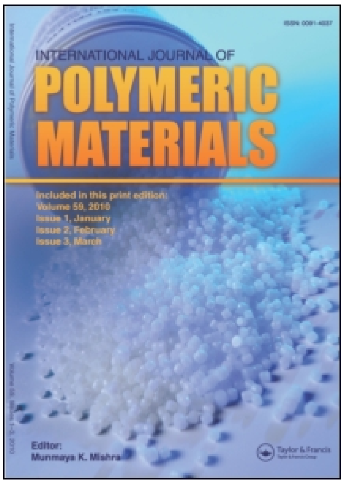

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Preparation and Characterization of Polypyrrole Silver Nanocomposites via Interfacial Polymerization

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Conducting polypyrrole silver (Ppy-AgNC) nanocomposite was synthesized by an interfacial polymerization method. Ag^+ ions from the $AgNO_3$ solution were taken in the formation of Ppy-AgNC. The incorporated silver was confirmed by X-ray diffraction (XRD). During the polymerization in a nitrate ion-containing solution, the impregnation leads to the formation of metallic silver. The size distribution of Ag into the polymer is confirmed by transmission electron microscopy (TEM), and proves the formation of a uniform species with spherical particles of Ag (mean diameter of 8-12 nm) branching at the border of Ppy. The thermal behavior of the material was studied by thermogravimetric measurements.

Keywords interfacial, nanocomposites, polypyrrole, TEM, thermogravimetric, XRD

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INTRODUCTION

Conducting polymers [1–2], which combine the advantageous properties of, mechanical strength, flexibility, stability, low cost and ease of processing, have prompted great interest as replacements for existing metals and semiconductors. The novel features associated with conducting polymers are the growing realistic applications including plastic batteries, sensors, electrochromic displays, EMI-shielding, fuel cells and biomedical devices [3–7].

Metal nanoparticles with different sizes and shapes can be combined with polypyrrole to form composite materials, which represent a new class of materials that may combine desirable physical properties characteristic of both their organic and metallic components within a single composite. The metallic portion offers the electrical properties, whereas the polymer part can provide thermal stability and mechanical properties, which eases the processing. Silver nanoparticles have applications in catalysis, conductive inks, thick film pastes and adhesives for various electronic components, in photonics and in photography [8–9]. In addition, silver nanoparticles exhibit significantly interesting conductive and optical properties [10]. Their size and shape-dependent optical properties arise from their surface plasmon resonance frequency, characteristic of noble metals with free electrons such as Au and Ag, which results in a characteristic absorption in the UV-visible spectrum [11].

Among the conjugated polymers, polypyrrole (Ppy) has attracted much attention due to its high conductivity, thermal and environmental stabilities, and relative ease of synthesis [12–14]. Nevertheless, few applications have been reported because conducting polymers based on Ppy exhibit poor physical and mechanical properties and are not soluble in common solvents. Recently, metal nanoparticles (Me-NPs), which have a large surface area and a high ratio of surface-to-bulk atoms, have attracted a lot of interest because of their possible use in many technologically relevant applications. Me-NPs have greater catalytic activities than the corresponding bulk metals. In particular, it has been reported that Me-NPs embedded in a conducting polymer matrix serve as an efficient electrocatalyst for oxidation and reduction reactions of various redox species [15].

In the synthesis of Ppy-Me composites, metal ions are often reduced in the presence of processed Ppy. In the resulting composites, metal nanoparticles are not often effectively dispersed into the polymer matrix, because metal ions and nanoparticles interact strongly with the imino groups of the polymer and are reduced at the point of contact [16]. Many chemical and physical methods have already been used to incorporate silver nanoparticles into polymer films [17]. However, homogeneous dispersion into the polymer matrix is difficult as suspensions or dispersion of Ag nanoparticles tend to aggregate [18]. Recently, we have reported on the preparation and characterization of polyaniline and polyaniline Ag nanocomposite via a similar route [19]. To the best of our knowledge this is the first time composite materials have been made in a single step without using any surfactants. Our method is significantly different from other authors.

Incorporating nanosized metal particles into polymer matrices, such as Ppy, is of current interest for many purposes. On one hand, the polymer can be a matrix for stabilizing the growth of nanoparticles and avoiding the agglomeration process. The stabilized nanoparticles then can be studied for their catalyses and optical, magnetic, mechanical and electrical properties. On the other hand, the nanoparticles can be deposited into polymer matrices to enhance some of the polymer properties, like Raman activities and conductivity, or to modify the polymer structures, and electronic, mechanical and electrical properties. Moreover, the nanoparticles can serve as fillers to modify the polymer surface morphology, or even to print nanoelectric circuits using some other templates or masks. Ag nanoparticles are of special interest due to their novel optical properties, surface-enhanced Raman scattering (SERS), and their abilities to attach bio-molecules to be used as biosensor applications. Mikalo et al. [20] used doped polypyrrole films for the evaporation of a small amount of Ag to make Ppy-AgNC. These authors [21] also showed that the conductivity of the Ppy films was not influenced by the evaporated Ag. In the same system, the authors study showed that Ag–polypyrrole is reactive because of charge transfer, which may in turn cause the formation of Ag-polymer alloy.

