

Novel Ni/Polypyrrole and Cu/Polypyrrole Composites Prepared in the Presence of Different Acids: Synthesis and Investigation of Thermal Stability

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ABSTRACT: We report the synthesis and characterization of new organic/inorganic hybrid materials constituted of Ni(0) and Cu(0) nanoparticles and polypyrrole (PPy). Copper and nickel nanoclusters were synthesized by a chemical reduction of aqueous metal salt solutions by sodium borohydride. PPy/Ni(0) and PPy/Cu(0) composites were obtained in the presence of two different acids (H₃BO₃, CH₃COOH), by polymerizing pyrrole-Ni and pyrrole-Cu particles by using iron (III) chloride. The composites have been characterized by scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and magnetic susceptibility techniques. Conductivity measurements of samples were taken using four-probe devices. The PPy/Ni(0) and

PPy/Cu(0) nanocomposites doped with different acids exhibited higher conductivity values than those of homopolymers. Among all samples, Ni/PPy-H₃BO₃ has the highest conductivity (1.42 S cm⁻¹). Homopolymers and composites showed a stable and increasing conductivity with increasing temperature, except Ni(0). We observed that from TGA analysis of polymers, metal composites of PPy synthesized in two different media are more stable than those of PPy-CH₃COOH and PPy-H₃BO₃. The magnetic susceptibility values of homopolymers and Cu are negative, whereas the other samples are positive. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3852–3860, 2007

Key words: nanocomposite; copper; nickel; polypyrrole

INTRODUCTION

Since the highly conducting polyacetylene (PA) was prepared in 1977,¹ many studies have already been reported regarding organic conducting polymers such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh) for their possibilities for devices combining optical, electrochemical, and conducting properties.

Among the conducting polymers, because of its high electrical conductivity, long-term environmental stability, and interesting technological applications, PPy is one of the most extensively studied polymers.^{2–4} It has been identified for certain specific applications such as rechargeable batteries,^{5,6} conducting textiles,^{7,8} and as membranes for gas separation processes.^{9,10} PPy can be easily synthesized by chemical^{11–16}

or electrochemical methods.^{17–20} The preparation conditions affect the chemical characteristics and electrical conductivity of final products. Thus, it is well known that the synthesis with different dopants influences the electrical properties. The chemical nature and the dimensions of the dopants as well as the doping level affect the extent of conductivity.^{18,19,21} A number of study have already reported on the synthesis of PPy using various dopants synthesis and characterization.^{22–27}

The development of nanocluster-based materials is a topic of great interest^{28–30} because of their vast technological applications. Nanoclusters are ultrafine particles of nanometer dimensions located in the transition region between atoms and bulk solids. Recently, nanocomposites of π -conjugated polymers (such as PANI, PPy, and PTh) and inorganic particles have been receiving much attention^{31–34} because of their broad range applications as battery electrodes in batteries, catalysis, and light emitting devices.³⁵

The electrical and thermal conductivities of polymers can be improved with the addition of metallic filler.^{36–38} In the recent years, there have been increasing interest in the optical properties of metal aggregates and conducting polymers due to their technological applications in heterogeneous catalysis,³⁹ environ-

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mental science,⁴⁰ microelectronics,⁴¹ and magnetism.⁴² Various methods could be changed in the literature for synthesizing the nanoclusters of noble metals.^{43,44} However, one of the most accepted way to prepare these materials is electrochemical method, which has been applied to produce composites such as copper⁴⁵ and nickel⁴⁶ nanoparticles have been successfully incorporated into PPy but their detailed characterization was absent.

Among these inorganic materials, transition metals play an important role in the production of polymeric materials. In addition to cost saving, other value-added properties are gained through the use of those inorganic fillers. They can improve mechanical^{47–49} and thermal^{50,51} properties, as well as optical and electrical properties,^{52–54} of a polymeric material.

In the past few years, there have been some reports on the synthesis of PPy/Ni and PPy/Cu nanocomposites with different methods in literature. Haseko et al. performed a reversal pulse potential technique to obtain a composite plating of nickel and PPy on the copper substrate.⁵⁵ Zouaoui et al. report that the inclusion of copper metal in poly(pyrrole-alkylammonium) films coated on carbon electrodes via the incorporation by ion-exchange of anionic copper(II)-oxalate complexes followed by an electrochemical reduction.⁵⁶ However, there was no report on the preparation and characterization of PPy/Ni and PPy/Cu nanocomposites synthesis in different dopant anions with chemical oxidation polymerization method and their detail characterization. We described a method to prepare PPy/Ni and PPy/Cu composites using *in situ* chemical polymerization of PPy doped with two different acids in presence of Ni(0) and Cu(0) aggregates. It was also attempted to describe a simple method to synthesize PPy containing aggregated Ni and Cu nanoparticles by reducing chemically. Characterization of samples was made by spectroscopic, thermal, conductivity, and magnetic susceptibility measurements. The conductivity of treated and control samples were measured during heating-cooling cycles. The isothermal stability of composites was carried out at 70, 85, and 100°C temperature, respectively.

