Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Özay Eraldemir[a]; Bekir Sari[a]; Ayşegül Gök[b]; Halil İbrahim Ünal[a]
[a] Department of Chemistry, Faculty of Arts and Science, Gazi University, Ankara, Turkey [b] Department of Chemistry, Faculty of Arts and Science, Suleyman Demirel University, Isparta, Turkey

To cite this Article Eraldemir, Özay , Sari, Bekir , Gök, Ayşegül and Ünal, Halil İbrahim(2008) 'Synthesis and Characterization of Polyindole/Poly(vinyl acetate) Conducting Composites', Journal of Macromolecular Science, Part A, 45: 3, 205 — 211

To link to this Article: DOI: 10.1080/10601320701839890

URL: http://dx.doi.org/10.1080/10601320701839890

Journal of Macromolecular Science®, *Part A: Pure and Applied Chemistry* (2008) **45**, 205–211

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320701839890

Synthesis and Characterization of Polyindole/Poly(vinyl acetate) Conducting Composites

ÖZAY ERALDEMIR,[1] BEKIR SARI,[1] AYŞEGÜL GÖK,[2] and HALIL İBRAHIM ÜNAL[1]

[1]*Faculty of Arts and Science, Department of Chemistry, Gazi University, Ankara, Turkey*
[2]*Faculty of Arts and Science, Department of Chemistry, Suleyman Demirel University, Isparta, Turkey*

Received August, 2007, Accepted September, 2007

Composites of a polyindole (PIN) and poly(vinyl acetate) (PVAc) were prepared chemically using $FeCl_3$ as an oxidant agent in anhydrous media. The composite compositions were altered by varying the indole monomer during preparation. The composites were characterized by FTIR and UV-visible spectroscopies, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), stress-strain experiments and conductivity measurements. Moreover, the film of PVAc and PIN/PVAc composites were prepared by casting on glass Petri dishes to examine their stress-strain properties. PIN/PVAc composites are thermally more stable than PIN. It was found that the conductivities of PIN/PVAc composites depend on the indole content in the composites.

Keywords: conducting composites; polyindole; poly(vinyl acetate)

1 Introduction

In the past 25 years, inherently conducting polymers, such as poly(*para*-phenylene), polyaniline, polythiophene and polypyrrole have attracted great attention because of their widespread fundamental interest and potential industrial applications (1). Polypyrrole has the advantages of good electrical conductivity, environmental stability, and ease of anodic electrodeposition of freestanding polypyrrole films. On the other hand, poly(*para*-phenylene) has the advantage of good thermal stability. Indole has both a benzene ring and a pyrrole ring. Thus, polyindole (PIN) may have the properties of both poly(*para*-phenylene) and polypyrrole. Interest in the electrochemical polymerization of indole is due to its close structural similarities to pyrrole; many statements about the structure and polymerization mechanism of PIN have been taken from polypyrrole studies (2–5). Therefore, PIN has received a significant amount of attention in the past several years and may be a good candidate for applications in various areas, such as electronics, electrocatalysis, anode materials in batteries, anticorrosion coatings, and pharmacology (6–10). PIN films have mainly been synthesized through electrochemical oxidation (11), except in several works concerning the direct chemical oxidation of indole by $FeCl_3$ (2). The chemical and electrochemical synthesis of polyindole have been discussed in detail by Billaud and coworkers (12–16).

The doped polyindole was obtained in the form of an air stable conducting polymer, green in color. Polyindole-5-carboxylic acid is an interesting conducting polymer because depending on the pH of the solution it can be self-doped (17). Bartlett and Farrington developed a micro pH sensor based on this polymer (18). The polymer showed good stability and rapid response to changes in solution pH. Also, the films could be stored dry and reused. Koleli et al. (19) reported the properties of the Schottky barrier formed on a polyindole-n-GaAs interface. However, PIN has disadvantage properties such as poor mechanical properties due to its powder form. There have been very few studies on the structural characterization of as-prepared PIN films because of the poor quality (20).

Therefore, it is necessary to improve the quality of freestanding PIN films. It is well known that freestanding films of polythiophene and its derivatives, poly(*para*-phenylene) and polypyrrole, can be produced by the direct anodic oxidation of the corresponding monomers in boron trifluoride diethyl etherate (BFEE) with good mechanical, electrical, and thermal properties (21). Additionally, the mechanical properties can be modify with preparing composite in the presence of host matrix (22, 23).

