polymerization of pyrrole was carried out in a three-compartment cell .The preparation of composites was done in an acetonitrile solution containing 0.05 mol/ L Pyrrole and 0.05 mol/ L TBAFB. The solutions were purged with N_2 before polymerizations for 5-10 minutes, and a blanket of N_2 was used during the experiments. In all cases, polymerizations were conducted at ambient temperature.

A polyacrylamide-coated electrode (PAA/Pt) was prepared by depositing a 1 wt% solution of PAA in water onto a Pt foil and allowing the water to evaporate completely in the oven. This film of dried polymer on Pt electrode was directly used for electrochemical polymerization of pyrrole. The electrochemical polymerization process was carried out potentiostatically at a constant voltage of 1.2 V vs. Ag/Ag^+ to speed up the pyrrole polymerizations and overcome the resistance caused by the insulating film on the anode. After a suitable polymerization period (depending on the desired composition of polypyrrole), the films were removed with a doctor blade. The films were washed with water and acetonitrile in order to remove the electrolyte and dried under vacuum. The polymerization was possible only for a certain thickness of the PAA onto platinum.

As a control experiment, we repeated the above experiment with no pyrrole monomer in the cell. We observed that the insulating polymer, PAA, does not undergo oxidation under the conditions of the polymerization of pyrrole. In addition to this, the FTIR spectra of the insulating polymer was taken before and after the electrolyses to rule out such a possibility. The gas sensing system consisted of a measuring compartment where the film was connected to a digital multimeter, traps for drying the gas a diluter, where dry nitrogen was used as the diluent and a flow-rate measurement compartment. The thicknesses of the composite films were 50-70 (μm) with a conductivity of 10^{-2} S cm^{-1}. These electrolytic films consisted of about 40-73% polypyrrole by weight Table 1.

CHARACTERIZATION

Fourier Transform Infrared Spectroscopy

A Mattson 1000 FTIR instrument was used to obtain spectra from (KBr) pellets of polyacrylamide and PP$_y$/PAA composites. All spectra were collected with 20 scans at a resolution of 16 cm^{-1}.

Thermal Characterization

Thermal characterization of the polyacrylamide and PP$_y$/PAA composites was carried out using Shimadzu TGA-50 and Setaram DSC 131. Thermal gravimetry experiments were carried out under dry nitrogen purge at a rate of 25 cm^3 min^{-1}. A constant heating rate of 10°C min^{-1}. was used.

Electrochemical Polymerization

The electrochemical preparation of PP$_y$/PAA composites were accomplished with a Wenking POS 73 potentiostat.

Scanning Electron Micrograph

SEM was performed using a Jeol JXA 840-A. Despite their intrinsically conducting nature, all specimens were coated with gold prior to examination.

TABLE 1. The Conductivity of PPy/PPA Films at Different Compositions Exposed to Ar, C_3H_8, and H_2 Gases

compositions	**%20PP$_y$+%80PAA**	**%49PP$_y$+%51PAA**	**%58PP$_y$+%42PAA**	**%73PP$_y$+%27PAA**
conductivity	0.75×10^{-2} S Cm^{-1}	1.25×10^{-2} S Cm^{-1}	1.50×10^{-2} S Cm^{-1}	2.00×10^{-2} S Cm^{-1}
exposed to Ar	0.78×10^{-2} S Cm^{-1}	1.30×10^{-2} S Cm^{-1}	1.58×10^{-2} S Cm^{-1}	2.12×10^{-2} S Cm^{-1}
exposed to C_3H_8	0.71×10^{-2} S Cm^{-1}	1.22×10^{-2} S Cm^{-1}	1.43×10^{-2} S Cm^{-1}	2.05×10^{-2} S Cm^{-1}
exposed to H_2	1.98×10^{-2} S Cm^{-1}	2.51×10^{-2} S Cm^{-1}	3.25×10^{-2} S Cm^{-1}	4.58×10^{-2} S Cm^{-1}

Cyclic Voltammetry Experiments

Cyclic voltammetry experiments of PP_y and PP_y/PAA were carried out with Wenking POS 73 potentiostat and Rikadenki RW-11T x/y recorder. HPLC-grade acetonitrile solutions containing 0.1M TBAFB and 10^{-3} M mono-mer were employed along with a Pt foil (1.5 cm^2) working and Pt foil (1.0 cm^2) counter electrodes and a Ag/Ag^+ reference electrode. Prior to all measurements solutions were purged with N_2 and CV runs an N_2 blanket was maintained over the solution.

RESULTS AND DISCUSSION

One of the first questions related to the growth of a polymer was based on the presence of the polyacrylamide on the electrode surface during the polymerization process. In this way, the voltammograms depicted in Figure 1 were obtained using the same working electrode which was coated with the polyacrylamide. The oxidation peak potential of 10^{-3} M pyrrole was determined by cyclic voltammetry (Figure 1, a, b).

Since pyrrole was electrochemically polymerized onto a PAA/Pt electrode, the transparent PAA film coated on Pt turned light green and gradually darkened finally becoming black. The washing procedure with the solvent of PAA was repeated for several days in order to see whether there was a change in weight or not. No marked changes were observed in conductivity and in the percolation composition of PAA in the composite.

Conductivity of PP_y/PAA Composite Films

The conductivity of the composite PAA/PP_y film was observed to increase as the electrochemical polymerization process of pyrrole persisted at a constant potential of 1.2 V in an acetonitrile/TBAFB solution. After the PAA film coated on the Pt electrode is sufficiently swollen by the electrolyte solution, pyrrole, and electrolyte penetrate through the PAA layer onto the Pt electrode surface. As a result, the pyrrole is electro-oxidatively polymerized on the Pt surface and doped by the counteranion at the same time. Reactants penetrating through the PAA layer afterwards will electrodeposit onto the surface of the PP_y layer that has formed in the PAA matrix. Having grown throughout the inside of the PAA substrate, PP_y grows out of the PAA outer surface and makes that surface conducting. The weight percentage of PP_y in the composite was determined

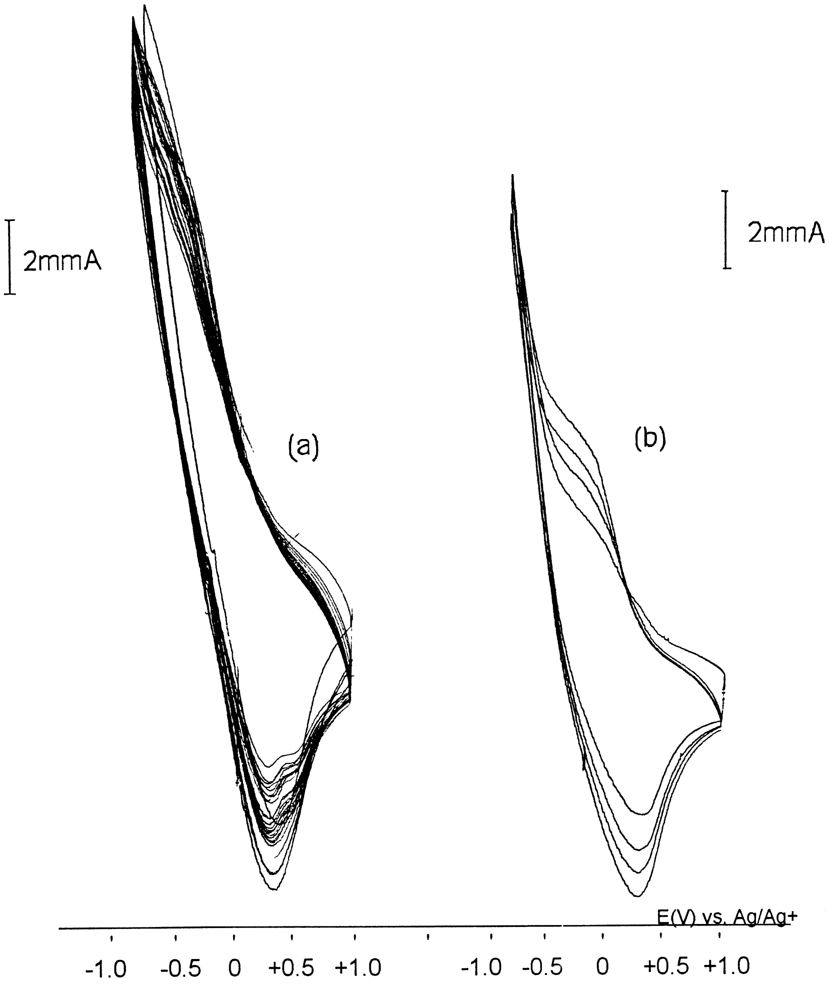

Figure 1. Multisweep cylic voltammograms of pyrrole (a) on bare Pt electrode and (b) on PAA coated Pt electrode.