EXPERIMENTAL

Materials

Pyrrole was provided by Merck, reagent ferric chloride, FeCl₃, obtained from Riedel de Haen, was used as an oxidizing agent for chemical polymerization of pyrrole. Pyrrole was distilled prior to use. All acids used (H₃BO₃ and CH₃COOH) were of HPLC grade reagent and were provided by Merck. Cu(NO₃)₂ · 3H₂O (Fluka), Ni(CH₃COO)₂ · 4H₂O (Fluka), and NaHB₄ (Fluka) were used as received without further purifi-

cation. Double-distilled water was used as a solvent throughout the experimental procedure.

Synthesis of PPy/Ni and PPy/Cu composites

Copper and nickel hydrosols were prepared by reducing the aqueous copper nitrate and nickel acetate solutions (40 mL) by adding an appropriate amount of reducing agent (NaHB₄) until the solution was colorless. In the reducing procedure, distilled water was used as solvent. Synthesized copper and nickel colloidal dispersion solutions were added into 60 mL containing 1.67M acid solution (CH₃COOH and H₃BO₃) with 10 mmol pyrrole monomer. The polymerization of pyrrole was initiated by the drop wise addition of 25 mmol ferric (III) chloride as the oxidizing agent in acidified solution (containing 1M acids) prepared using distilled water under constant stirring at 0–5°C. The molar ratio of oxidizing agent to monomer was 2.5. After complete addition of the oxidizing agent, the reaction mixture was kept under constant stirring for 16 h. The precipitated composite was filtered and washed with acid solution and distilled water until the filtrate was colorless. Finally, the polymer was dried at 50°C for 24 h under vacuum environment. The amounts of Ni and Cu nanoparticles in Ni/PPy-H₃BO₃, Ni/PPy-CH₃COOH, Cu/PPy-H₃BO₃, and Cu/PPy-CH₃COOH composites were found to be between 11.5–12.8% (w %) and 10.6–10.4% (w %) calculating from the amounts of pure Ni and Cu nanoparticles, respectively. Figure 1(a,b) shows the schematic process of the formation of the metal/PPy composites and chemical reaction of PPy synthesis.

Characterization of samples

Scanning electron microscopy (SEM) and EDS studies of the polymers were performed using JEOL, JEM 100CX (Tokyo, Japan) model scanning electron microscopy. FTIR spectra of the polymers were recorded on a Perkin Elmer model spectrometer (Beaconsfield, Beuckinghamshire, HP91QA, England). Thermograms of the polymers were recorded using a Perkin Elmer (Beaconsfield, Beuckinghamshire, HP91QA, England) thermogravimetric analyzer in the presence of N₂ atmosphere from 50 to 900°C with a heating rate of 10°C min⁻¹. The electrical conductivity of polymers was measured using the standard four-probe technique. The direct current electrical conductivity of samples was measured by standard four-probe method using PCI-DAS6014 for a current source, voltmeter, and temperature controller. Dry powdered samples were made into pellets using a steel die having 13 mm diameter in a hydraulic press under a pressure of 200 MPa. Temperature-dependent electrical conductivity of the polymer samples was measured by four-probe system with PCI-DAS6014 connected to

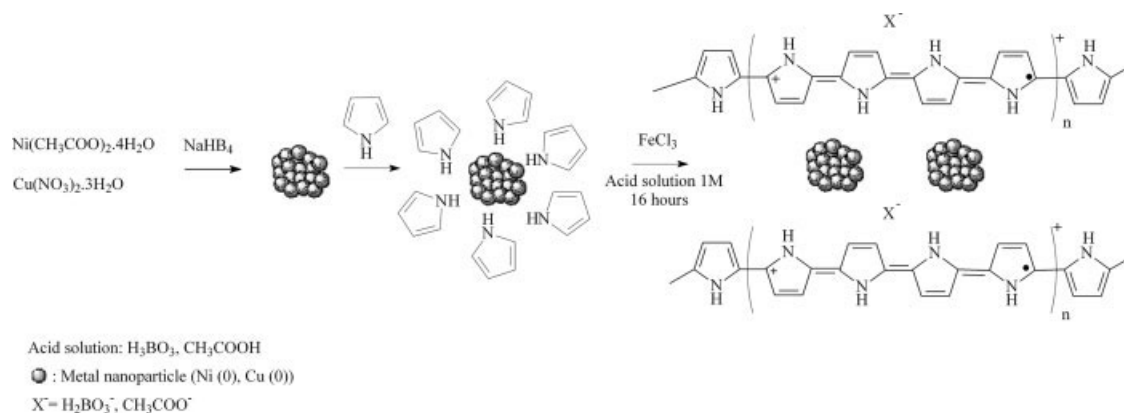


Figure 1 Schematic process of the formation of the metal/PPy composites.

computer and, the temperature of pellets was recorded with a thermocouple. All samples were in pellet forms. And the thicknesses of pellets were measured by digital micrometer. Conductivity values of samples were calculated according to Van der Pauw equation.⁵⁷ The dependence of the electrical conductivity of polymers was measured over a temperature range from 25 to 100°C. Electrical properties of polymers were investigated between 25 and 100°C with heating–cooling cycles and thermal aging studies were made at 70, 85, and 100°C. Magnetic susceptibility measurements were taken on a Sherwood Scientific model (Sherwood Scientific) Gouy balance.