To the best our knowledge, there are no reports in the literature on the synthesis and characterization of polyindole/poly(vinyl acetate) composites. The present work, reports

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Address correspondence to: Bekir Sari, Faculty of Arts and Science-Department of Chemistry, Gazi University, 06500 Ankara, Turkey. E-mail: bsari@gazi.edu.tr

the results obtained on the chemical synthesis and the characterization of polyindole/poly(vinyl acetate) composites using poly(vinyl acetate) as an insulator polymer matrix. Poly(vinyl acetate) (PVAc) has strong adhesive properties and was thus used as the matrix polymer in this study. Films of PVAc homopolymer and the PIN/PVAc composites were prepared by casting on glass Petri dishes.

2 Experimental

2.1 Materials

Indol was purchased from Across Organics. Indole, $FeCl_3$ (Aldrich), $CHCl_3$ (Merck), and C_2H_5OH (Merck) were used such as purchased. Poly(vinyl acetate) was obtained from Aldrich.

2.2 Synthesis of Polyindole (PIN)

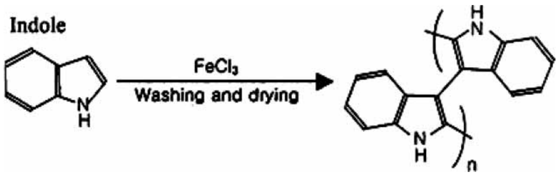
Polyindole were chemically synthesized using $FeCl_3$ as an oxidant (Scheme 1). The molar ratio of oxidant to monomer was taken as two. 4.99 g of oxidant was dissolved into 36 mL of $CHCl_3$. The monomer solution into 10 mL $CHCl_3$ was added dropwise into an oxidant solution. The reaction was continued under nitrogen atmosphere for 5 h. The pristine polymer was collected by filtration and then washed with distilled hot water (90°C). Finally, the precipitate was dried in vacum oven at 70°C for 24 h.

2.3 Synthesis of Polyindole/Poly(vinyl acetate) Composites

2.87, 3.48, 4.10, 4.70, 5.40, and 6.05 g PVAc were dissolved in 35 mL of $CHCl_3$, respectively. After 1.82 g monomer was added to PVAc solutions, indole was polymerized by adding 4.99 g $FeCl_3$ in 30 mL ethyl alcohol. The reaction mixture was continuously stirred for 5 h at 15°C. Then, the reaction solutions were cast on glass Petri dishes. PIN/PVAc composites were dried by an evaporating solvent. The precipitates were washed with distilled hot water and dried at room temperature for 36 h. The PIN/PVAc composites, including PIN at different amounts, were prepared.

2.4 Film Preparation

To prepare PIN/PVAc composite films, 2 g powder of composite was dissolved in $C_2H_5OH + CHCl_3$ (40 + 10, mL) solvent mixture. Then, the solution was cast on a glass Petri dish. The film was dried at room temperature for 48 h, and removed from the glass Petri dish by exposing the film to a water steam. The PIN amount in every composite film was calculated by dissolving PVAc in $CHCl_3$.



Sch. 1. Polymerization of indole using $FeCl_3$.

2.5 Characterization

Conductivities of samples were measured by a four-probe technique. Fourier transform infrared (FTIR) spectra of the samples were taken on KBr disks and recorded on an ATI UNICAM spectrometer. TGA analysis was carried out using a Setaram 8 ET 8 V8 Evolution 1760 model thermogravimetric analyzer in the presence of nitrogen atmosphere up to 800°C, at a heating rate of 10°C min^{-1}. DSC of the polymer samples was recorded using a SETARAM 8 ET8 V 8 Evolution 1760 model calorimetry under nitrogen atmosphere up to 800°C at heating rate of 10°C min^{-1}. The surface morphologies of the polymers were utilized using A Jeol model JSM 5600 scanning electron microscope (SEM). The UV-vis spectra were recorded using a ATI UNICAM UV-2 model spectrometer. The strain stess experiments of the polymers were carried out using a Shimadzu AG-I 5 kN model machine.