gravimetrically. The PAA-coated Pt foil electrodes were weighed before and after electrolyses. In Figure 2, the electrical conductivity, σ, is plotted as a function of PP_y content of the composite film. From the conductivity measurements it was found that the conductivity of the film surface that was not in contact with Pt was about the same order of magnitude compared to that of the electrode side. According to SEM (Figure 3, c, d), the polyacrylamide as the host matrix does not seem to interact with monomer molecules but we observed that the pyrrole does not attach itself to the polyacrylamide molecular through hydrogen bond (σ). A homogeneous distribution of PP_y in the matrix PAA would lead to a sud-

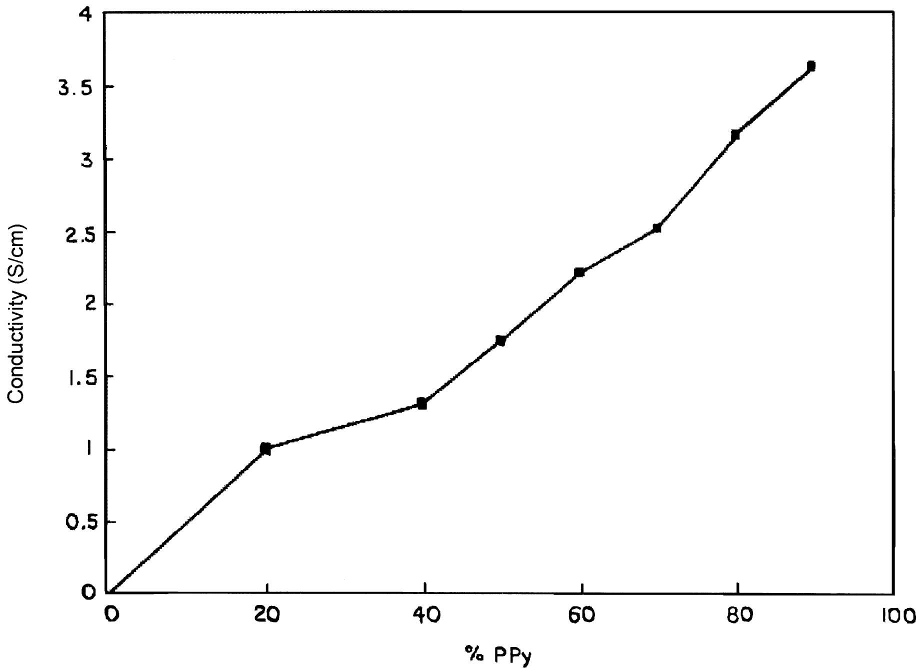

Figure 2. Conductivity vs. percent composition of PP_y.

den small increase in conductivity. The first penetrating pyrrole forms a very fine particle of PP_y on the electrode surface due to fast oxidation. These polymers gradually clog the pores and reduced the conductivity, hence reduces the oxidation rate.

The conductivity of composite materials are less than those of pure Pp_y. The composite film obtained on the surface of electrode is less fragile than pure PP_y. we conclude that the initial deposition of PP_y mainly occurs at the PAA and the metal electrode interface and then reaches the surface of the insulating film. The conductivity was found to be proportional to weight percentage of PP_y present in the alloys as shown in Figure 2.

Morphology of Composites

Figure 3 shows scanning electron micrographs (SEM) for PAA/PP_y composite films. A composite PAA/PP_y film's solution side (facing the electrolyte) has many cauliflower-like projections bulging from the network of PAA. An obvious difference could be detected between the micrographs of electrolytic film and that of the film washed with water. The electrode sides of both films PAA/PP_y also have the same appearance which is not an indication of a chemi-

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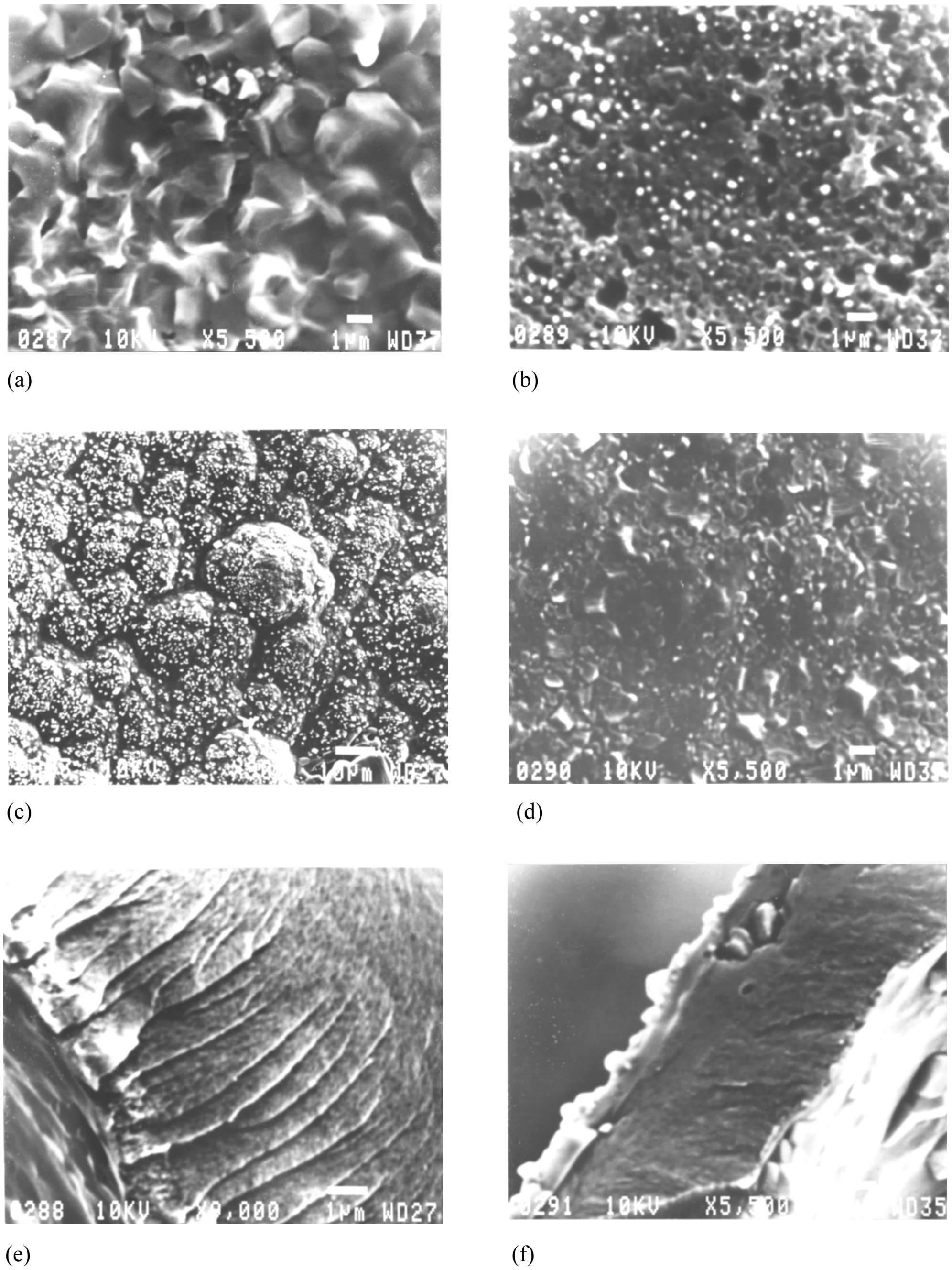


(a) (b)

(c) (d)

(e) (f)

Figure 3. Scanning electron micrographs of (a) electrode side of pure PP_y, (b) electrode side of PAA/PP_y film, (c) solution side of PAA/PP_y film, (d) solution side of washed film, the cross section of the composite film, and (f) the the cross section of the pure PP_y.

cal interaction between the two polymers (Figure 3d). The side of the PP_y layer, which was in contact with the insulating polymer layer, was smoother than the other side. Furthermore, the cross sections of the composite films were investigated.