RESULTS AND DISCUSSION

FTIR studies of samples

Figure 2(a,b) represents the FTIR spectra of the PPy doped with organic acids and its formed composites. The infrared spectra of samples were taken in the region from 4000 to 400 cm^{-1} with a 4 cm^{-1} resolution. The band at 1539 cm^{-1} in the spectrum of PPy- CH_3COOH [Fig. 2(a)] corresponds to the C–C stretching vibrations in pyrrole ring. This band has been observed at 1537 cm^{-1} for PPy- H_3BO_3 [Fig. 1(b)]. As seen from Figure 2(a,b), the bands belonging to PPy- H_3BO_3 are sharper than those of PPy- CH_3COOH .

The bands at 1443 and 1447 cm^{-1} in the spectra of homopolymers correspond to C–N stretching vibration in the aromatic ring. The band at 1295 cm^{-1} in the spectrum of PPy- H_3BO_3 is attributed to C–H or C–N in-plane deformation modes. This band was observed at 1292 cm^{-1} for PPy- CH_3COOH . Spectroscopic properties of the polymers are found to be affected by the type of the dopant ion used for doping purpose.³⁴ The band at 1165 cm^{-1} , which is attributed to the vibration of dopant anion observed for PPy- H_3BO_3 , was seen at 1156 cm^{-1} for PPy- CH_3COOH ,⁵⁸ as well. This value (1156 cm^{-1}) for PPy- CH_3COOH homopolymer shifted to 1165 and 1174 cm^{-1} , for Ni/

PPy- CH_3COOH and Cu/PPy- CH_3COOH composites, respectively. Similarly, the dopant anion peaks of Ni/PPy- H_3BO_3 and Cu/PPy- H_3BO_3 was observed at 1166 and 1173 cm^{-1} . Moreover, the new peak at 1122 cm^{-1} appears in spectrum of Ni/PPy- H_3BO_3 composite. These shifts in the peak positions of homopolymers and nanocomposites show changing doping levels due to the size and basicity of the dopant anion.

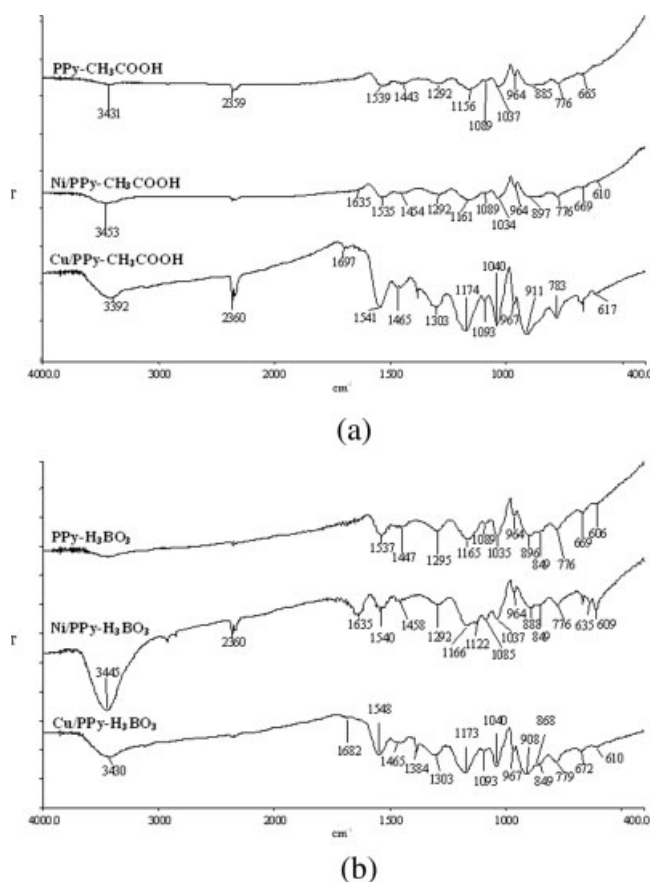


Figure 2 FTIR spectrum of metals and homopolymers, composites, which are synthesized in (a) acetic acid and (b) boric acid medium.

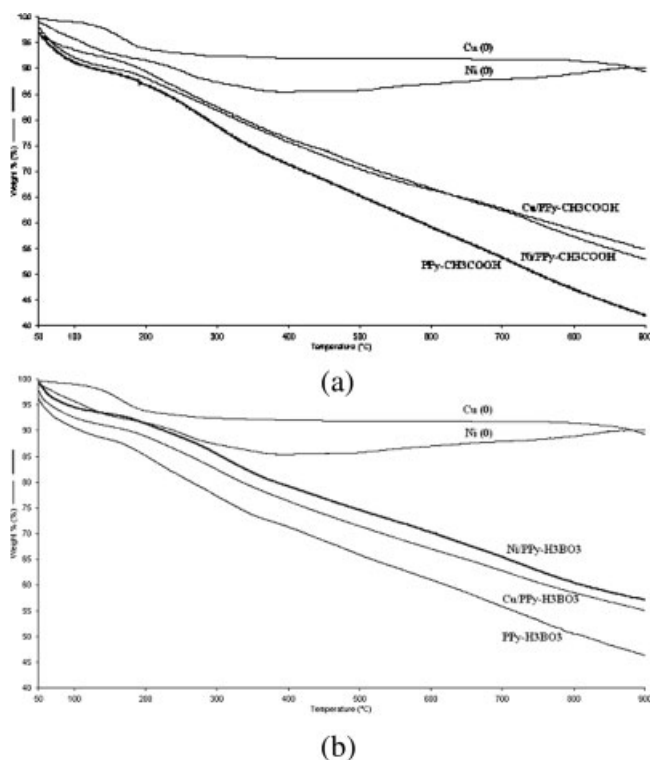


Figure 3 TGA curves of PPy-CH₃COOH and its composites (a), PPy-H₃BO₃ and its composites (b).