3 Results and Discussion

3.1 Yield and Conductivity Results

Table 1 show the yield percentage and conductivity values of PIN and PIN/PVAc composites containing different percentages of PIN. The conductivity of PIN was determined as 9.64×10^{-3} S cm^{-1}. This conductivity value is higher than that of PIN reported in the literature (24). As shown in Table 1, the conductivity of PIN/PVAc composites was slightly increased with increasing the content of PIN. In other words, conductivity values of the composites decreased with increasing the amount of PVAc in the composites. Among the composites, PIN/PVAc containing 35 wt% of PIN had the highest conductivity with a value of

Table 1. Yield and conductivity results of PIN and PIN/PVAc composites

Polymer/ composite	Polymerization yield of PIN in composite (wt%)	Conductivity (S/cm)
PIN	—	9.64×10^{-3}
PIN/PVAc(13/87)	46	1.61×10^{-5}
PIN/PVAc(14/86)	47	1.98×10^{-5}
PIN/PVAc(18/82)	55	2.45×10^{-5}
PIN/PVAc(22/78)	63	2.86×10^{-5}
PIN/PVAc(28/72)	74	3.89×10^{-5}
PIN/PVAc(35/65)	83	4.83×10^{-5}

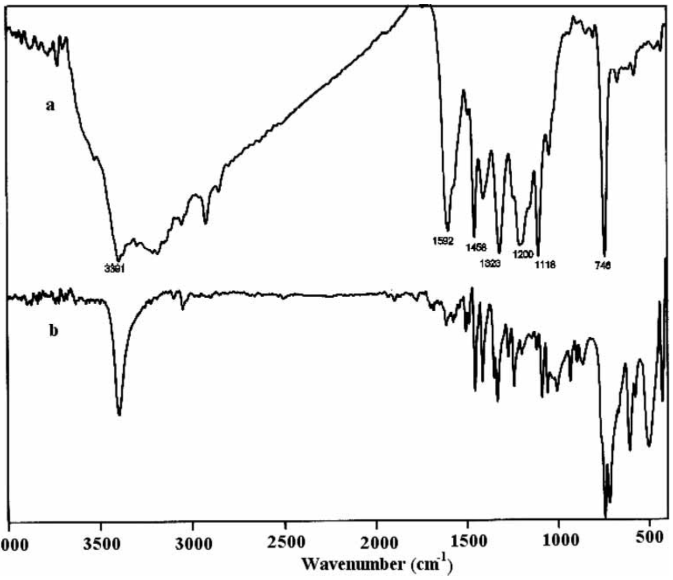


Fig. 1. FTIR spectra of PIN (a) and indole (b).

4.83×10^{-5} S cm^{-1}. The highest PIN yield was also obtained in PIN/PVAc (35/65) with a value of 83%.

3.2 *FTIR Results*

Figures 1 and 2 show FTIR spectra of PIN, indole and PIN/PVAc composites and PIN, respectively. The bands at 3391, 1540, and 1406 cm^{-1} indicate the presence of the N-H stretching in the spectra of PIN (Figure 1a). The band at 1590 cm^{-1} assigned to the vibration of the $C_2{=}C_3$ aromatic bonds typical of indoles. Two bands at 746 and 739 cm^{-1} show C-H vibration of indole (Figure 1b). However, PIN has one band at 746 cm^{-1} showing a hydrogen bond at the end of the chain. Also, the band at 1540 cm^{-1} can be related to the N-H stretch and $C_2{=}C_3$ deformation. The bands at 1458 and 1200 cm^{-1} attributed to the benzene and aromatic rings of PIN structure. FTIR spectrum of PIN strongly suggests that the monomers are linked via the positions 2 and 3 of the pyrrole ring (25, 26). The polymerization mechanism of indole shows two different postulated mechanisms concerning the propagation reactions (coupling between two radical-cations or between a radical-cation and a neutral species) to give conducting polymer (25). PIN/PVAc composite indicates the bands coming from both PIN and PVAc (Figure 2). There are four characteristic bands at 2928, 1721, 1375, and 1252 cm^{-1} for PVAc. Additionally, the peak at 2982 cm^{-1} belongs to aliphatic C-H stretching and the band at 1721 cm^{-1} has C=O vibrations (27). The band at 1252 cm^{-1} comes from C-O vibrations. However, the similar bands to those of PIN are seen, the values of the bands shifted due to interaction between PIN and PVAc.