In Figure 3 (e, f), a layered structure consisting of two different phases was observed. From a comparison of pure PP_y and PAA/PP_y it was concluded that one layer consisted of pure PP_y and the other of pure PAA. Thus, no interaction in the formation of the layered structure is probably due to the immiscibility of the two polymers. The electropolymerization of pyrrole occurs at the surface of the electrode and grows through the PAA film, forming a continuous layer on PAA. The cross section of PP_y is uniform throughout the surface, whereas cauliflower protuberances are observed in PAA/PP_y alloys. We have observed homogeneous composites of uniform conductivity and microstructures for both sides of the composite films.

Thermal Analysis

In thermogravimetry studies of the PP_y/PAA composite it was seen that the TG curve of the composite is a simple addition of the pure polymers. The TG curves of pure polymers and composite film are given in Figure 4 (a, b). In the thermogravimetry analysis of PAA, there exists about 10.52% weight loss at 216°C and 23.25% loss at 280°C and 35% loss at 344.50°C (Figure 3b).The glass transition temperature of PAA is 240°C. On the other hand, the electrolytic film shows 8.5% and 10% weight losses around 100-300°C. Figure 4 (a) and (c) shows the thermal gravimetry curves of the pure PAA and the mechanical mixture. It seems that the behavior of the new material is quite different according to SEM and thermal analyses from that of either polypyrrole or polyacrylamide.

FTIR Analysis

FTIR characteristic peaks for polyacrylamide, 1660 cm^{-1} (c=0 stretching), 3240-3345 cm^{-1} (N-H stretching), and 2750-2790 cm^{-1} ($-CH_2-$ stretching), were observed. Polyacrylamide displays one stretching band in the carbonyl region. These characteristic peaks are present in the spectrum of composite film. The FTIR spectrum of composite shows additional bands at 1161, 1416, 1463, and 1551 cm^{-1} due to C-N and C-C stretching in addition to an N-H wagging band between 908-669 cm^{-1}. These are characteristic peaks of PP_y. The spectrum of the electrolytic film reveals the same bands coming from pure PP_y and PAA just as the spectrum of the mechanical mixture (Figure 6d). In the composite there are two carbonyl peaks (Figure 6c). It is apparent that, as if in the carbonyl region, there was a weakly H-bond; however, in reality it is not a H-bond at all. Both washed and unwashed films have 1780 cm^{-1} carbonyl asymmetric and at 1720 cm^{-1} carbonyl symmetric and at 1380 cm^{-1} C-N stretchings. The strongest band at 1080 cm^{-1} stands for BF_4^- dopant ion.

Electroactivity of PP_y and PAA/ PP_y Composite Film

The anion doping-undoping process for the PAA/PP_y films was examined by the usual electrochemical techniques. Cyclic voltammetry experiments were performed with a potential scan from −0.3 to +1.4 V on bare Pt and –0.3 to +1.4 V on a PAA-coated electrode versus Ag/Ag^+. The two cyclic voltammograms with PAA/Pt and Pt as the working electrode are compared in Figure 5. At the Pt electrode, pyrrole starts to polymerize at +0.35 V. The corresponding reduction peak is at around −0.25 V. The anodic peak potential of the polymer shifted slightly toward the anodic direction with repeated cyclings. The anodic peak potential which is at +0.35 V at the first run shifts to +0.45 V. A multisweep cyclic voltammogram of the composite electrode is given in Figure 1. It has an oxidation peak at around +0.4 V and the corresponding cathodic peak at −0.2 V. There is a shift during cycling resembling a PP_y cyclic voltammogram. The cathodic peak potential shifts to −0.35 V, and that of the anode, to +0.75 V.

These differences result from the fact that before electropolymerizing at the PAA/Pt electrode, P_y and electrolyte have to diffuse onto Pt surface a PAA layer after having diffused to the PAA layer's outer surface from the electrolyte solution. Repeated scanning over the potential range –0.3 to 1.4 +V results in small changes in the size of cyclic voltammetric redox peaks, indicating the electrochemical switching capacity of the PP_y/PAA composite film. The conductivities of the films obtained at different concentration were measured in the presence of Ar. C_3H_8 and H_2 separately. It was observed that the conductivity changed just a little in the presence of H_2 only (Table 1).

CONCLUSION

By electrochemically polymerizing pyrrole in the PAA matrix we obtained composites of PP_y and PAA with good environmental stability, and flexibility but with little decrease in conductivity.

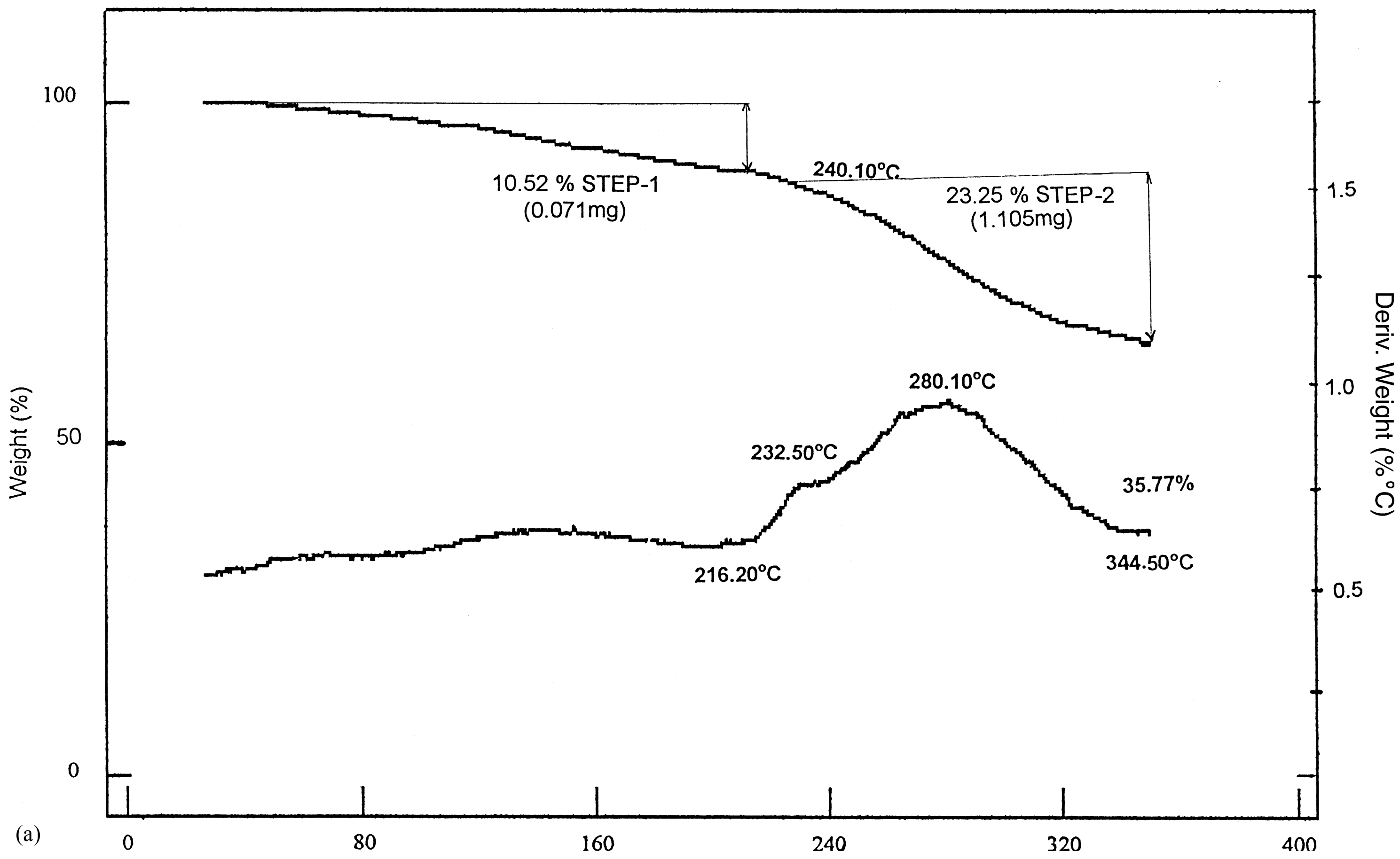


Figure 4. Thermal gravimetry analyses of (a) pure PAA, (b) PAA/PP_y composite film, and (c) mechanical mixture.