The band at 1037 cm⁻¹, which corresponds to C—H and N—H in-plane deformation vibration presents in both homopolymers. The band at 964 cm⁻¹, which is attributed to C—C out of plane ring deformation vibration, is situated at the same position in the spectra of both samples. The band of C—H out of plane deformation vibrations of ring has a maximum at 776 cm⁻¹ for PPy-CH₃COOH and PPy-H₃BO₃, respectively. All these peaks can be observed well in the metal/PPy composites synthesized in two different acid media. The spectra of PPy composites are very similar to that of PPy formed in the absence of Ni and Cu nanoparticles but their intensities are higher than those of homopolymers. The bands observed at 1535–1635 cm⁻¹ and 1697–1541 cm⁻¹ in the FTIR spectra of Ni/PPy-CH₃COOH and Cu/PPy-CH₃COOH composites clearly exhibited a large extension of the conjugated system in the pyrrole chain.²⁸

TGA results

The TGA curves of PPy homopolymers, metals, and their composites are shown in Figure 3(a,b). All samples showed low weight loss at low temperatures (about at 80°C) indicating the expulsion of water molecules/moisture from the polymer matrix.⁵⁹ Thermal degradation temperatures and percentage residue at 900°C obtained from these curves can be seen in Table I. The homopolymers and composites synthesized in the different media showed thermal degradation with one

step, whereas Ni/PPy-H₃BO₃ has weight loss in two steps. This degradation step shows thermal decomposition of polymer chains together with removing dopant anions from polymer structures.^{60,61} PPy-CH₃COOH has higher initial thermal degradation temperature (200°C) than that of PPy-H₃BO₃ (180°C). The similar result was obtained by Gök et al. for poly(toluidine) synthesized in the H₃BO₃ and CH₃COOH media.⁶² On the other hand, PPy-CH₃COOH sample has higher weight loss than that of PPy-H₃BO₃. This result can be explained on the basis of the ionic nature of the conducting PPy, which is also found to be varied depending on the type of the anion used for doping purpose.⁵⁷ Fifty percent of the original weight of PPy-H₃BO₃ is found to be stable up to 800°C while, it is 770°C in PPy-CH₃COOH. It is observed that PPy-H₃BO₃ is thermally more stable than PPy-CH₃COOH. PPy-CH₃COOH and PPy-H₃BO₃ showed the similar residue amounts (42 and 45%) and they have more stable values than those given in the literature.⁶³

Cu and Ni exhibited low weight loss due to removing of volatiles adsorbed on the surface of the nanoparticles. Ni/PPy-H₃BO₃ composite has the highest thermal stability (210°C) among all samples. The increase in the amount of residue (%) in the composites corresponds to about 11–14% and this amount confirmed incorporation of the Ni and Cu nanoparticles to PPy structure. Initial degradation temperatures of metal/PPy-H₃BO₃ nanocomposites (210 and 195°C) were higher than that of their homopolymer (180°C), while initial degradation temperatures of metal/PPy-CH₃COOH (170 and 180°C) nanocomposites were lower than that of their homopolymer (200°C). Thermal stabilities of nanocomposites varied depending on the type of the anion used with doping purpose.⁵⁷ Moreover, the residue amounts of composites at 900°C are very closed to each other and these values are higher than those of homopolymers.

SEM-EDS studies of samples

The morphological study of the deposit by SEM examination coupled with an EDS analysis were conducted to confirm the presence of metal (Cu(0), Ni(0)) particles on

TABLE I
Thermal Degradation Temperatures of Samples

Sample	T_i (°C)	T_m (°C)	T_f (°C)	Residue % at 900°C
PPy-CH ₃ COOH	200	340	480	42
Ni/PPy-CH ₃ COOH	170	350	530	54
Cu/PPy-CH ₃ COOH	180	428	675	56
PPy-H ₃ BO ₃	180	370	560	45
Ni/PPy-H ₃ BO ₃	210	290	370	57
Cu/PPy-H ₃ BO ₃	195	318	440	56

T_i , Initial decomposition temperature; T_m , Maximum decomposition temperature; T_f , Final decomposition temperature.