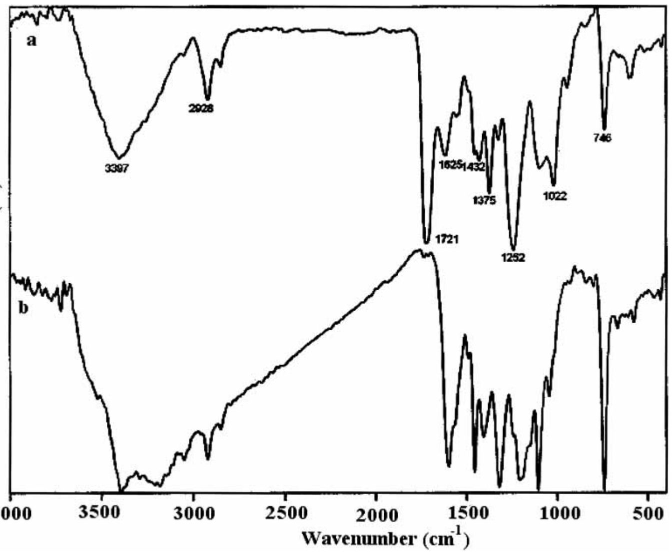


Fig. 2. FTIR spectra of PIN/PVAc (a) and PIN (b).

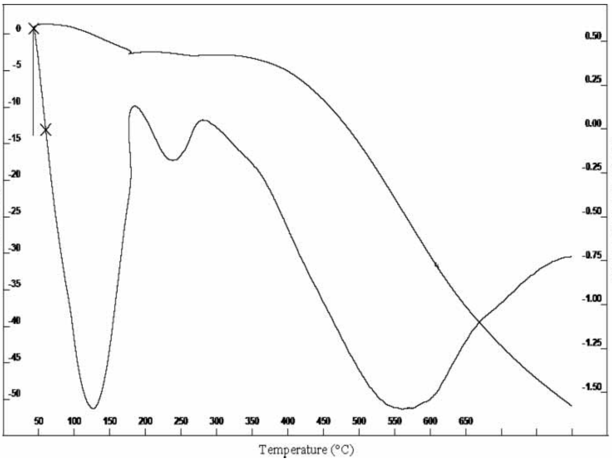


Fig. 3. TGA curve of PIN.

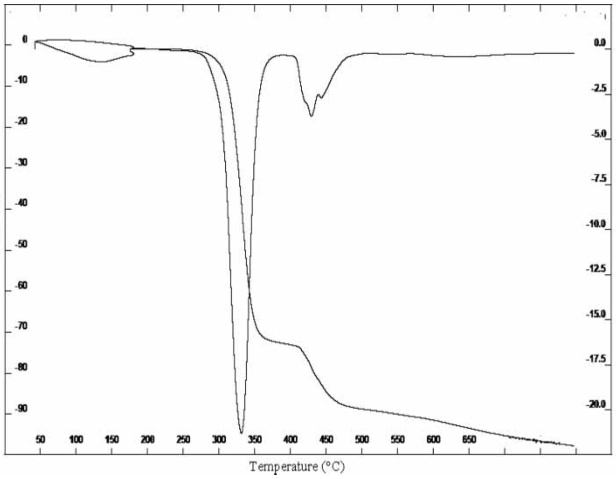


Fig. 4. TGA curve of PVAc.

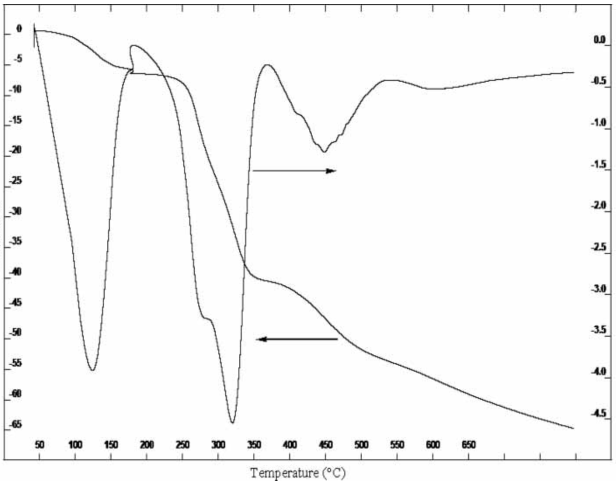


Fig. 5. TGA curve of PIN/PVAc, with 35% of PIN.