(continued)

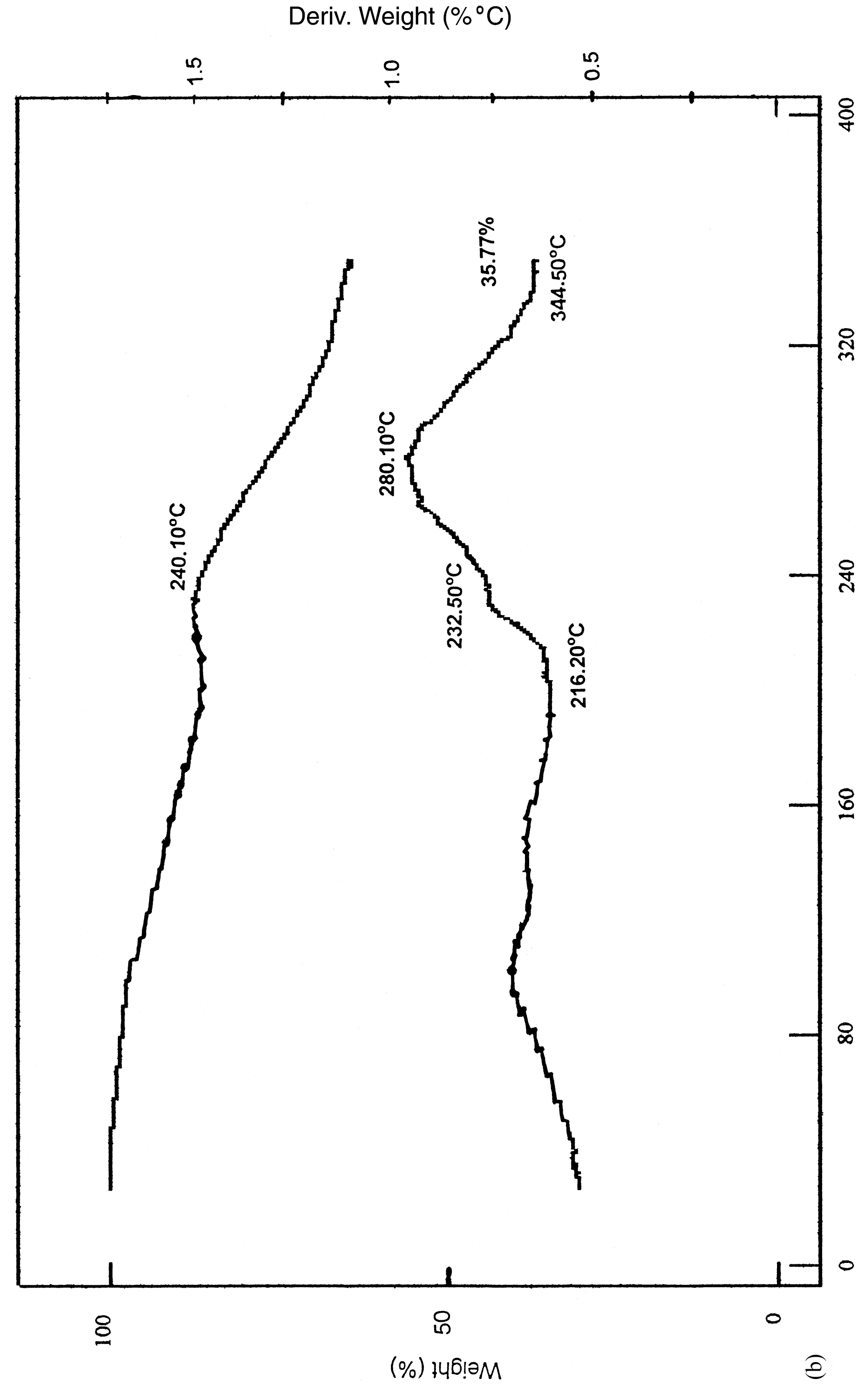


Figure 4. (continued)