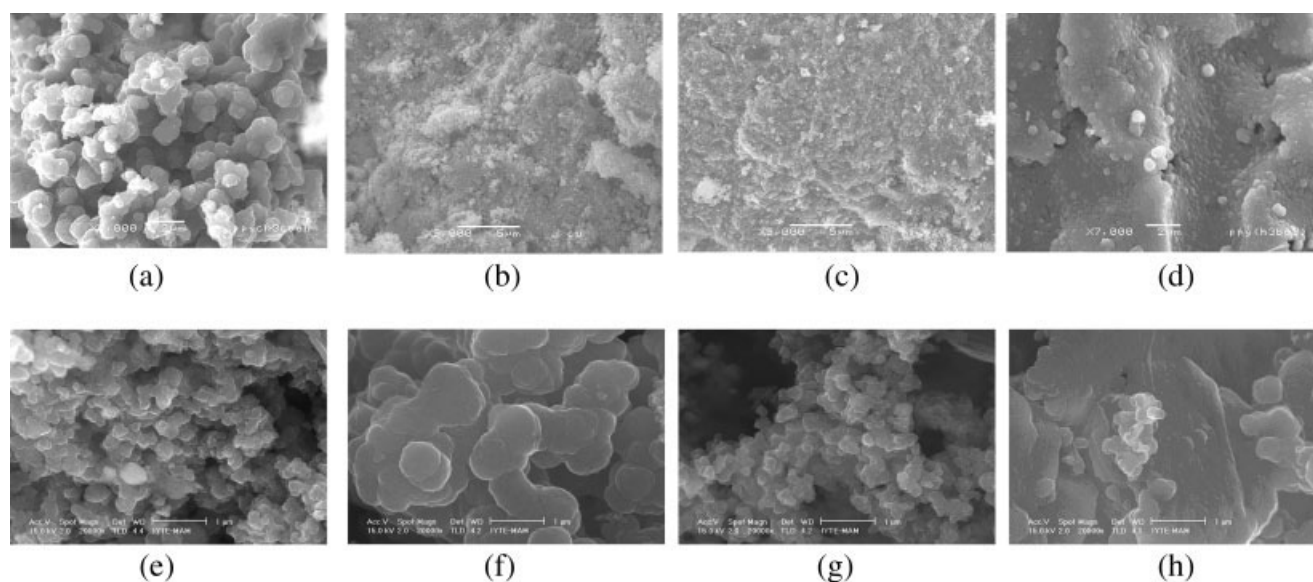


Figure 4 SEM images of samples (a) PPy-CH₃COOH, (b) Cu, (c) Ni, (d) PPy-H₃BO₃, (e) Cu/PPy-CH₃COOH, (f) Ni/PPy-CH₃COOH, (g) Cu/PPy-H₃BO₃, and (h) Ni/PPy-H₃BO₃.

the matrix of PPy films. Figure 4(a–h) shows the scanning electron microscopy (SEM) images of homopolymers and composites. It was clearly observed that resulting metal/PPy composite morphologies were con-

siderably different from homopolymers and metals. The size of metal nanoparticles [Fig. 4(b,c)] is much smaller ($\ll 1 \mu\text{m}$) than those of homopolymers and composites. The metal particles were also confirmed by