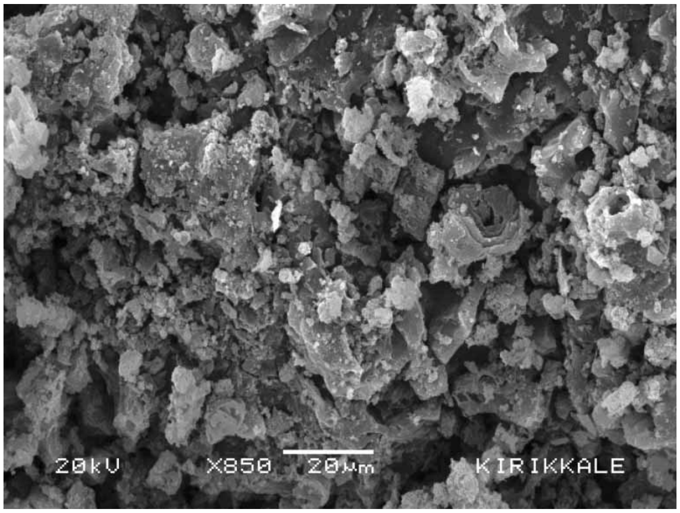


Fig. 6. SEM micrograph of PIN.

3.3 TGA Results

TGA curves of the PIN, PVAc and PIN/PVAc, with 35% of PIN, are given in Figures 3–5 and, the decomposition temperatures obtained from the all curves were tabulated in Table 2. As can be seen from Table 2, PIN and composites indicate three different decomposition temperatures (T_i, T_m, T_f). PVAc shows decomposition with two steps, whereas PIN has three degradation steps. The first weight loss (100–180°C) indicates the loss of small units such as solvents and monomers in the polymers. The second weight loss, between 180°C and 370°C, attributes removal of the dopant anions from the polymer structure. The final step at 415°C–680°C, shows degradation of the polymer (28). There were two degradation steps for PVAc (320–350°C and 420–465°C). According to initial decomposition temperature (T_i) among the composites, the PIN/PVAc composite, which included 35% of PIN, has the highest decomposition temperature, 270°C. However, the thermal stability of the composites increased with increasing the amount of PIN in PIN/PVAc composites. As seen in Table 2, the composites show three decomposition steps. The first step occurred between 85–190°C, and it could be attributed to the loss of small units

Table 2. TGA results of samples

Polymer/ composite, (wt%)	Decomposition temperature (°C) T_i^a	T_m^b	T_s^f
PIN	100	125	180
	180	235	370
	415	570	680
PVAc	320	335	350
	420	435	465
PIN/PVAc(13/87)	100	145	190
	255	325	350
	400	445	495
PIN/PVAc(14/86)	95	140	170
	255	325	345
	400	445	495
PIN/PVAc(18/82)	100	150	185
	255	325	350
	400	450	485
PIN/PVAc(22/78)	85	115	150
	260	325	345
	415	450	480
PIN/PVAc(28/72)	100	150	180
	260	300	350
	405	450	480
PIN/PVAc(35/65)	95	125	160
	270	320	345
	400	450	480

T_i^a: initial temperature; T_m^b: maximum decomposition temperature; T_s^f: final temperature.

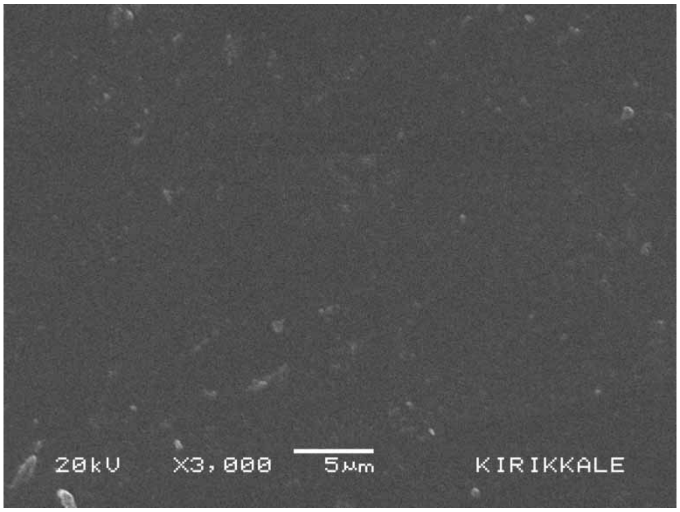


Fig. 7. SEM micrograph of PVAc.