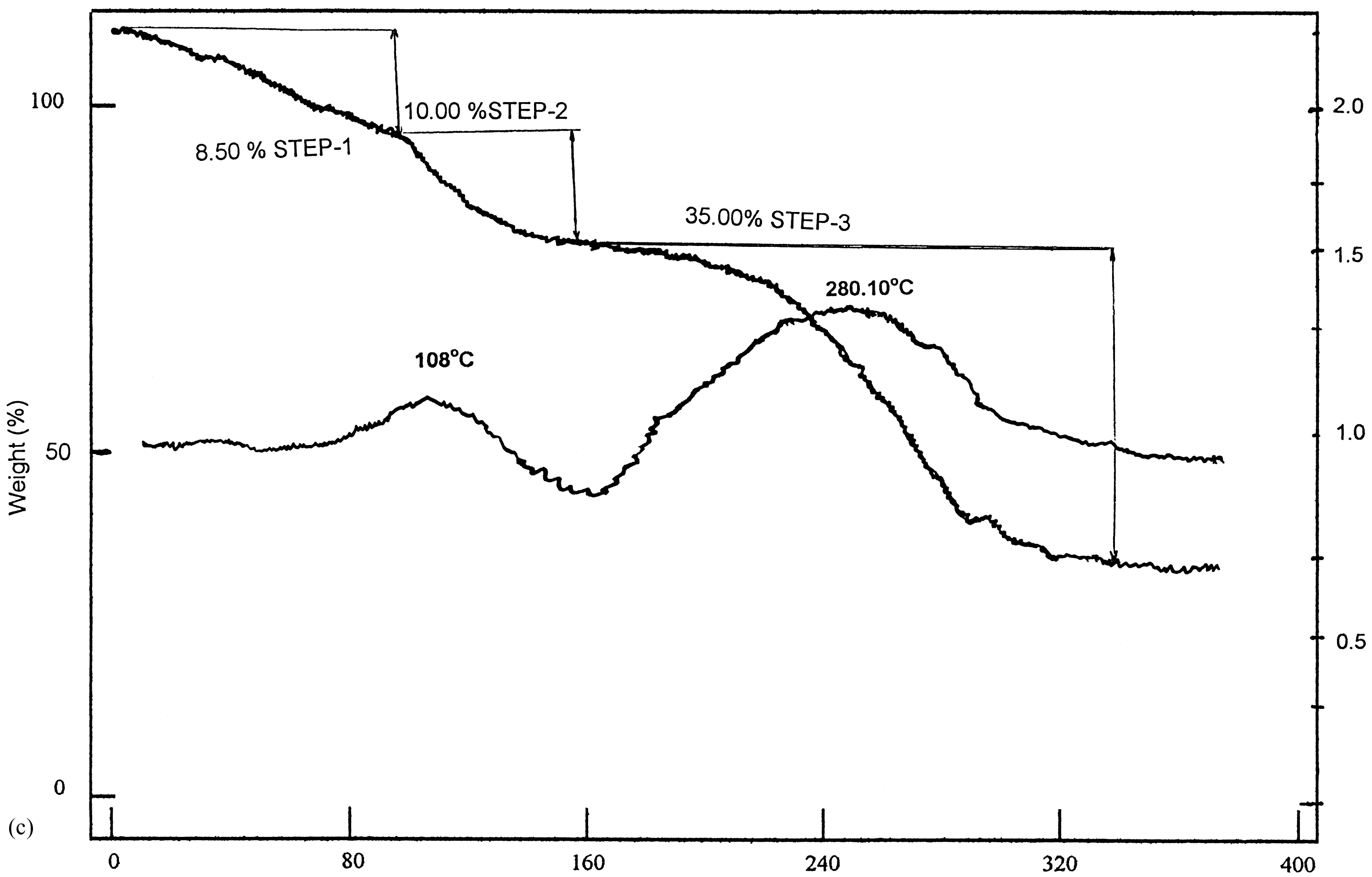
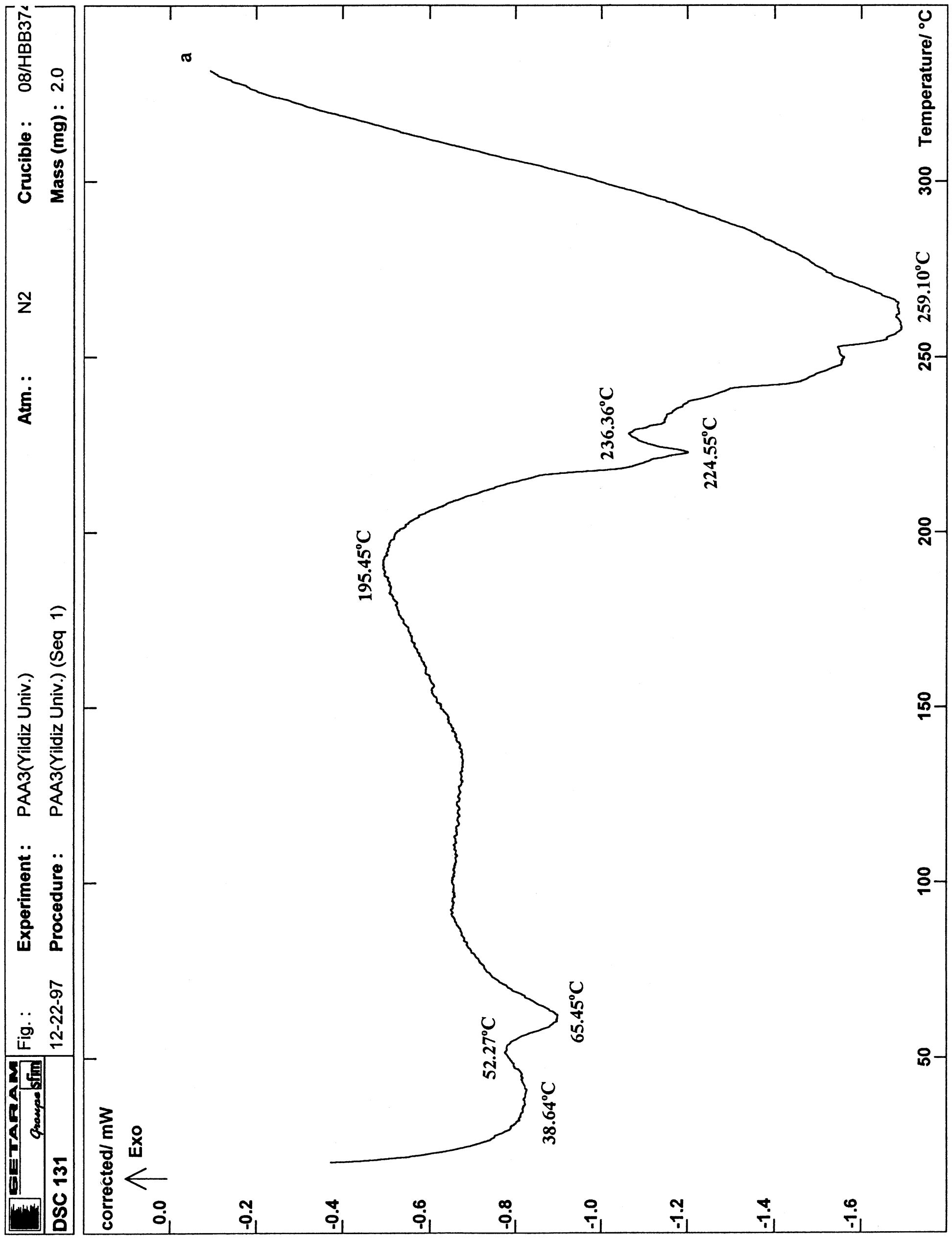


Figure 4. (continued)



(a)

Figure 5. Differential scanning calorimetry of (a) pure PAA, (b) mechanical mixture, and (c) PAA/PP$_y$ composite film.