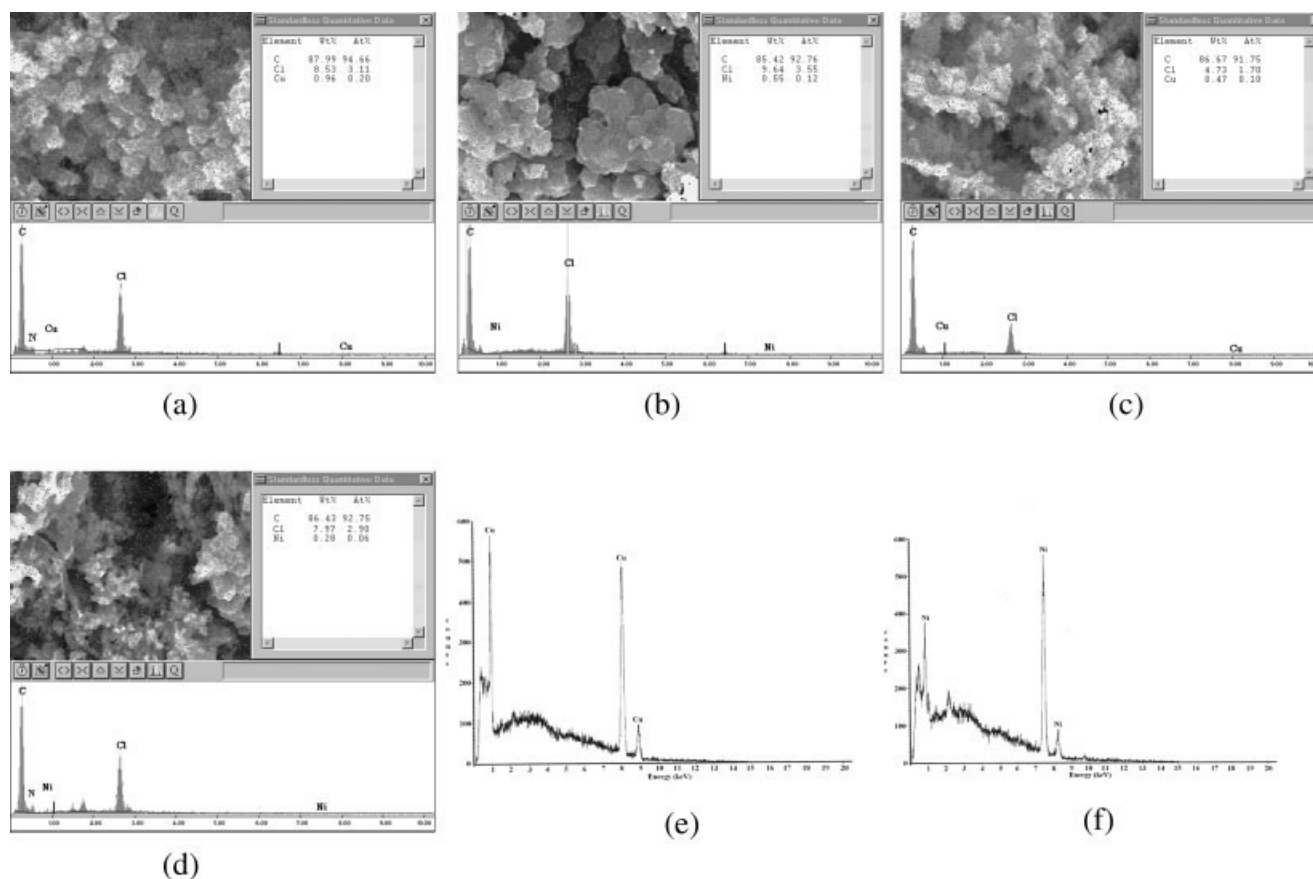


Figure 5 EDS histograms of samples (a) Cu/PPy-CH₃COOH, (b) Ni/PPy-CH₃COOH, (c) Cu/PPy-H₃BO₃, (d) Ni/PPy-H₃BO₃, (e) Cu, and (f) Ni.

TABLE II
Room Temperature Conductivity, Mass Magnetic Susceptibility, and Yield Values of Samples

Sample no.	Polymer	Conductivity (S/cm)	Mass magnetic susceptibility (χ_g)	Yield (%) of PPy
1	PPy-CH ₃ COOH	1.2×10^{-2}	-1.5×10^{-6}	99
2	PPy-H ₃ BO ₃	2.1×10^{-2}	-2.3×10^{-6}	100
3	Cu(0)	8.0×10^{-4}	-1.22×10^{-7}	32
4	Ni(0)	1.69	1.27×10^{-6}	30
5	Cu/PPy-CH ₃ COOH	2.08×10^{-1}	3.94×10^{-6}	99
6	Ni/PPy-CH ₃ COOH	2.05×10^{-1}	7.34×10^{-6}	83
7	Cu/PPy-H ₃ BO ₃	1.08×10^{-1}	1.45×10^{-6}	97
8	Ni/PPy-H ₃ BO ₃	1.42	4.64×10^{-7}	92

elemental mapping. PPy-CH₃COOH [Fig. 4(a)] has a more globular surface than PPy-H₃BO₃ [Fig. 4(d)]. It was observed from SEM results that metal/PPy composites have formed from the particles having different sizes at nanometer levels (under 1 μ m). Ni/PPy-CH₃COOH has relatively bigger particle size than other nanocomposites.

Ni/PPy-CH₃COOH and Ni/PPy-H₃BO₃ composites [Fig. 4(f,h)] also show fairly different structures compared to homopolymers and Ni(0). Morphologies of composites are more flat and leafly according to homopolymer and Ni(0).

EDS was used to determine whether the small particles observed in the microstructure of the nanocomposites are copper and nickel nanoparticles or not. The SEM image, the SEM-EDS metal-mapping photograph, and the EDS images are presented in [Fig. 5(a-d)], respectively. It can be seen that the copper and nickel nanoparticle aggregates observed in the nanocomposites are distributed uniformly in the matrix in general. The chemical composition of the metal/PPy composite surfaces was examined by EDS and mapping analysis. The results indicate the existence of elements Ni and Cu (from metal), C and N (from pyrrole), and Cl (from FeCl₃).

EDS histograms of samples [Fig. 5(a,c)] confirm that Cu/PPy-CH₃COOH and Cu/PPy-H₃BO₃ nanocomposites have a similar peaks surface compared to Cu(0) [Fig. 5(e)], however with a significant decrease in the counts of Cu peaks.⁵³ It was seen that intensities of peaks of nanoparticles in Cu/PPy-CH₃COOH, Cu/PPy-H₃BO₃, Ni/PPy-CH₃COOH, and Ni/PPy-H₃BO₃ [Fig. 5(b,d)] composites decreased due to PPy coated onto Ni(0) [Fig. 5(f)] and Cu(0) [Fig. 5(e)] surfaces. The metal particles would be present not only on the composite particle surface but also distributed through their interior. Thus, the intensities of metal peaks in composites might be decreased in EDS histograms.

Conductivity, magnetic susceptibility and yield (%) results of samples

The conductivity, magnetic susceptibility, and yield (%) values of all samples are given in Table II. The PPy nanoparticles prepared in different media showed an

enhanced electrical conductivity in the presence of metal particles. The conductivity properties of PPy-CH₃COOH increased from 1.2×10^{-2} S/cm to 2.08×10^{-1} ; 2.05×10^{-1} S/cm in the Cu/PPy-CH₃COOH