The novel features of metal nanoparticles and conductive polymers lead to an increasing interest in the synthesis of composite materials consisting of finely and homogenously dispersed nanoparticles in polymer matrices [22]. However, one major problem when synthesizing nanocomposite materials derived from the dispersion of nanoparticles in polymer matrices will entail the aggregation of nanoparticles [23]. Therefore, the aim of our present work is to study the interfacial polymerization of pyrrole and to prepare Ppy-Ag nanocomposite materials with variable concentrations of Ag in the polymers. Also, we have studied morphological changes and thermal stability of a prepared nanocomposites.

EXPERIMENTAL PART

Materials and Methods

All the chemicals and reagents used were of analytical grade reagents. Double-distilled water was used throughout the work. $AgNO_3$ and ammonium persulphate (APS) was procured from Qualigens; pyrrole was double-distilled before use and AR grade HNO_3 was purchased from Aldrich Chemicals.

Synthesis of Polypyrrole Silver Nanocomposites (Ppy-AgNC)

In a typical synthesis, 0.1 N mol $AgNO_3$ is dissolved in 1 N HNO_3 and is added to the organic phase which contains a known amount of pyrrole in 100 ml of $CHCl_3$, while ammonium persulphate is dissolved in 1 N HNO_3 and is slowly added to the aqueous phase and organic phase. After 5 min, blackish green Ppy-AgNC is formed slowly at the interface and then gradually diffuses into the aqueous phase. After 24 h, the entire aqueous phase was filled homogenously with blackish green Ppy. The aqueous phase was then collected, and washed with ethanol and water to remove the unreacted pyrrole. The residue thus obtained was a purified Ppy-AgNC, dried in a vacuum oven at 40°C for 36 h. This dried Ppy-AgNC sample was then used for characterization and study.

Characterization Techniques

The powder X-ray diffraction patterns were recorded on a JEOL JDX-8P diffractometer using $CuK_\propto$ radiation (1.5406 Å) at 30 kV. UV-visible spectra of the polymer solution in m-cresol were recorded by using an Elico double-beam spectrophotometer in the range of 200–1100 nm. The Fourier transform infrared (FTIR) spectra of the samples were recorded on a Perkin-Elmer FTIR (Model No. 1000) in the range 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. Thermogravimetric analyses (TGA) and differential thermal analysis (DTA) experiments were performed using NETZSCH STA 409PC. TGA and DSC data were obtained at a heating rate of 10°C/min under an argon atmosphere. Dark field transmission electron microscopy images were obtained from JOEL 100 CX operated at 190 KeV.

RESULTS AND DISCUSSION

UV-Visible Studies

The UV-visible spectra of the Ppy-Ag nanocomposites formed in the aqueous phase are shown in Figure 1(a–b). In the two spectra, two bands developed at 442 nm and 454 nm represent the π-π^* and bipolaron excitations and Me-NPs bonding, which are in agreement with the work of Dallas et al. [22–26]. The development of an absorption band at 652 nm for these two samples of Ppy-Ag composites continues to extend to the near IR region, indicating that the oligomers are in the doped state, which has been previously reported for water-soluble Ppy [22,25].

Infrared Spectroscopy

The molecular structure of the resulting Ppy-AgNC is characterized by Fourier transform infrared (FTIR) spectroscopy. Figure 2 shows the FTIR

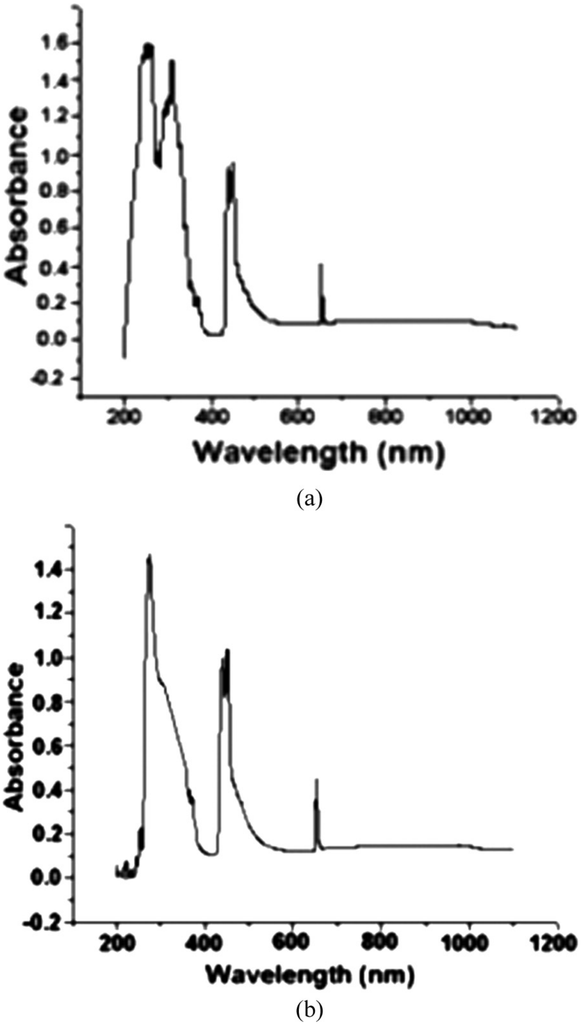


Figure 1: (a) UV-visible spectra of Ppy-Ag_1; (b) UV-visible spectra of Ppy-Ag_2.