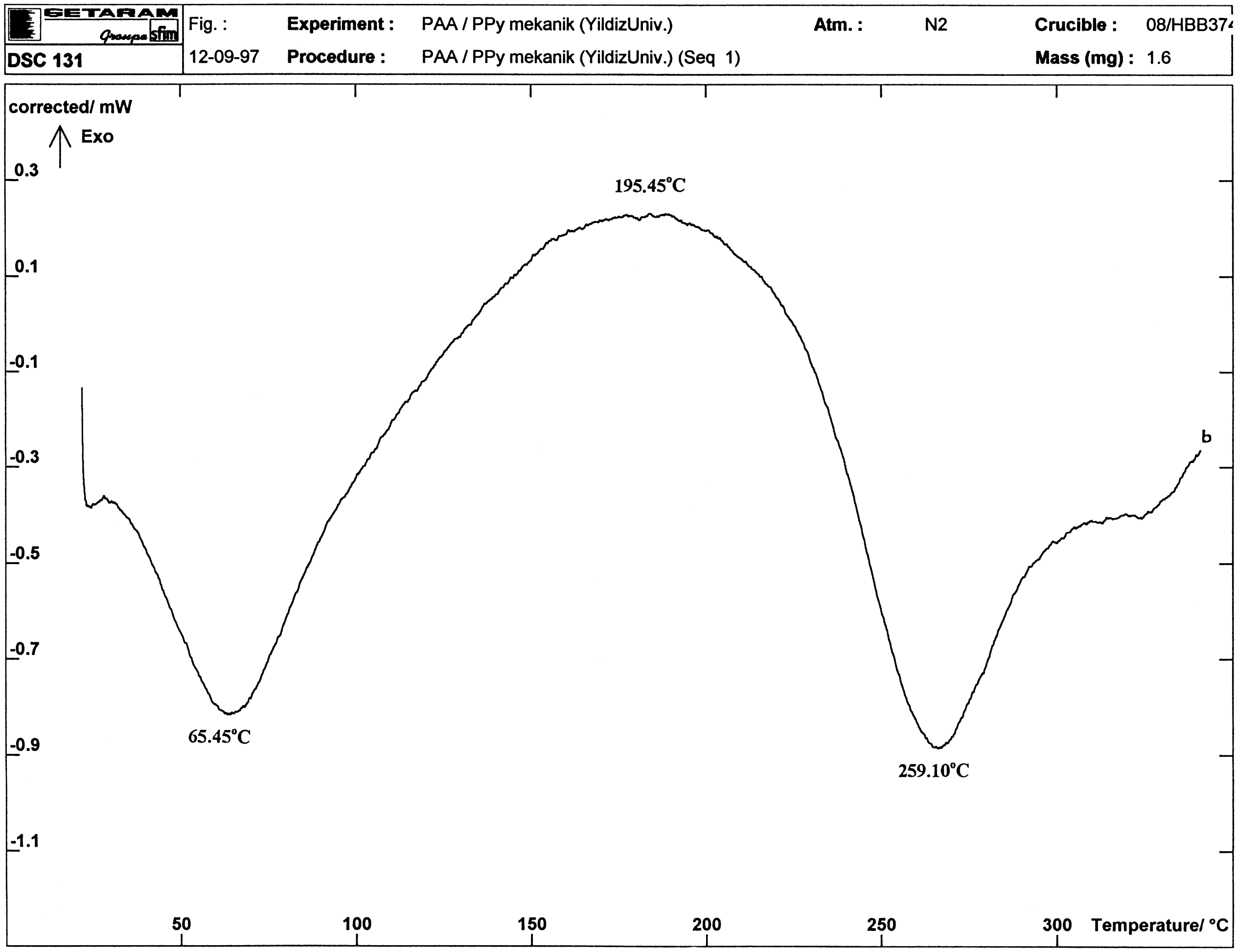
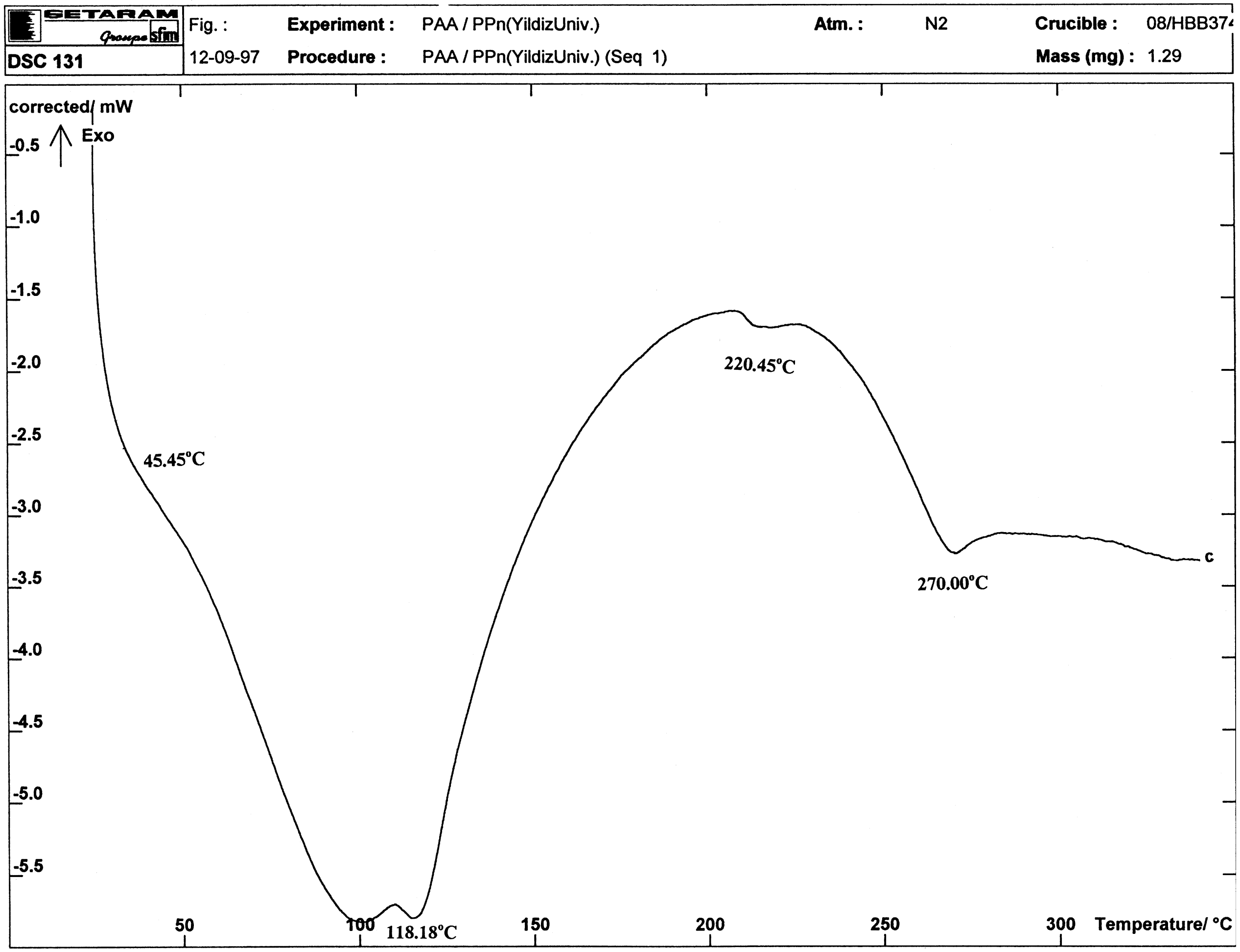


Fig. : 12-09-97
Experiment : PAA / PPy mekanik (YildizUniv.)
Procedure : PAA / PPy mekanik (YildizUniv.) (Seq 1)
Atm. : N2
Crucible : 08/HBB374
Mass (mg) : 1.6

(b)

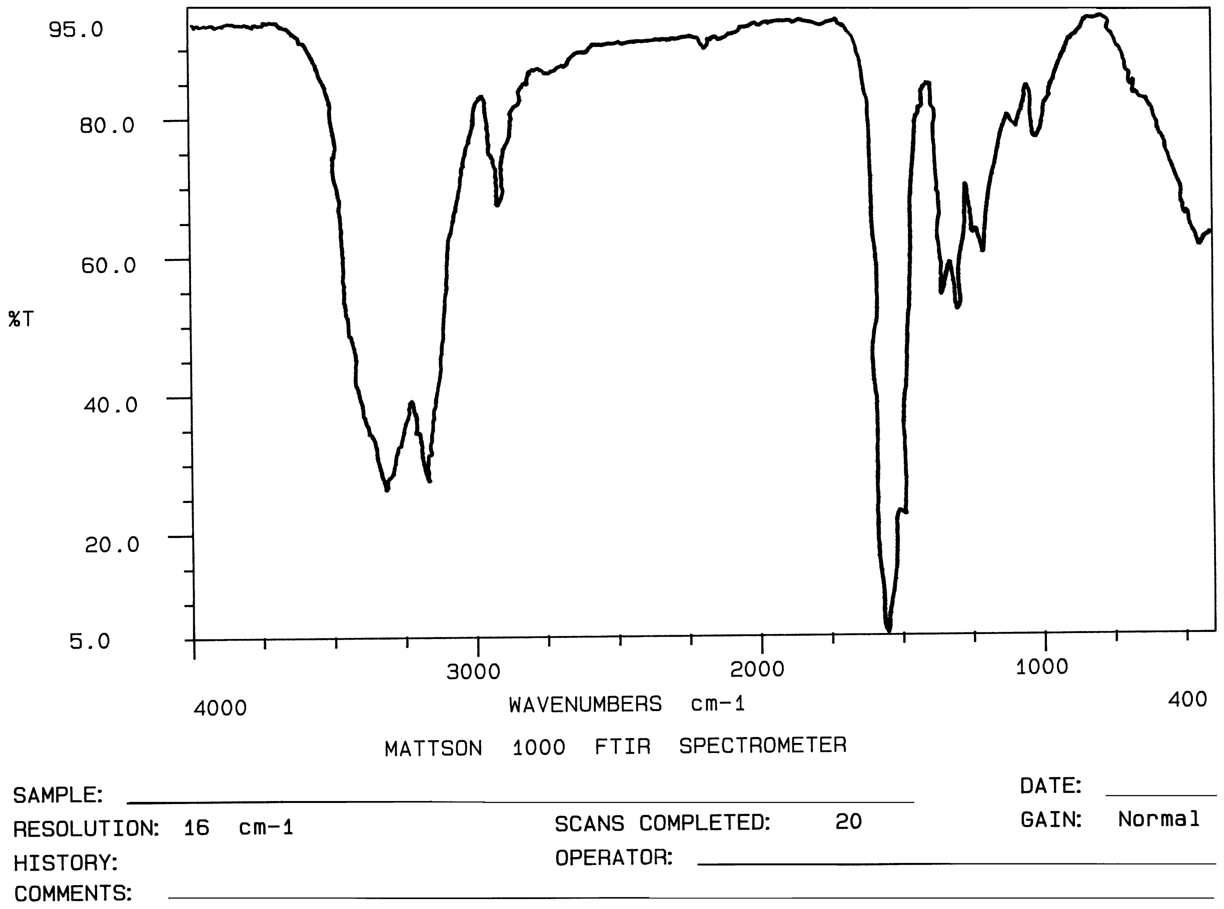
Figure 5. (continued)

(continued)



(c)

Figure 5. (continued)



SAMPLE:
RESOLUTION: 16 cm-1
HISTORY:
COMMENTS:
SCANS COMPLETED: 20
OPERATOR:
DATE:
GAIN: Normal

(a)

Figure 6. FTIR spectrums of (a) pure PAA, (b) PP_y, (c) PAA/PP_y composite film, and (d) mechanical mixture.