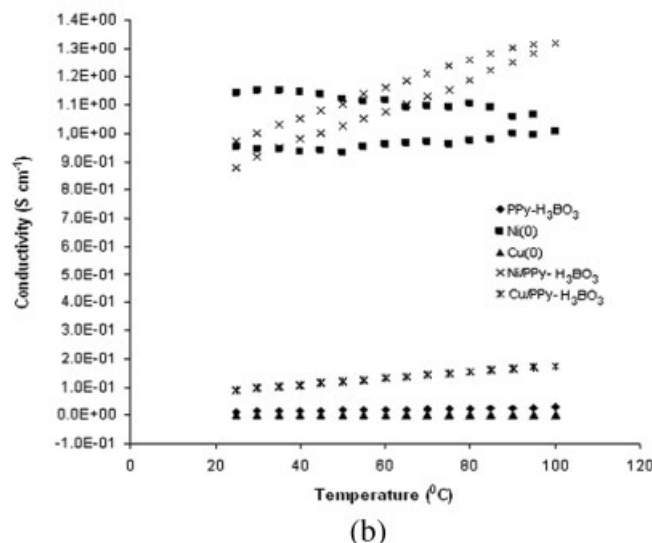
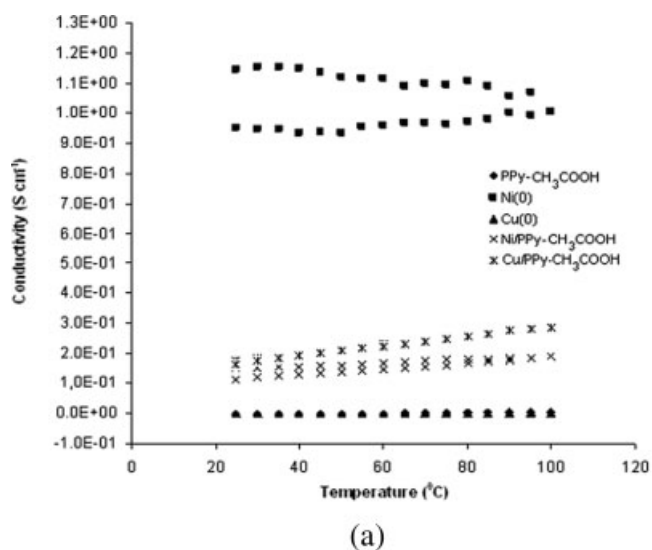


Figure 6 Temperature-dependent conductivity plots of metals, homopolymers, composites doped with two different organic acids (a) CH₃COOH media, (b) H₃BO₃ media.

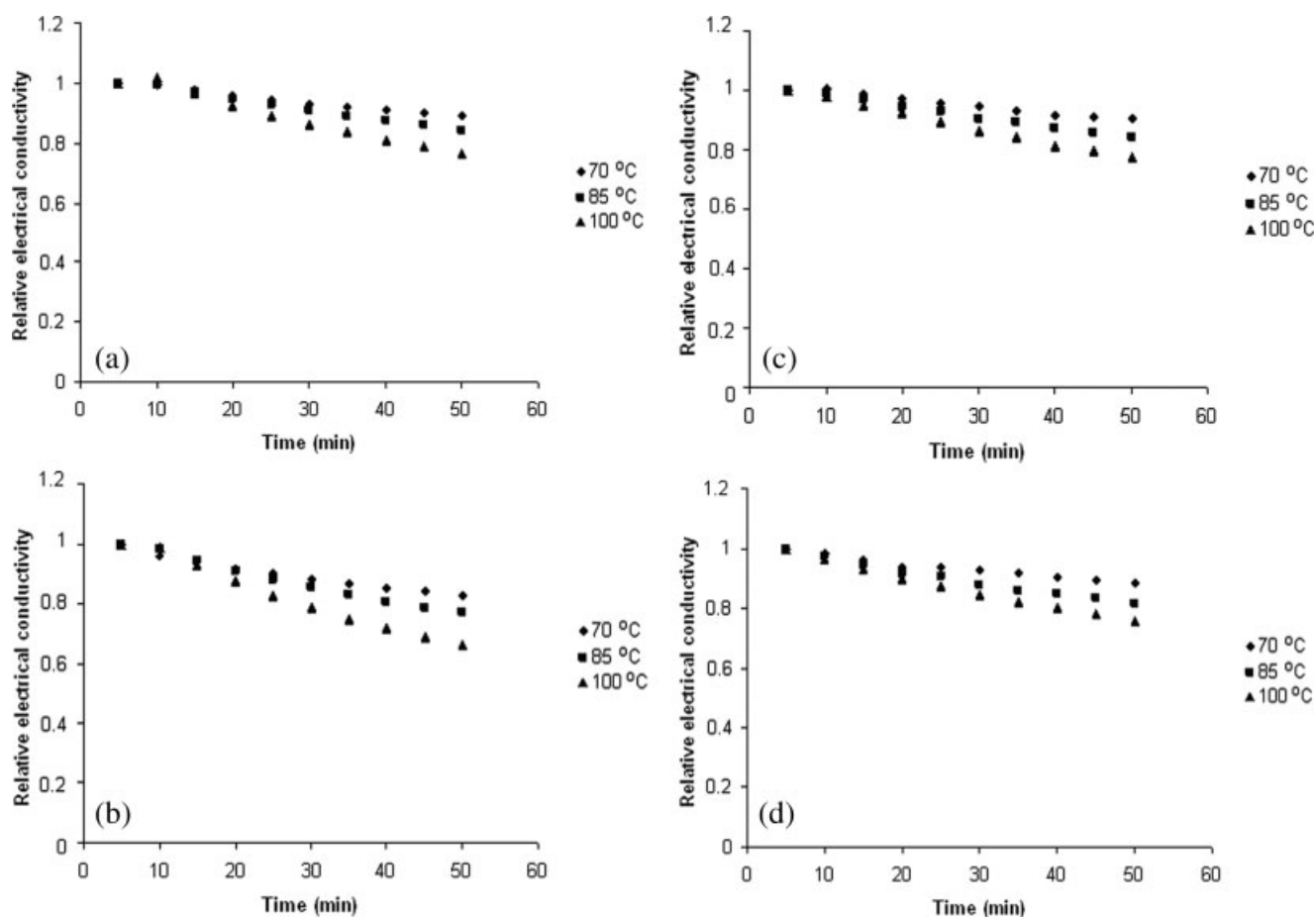


Figure 7 Isothermal stability of (a) Cu/PPy-CH₃COOH, (b) Ni/PPy-CH₃COOH, (c) Cu/PPy-H₃BO₃, and (d) Ni/PPy-H₃BO₃ composites in terms of retention of σ with respect to time at 70, 85, and 100 °C.