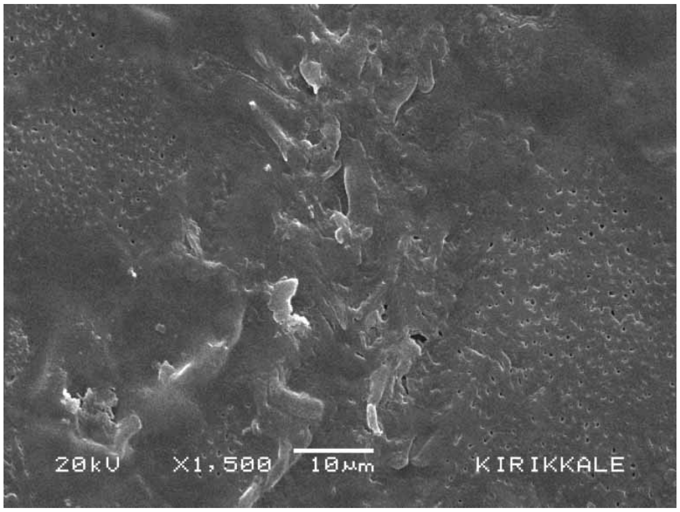


Fig. 8. SEM micrograph of PIN/PVAc, with 35% of PIN.

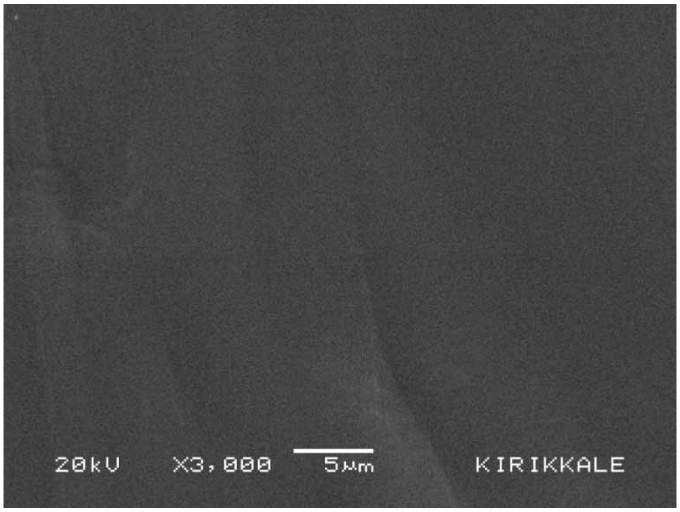


Fig. 9. SEM micrograph of PIN/PVAc, with 22% of PIN.

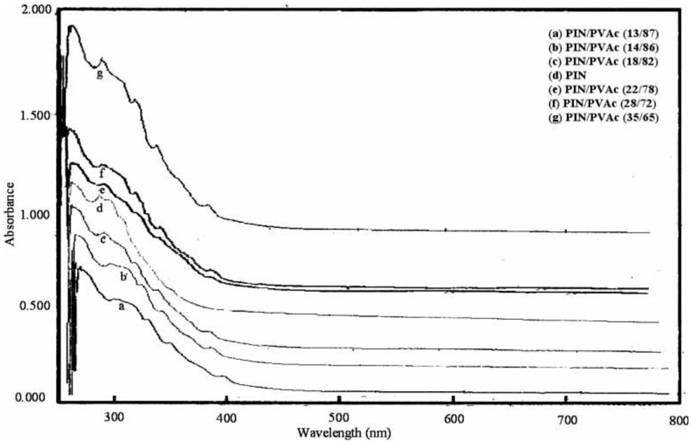


Fig. 10. UV-Vis spectra of samples.

such as solvents and monomers in the composites (29, 30). The second step stage of decomposition occurred between 255–350°C. This step is due to the removal of the dopant anions from the polymer structure. The last step, occurred between 400 and 495°C, shows the degradation of the polymer structure. Finally, PIN/PVAc composites exhibit adequate thermal stability.