(*continued*)

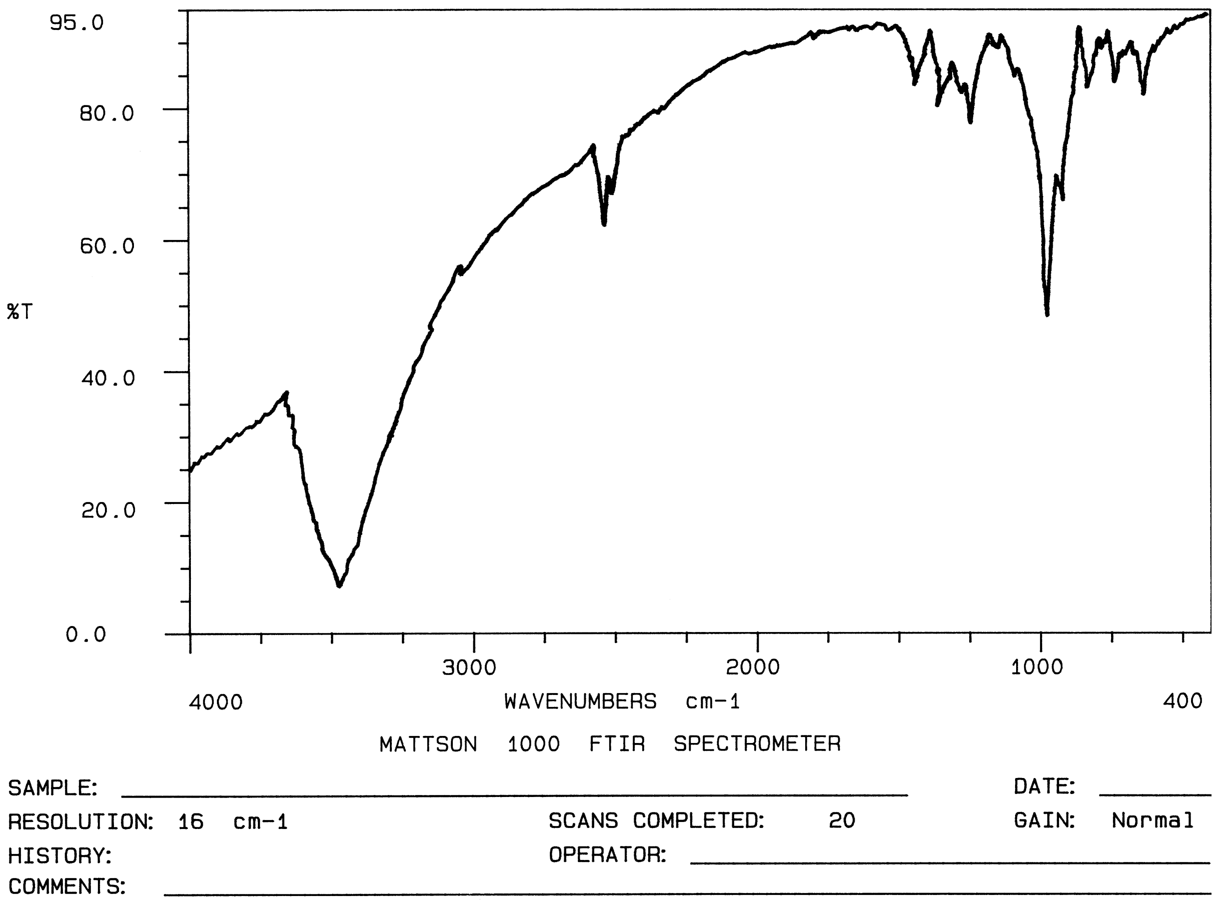


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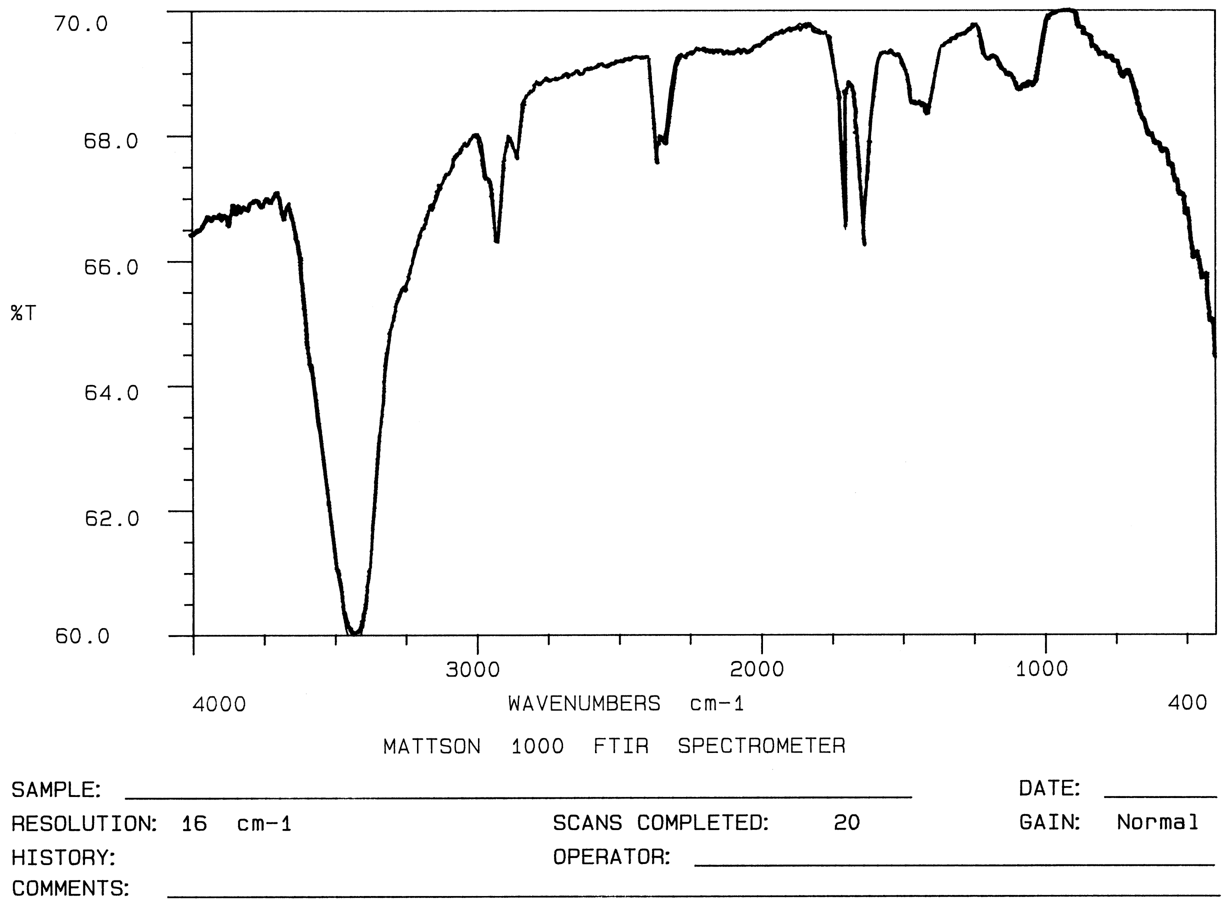
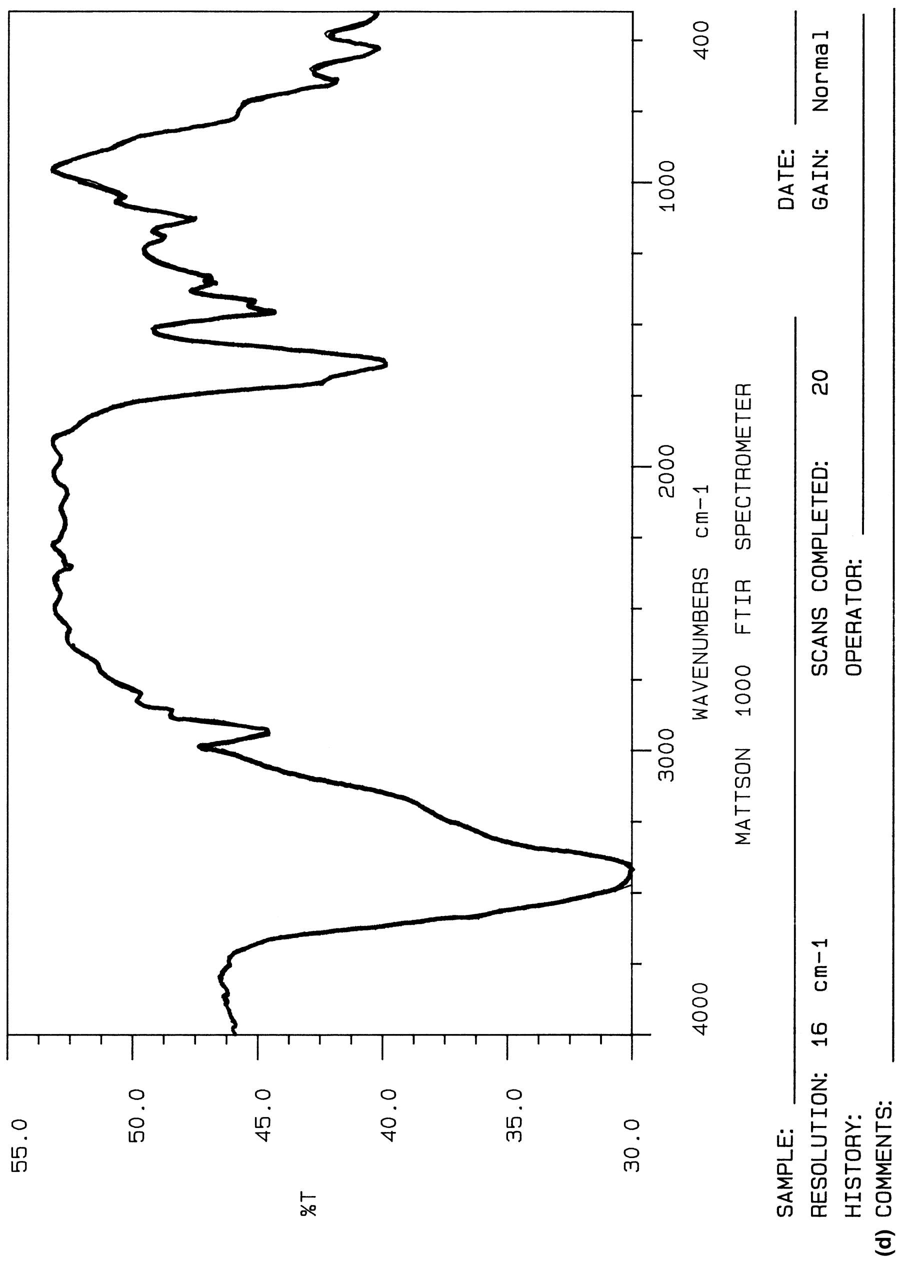
Figure 6. (continued)