and Ni/PPy-CH₃COOH composites, respectively. There was an increase in conductivity of about one to two orders of magnitude upon the incorporation of Cu and Ni nanoparticles in the conductive PPy. However, the highest conductivity was observed in the Ni/PPy-H₃BO₃ composite. This value is a conductivity near to Ni(0) metal; furthermore, it is higher than that of PPy-H₃BO₃. On the other hand, Cu/PPy-H₃BO₃ and Cu/PPy-CH₃COOH exhibited the higher conductivity than both that of PPy homopolymers and Cu(0) nanoparticles.

The magnetic properties of the composites have been considered by measuring the magnetic susceptibility. As seen in Table II, the mass magnetic susceptibility values of PPy-CH₃COOH, PPy-H₃BO₃, and Cu(0) are negative, whereas the other samples are positive. Negative magnetic susceptibility values reveal diamagnetism and positive values demonstrate paramagnetism.⁶⁰ These analyses indicate that the conducting mechanism of homopolymers⁶⁶ and Cu(0) is bipolaron by nature, whereas the nanocomposites and Ni(0) are polaron by nature.⁶¹ When the yield (%) of samples was compared to each other, the quite high values were obtained in all samples (Table II).

Thermal stability of conductivity

The conductivity of the metals, PPy and composites were measured *in situ* during thermal aging. The samples were placed in the temperature-controlled chamber and characterized during heating-cooling cycles [Fig. 6(a,b)]. An increase in conductivity of all samples was observed during the run of thermal aging, as shown in Figure 6(a,b). Temperature-dependent conductivity measurements show the characteristic "thermal activation behavior."⁵¹ The possible explanation for increase in conductivity is the increase of efficiency of charge transfer between the polymer chain and the dopant with increase in the temperature.⁵² However, there can be thermal curing. It affects the chain alignment of the polymer and leads to the increase of the conjugation length, which brings about the increase of conductivity. Also, there had to be molecular rearrangement on heating, which made the molecular conformation favorable for electron delocalization.⁵⁹ As seen from Figure 6(a), Cu/PPy-CH₃COOH exhibited higher conductivity than both PPy-CH₃COOH and Cu(0). This can be explained as synergic effect of pyrrole and copper. The conductivity value of Ni/PPy-CH₃COOH composite was between the conductivity

values of Ni(0) and its homopolymer [Fig 6(a)]. As seen from Figure 6(a,b), Ni(0) shows metallic behavior. Its conductivity was decreased with the increasing temperature due to confusion of electron motions. The conductivity values of Cu(0) and Cu/PPy-H₃BO₃ exhibited similar behavior that of the Cu/PPy-CH₃COOH composite with increasing temperature.

Figure 7(a–d) shows the electrical conductivity measured respect to the time of accelerated aging and the stability of electrical conductivity of nanocomposites under isothermal conditions at 70, 85, and 100°C, respectively. The temperature of the composite films was maintained, and the conductivity was measured for every 5 min in an accelerated aging experiment. For all composites, the electrical conductivities were quite stable at 70, 85, and 100°C, and this supported the fact that the electrical properties of the composites were sufficiently stable below 100°C under a thermooxidative atmosphere.⁶⁵ The electrical conductivity of Cu/PPy-CH₃COOH and Ni/PPy-CH₃COOH slightly decreased [Fig. 7(a,b)]. Cu/PPy-H₃BO₃, Ni/PPy-H₃BO₃ [Fig 7(c,d)] and Cu/PPy-CH₃COOH lost 20% of conductivity values at 100°C whereas Ni/PPy-CH₃COOH showed lower thermal stability of conductivity at the same conditions.

CONCLUSION

PPy composites were synthesized with two different transition metals (Cu, Ni) by oxidative chemical polymerization method in the presence of different acid media. The transition metals selected for this study possessed good conductivity properties. All of the samples were successfully characterized with FTIR, SEM, EDS, TGA, electrical conductivity, and magnetic susceptibility measurements. Spectroscopic, morphological, thermal, and conductivity properties of the prepared composites were affected by the type of dopant ions and metal nanoparticles used in the experiments. Ni/PPy-H₃BO₃ has the highest conductivity; however, Ni/PPy-H₃BO₃ showed the best thermal stability of conductivity. The structural thermal stability of composites changed with changing metal and dopant anions. The metal/PPy composites have higher conductivities and thermal stabilities than those of PPy homopolymers. The presence of different acids has important effect on the properties of homopolymers and nanocomposites. An interaction exists between PPy and metals, which gives rise to changes in surface properties and DC electrical conductivity of the composite, and they also improve thermal stability of the composite. The PPy composites obtained are quite stable polymers as both structural stability and thermal stability of conductivity. These stable materials could be possible to find applications in the area of conducting nanopolymers.

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