3.4 SEM Results

SEM micrographs of PIN, PVAc and PIN/PVAc composites, with 35 and 22% of PIN, have been seen in Figures 6–9. The SEM micrograph of PIN (Figure 6) shows both a granular and porous structure (31), (whereas the SEM micrograph of PVAc has a non-porous and uniform structure on the upper surface (Figure 7). It can be seen that morphological structures of composites are different from PIN. PIN/PVAc composite including 35% of PIN has a non-uniform structure (Figure 8). By decreasing the PIN content in the composites (Figure 9), the surface properties of the composites indicate similar morphology of PVAc. In general, composites show similar structures. But, some of them have a porous structure due to structure with porous and granular of PIN. The composites including 18, 22, and 28, wt% PIN show non-porous and uniform structure.

3.5 Stress-Strain Results

The stress-strain experiments were carried out in order to determine the mechanical stability of films. For stress-

Table 3. Results of stress-strain experiments of PVAc and composites

Polymer/ composite, (wt%)	Thickness (mm)	Max force (N)	Maz dispersion (mm)	Max stress (N/mm^2)	Max strain (%)	Energy (J)
PIN/PVAc(13/87)	0.4750	7.81	3.28	1.64	65.66	0.0181
PIN/PVAc(14/86)	0.4250	4.06	3.07	0.95	30.75	0.0079
PIN/PVAc(18/82)	0.3750	3.59	2.09	0.95	14.99	0.0068
Pure PVAc	0.3250	3.43	97.26	1.05	572.17	0.1470
Pure PVAc	0.3000	3.28	47.00	1.09	276.52	0.1241
Pure PVAc	0.2750	3.17	17.52	1.19	109.54	0.0499

Table 4. UV-Vis results of samples

Polymer/ composite, (wt%)	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)	λ_5 (nm)	λ_6 (nm)	λ_7 (nm)
PIN	268	294	308	—	—	—	—
PIN/PVAc(35/65)	271	298	307	345	369	422	428
PIN/PVAc(28/72)	271	298	307	345	369	422	428
PIN/PVAc(22/78)	271	298	307	345	369	422	428
PIN/PVAc(18/82)	269	299	306	345	369	422	428
PIN/PVAc(14/86)	269	299	308	345	369	422	428
PIN/PVAc(13/87)	268	298	307	345	369	422	428

strain tests, PIN/PVAc composites including 13, 14, and 18 wt%. PIN were selected due to their good resistance. The data of the stress-strain experiments is shown in Table 3. By the increasing the PVAc percentage in films, the value of thickness, maximum force, maximum dispersion, maximum strain, maximum stress and energy of composite films are increased. PVAc film is mechanically more flexible than composite films. It can be seen that PVAc modiies mechanical properties of PIN from Table 3.

3.6 UV-Vis Results

The UV-Vis spectra of PIN and PIN/PVAc composites are shown in Figure 10 and Table 4. The UV-Vis spectrum of PIN shows three peaks at 268 nm, 294 nm and 308 nm; the 268 nm peak corresponds to π-π^* transitions of the polymer chain (32) and, the peaks at 294 and 308 nm belong to conjugation and π-π^* transitions of benzene ring (33). The UV-Vis spectra of PIN/PVAc composites show seven peaks. The first absorption is assigned to the conjugation of monomers (32). The second band, corresponds to n-π^* transition of C=O, coming from PVAc. The third band corresponds to π-π^* transitions of benzene ring (33).

4 Conclusions

Freestanding PIN/PVAc composite films with conductivity of 2.45×10^{-5} S cm^{-1} were chemically synthesized in the presence of PVAc containing 18 wt% of PIN. Chemical, structural, and morphology studies indicated that PIN/PVAc composite films with better quality could be obtained from PVAc. According to FTIR spectra, the existence of the N-H bond implied that coupling between the monomer units occurred at the C_2 and C_3 positions. PIN/PVAc composites indicated good mechanical properties and thermal stability. These features are expected to introduce more applications for conducting PIN in the future.

5 Acknowledgements

This study was supported by the state planning organization of Turkey (Grant No: 2001K120590). The authors thank Dr Metin Gürü for TGA, Yüksel Akyüz for Stress-Strain measurements, and to Erdem Yaşar for SEM.

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