(c)

Figure 6. (continued)

(continued)



SAMPLE:
DATE:
RESOLUTION: 16 cm-1
SCANS COMPLETED: 20
GAIN: Normal
HISTORY:
OPERATOR:
(d) COMMENTS:

Figure 6. (continued)

Based on the conductivity measurements, SEM and thermal analyses it is deduced that PAA and PP_y coexist as two separate phases in the composite. Despite the fact that there films have shown little sensitivity to H_2 only, yet further investigation on this matter should be carried out.

ACKNOWLEDGEMENT

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REFERENCES

[1] T. F. Otero, R. Tejada, and A. S. Elola, *Polymer, 28,* 651-656 (1987).
[2] E. M. Genies and M. Lapkowski, *Synth. Met., 21,* 220 (1987).
[3] A. G. MacDiarmid, J. C. Chain, and A. F. Richter*, Synth. Met., 18,* 285 (1987).
[4] G. Zotti, G. Schianon, and N. Comisso*, Synth. Met., 36,* 337 (1990).
[5] T. F. Otero, J. Rodriguez, and E. de Larreta-Azelain, *Polymer, 31,* 220-228 (1990).
[6] R. H. Baughman, R. R. Chance, H. Eckhardt, and R. L. Elsenbaumer, *Polymer Preprints, 23,* 130 (1982).
[7] E. M. Genies, G. Bidan, and A. F. Diaz, *J. Electroanal. Chem., 149*, 101 (1983).
[8] M. Takuba, *J. Electroanal. Chem., 258*, 303 (1989).
[9] X. Bi, Y. Yao, M. Wan, P.Wan, K. Xiao, Q.Yang, and R. Qian, *Macromol. Chem., 186,* 1101 (1985).
[10] T. F. Otero and E. de Larreta-Azelain, *Polymer, 29,* 1522-1526 (1988).
[11] T. Osaka, K. Naoi, S. Ogano, and S. Nakamura*, J. Electrochem. Soc., Electrochem. Sci. Tech., 134,* 2096 (1987).
[12] T. F. Otero and E. de Larreta-Azelain*, J. Chem. Phys., 86,* 131 (1989).
[13] T. F. Otero, E. de Larreta-Azelain, and R. Tejada, *Macromol. Chem., Macromol. Symp., 20-21,* 615 (1988).
[14] V. Bocci and G. P. Gardini, *J. Chem. Soc. Chem. Comm., 148* (1986).
[15] O. Niwa and T. Tamamura, *J. Chem. Soc. Chem. Comm., 817* (1984).
[16] M. dePaoli, R. J. Waltmann, A. F. Diaz, and J. Bargon, *J. Chem. Soc. Chem. Comm., 1015* (1984).

[17] B. Tieke and W. Gabriel, *Polymer, 31,* 20 (1980).

[18] H. L. Wang, L. Toppare, and J. E. Fernandez, *Macromolecules, 23,* 1053 (1990).

[19] G. P. Zhang, G. R. Peng, and X. Bi, *Synth. Met., 55-57,* 1123-1128 (1993).

[20] E. Ruckenstein, J. H. Chen, *J. Appl. Polym. Sci., 43,* 1209-1218 (1991).

[21] B. Zinger and D. Kijel, *Synth. Met., 41-43,* 1013-1023 (1991).

[22] E. Ruckenstein and J. H. Chen, *Polymer, 32,* 1230-1235 (1991).

[23] L. Toppare, *Tr. J. of Chem., 21,* 30-34 (1997).

[24] F. Selampinar, U. Akbulut, T. Yalcin, S. Süzer, and L. Toppare, *Synth. Met., 62,* 201-205 (1994).

[25] S. Erturan, B. Yalvac, and S. Toraman, *Tr. J. of Chem., 22-2*, 161-166 (1998).

[26] F. Selampinar, U. Akbulut, E. Yildiz, , A. Güngör, and L. Toppare, *Synth. Met., 89,* 111-117 (1997).

[27] F. Selampinar, U. Akbulut, and L. Toppare, *Synth. Met., 84,* 185-186 (1997).

[28] N. Balci, U. Akbulut, L. Toppare, D. Stanke, M. L. Hallensleben, *Mat. Res. Bull., 32*, 1449-1458 (1997).

[29] F. Selampinar, U. Akbulut, T. Yilmaz, A. Güngör, and L. Toppare, *J. Polym. Sci., 35,* 3009-3016 (1997).

[30] C. Nylander, M. Armgarth, and I. Lundstrom, in *Proc. Int. Meeting on Chemical Sensors,* Fukuoka, T. Seiyama, K. Fueki, J. Shiokowa, and S. Suziki, Eds. Elsevier, 203, 1983.

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