spectra of Ppy-Ag_1 and Ppy-Ag_2. All the characteristic absorption peaks correspond to Ppy [27]. The main peak at 1557 cm^{-1} can be assigned to the pyrrole ring fundamental vibration (C=O stretching of the quinone ring). Moreover, the absorptions at 928 cm^{-1}, the characteristic peak present in all samples, is due to C–H out of plane deformation of the pyrrole unit [28–29]. The peak at 1048 cm^{-1} corresponds to the =C–H in plane vibration. A broad peak at 1199 cm^{-1} is assigned as the N–C stretching band and band observed at 791 cm^{-1} for the presence of polymerized pyrrole. The peak at 1385 cm^{-1} is attributed to the NO_3^- balancing anion [30]. Moreover it is clear that the intensity of the -NH- stretching vibration at 3240 cm^{-1} is considerably decreased due

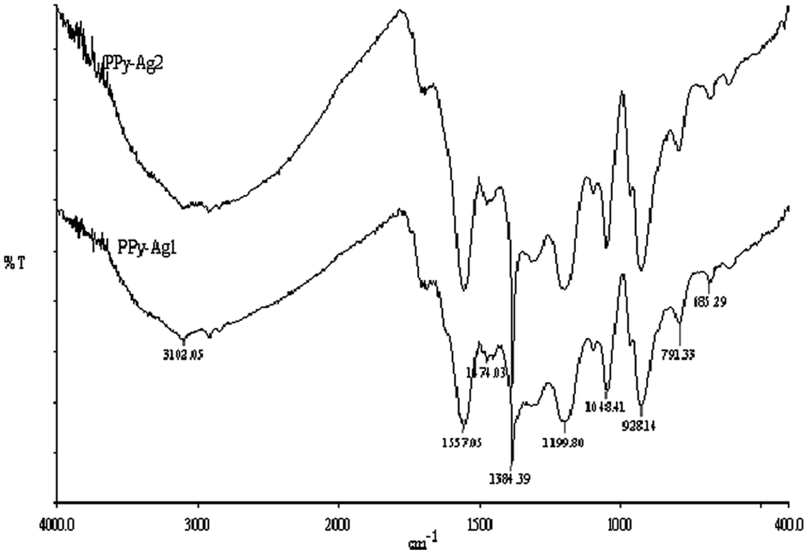


Figure 2: FTIR Spectra of Ppy-AgNC.

to the interaction of these groups with Ag particles, as the -NH- groups of the polymers are always positioned outside of the polymer backbone and facing the electrolyte side [31]. It is believed that the polymer is possibly stabilized by the lone pair of the heteroatom. Based on the study discussed, we understand that the uptake of the Ag nanoparticles is similar to palladium nanoparticle migration [32].

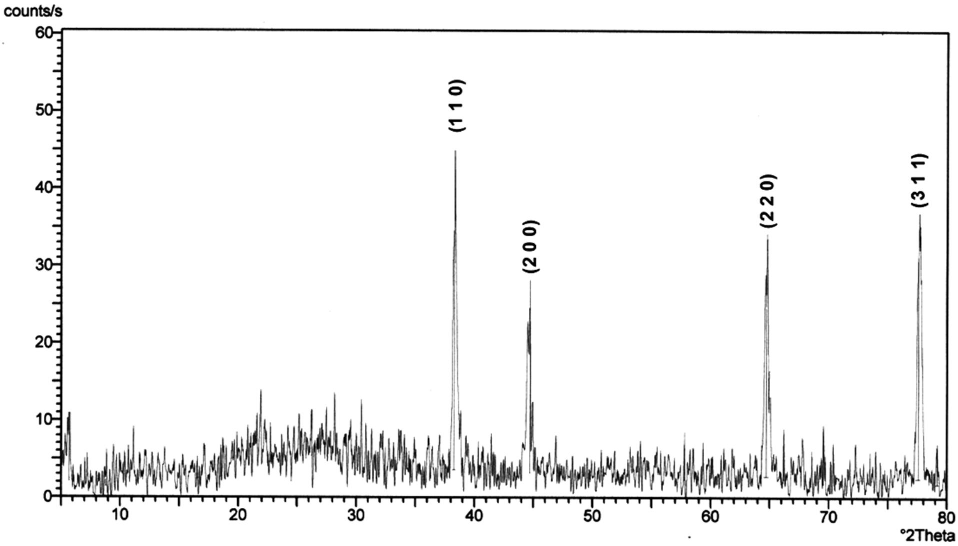
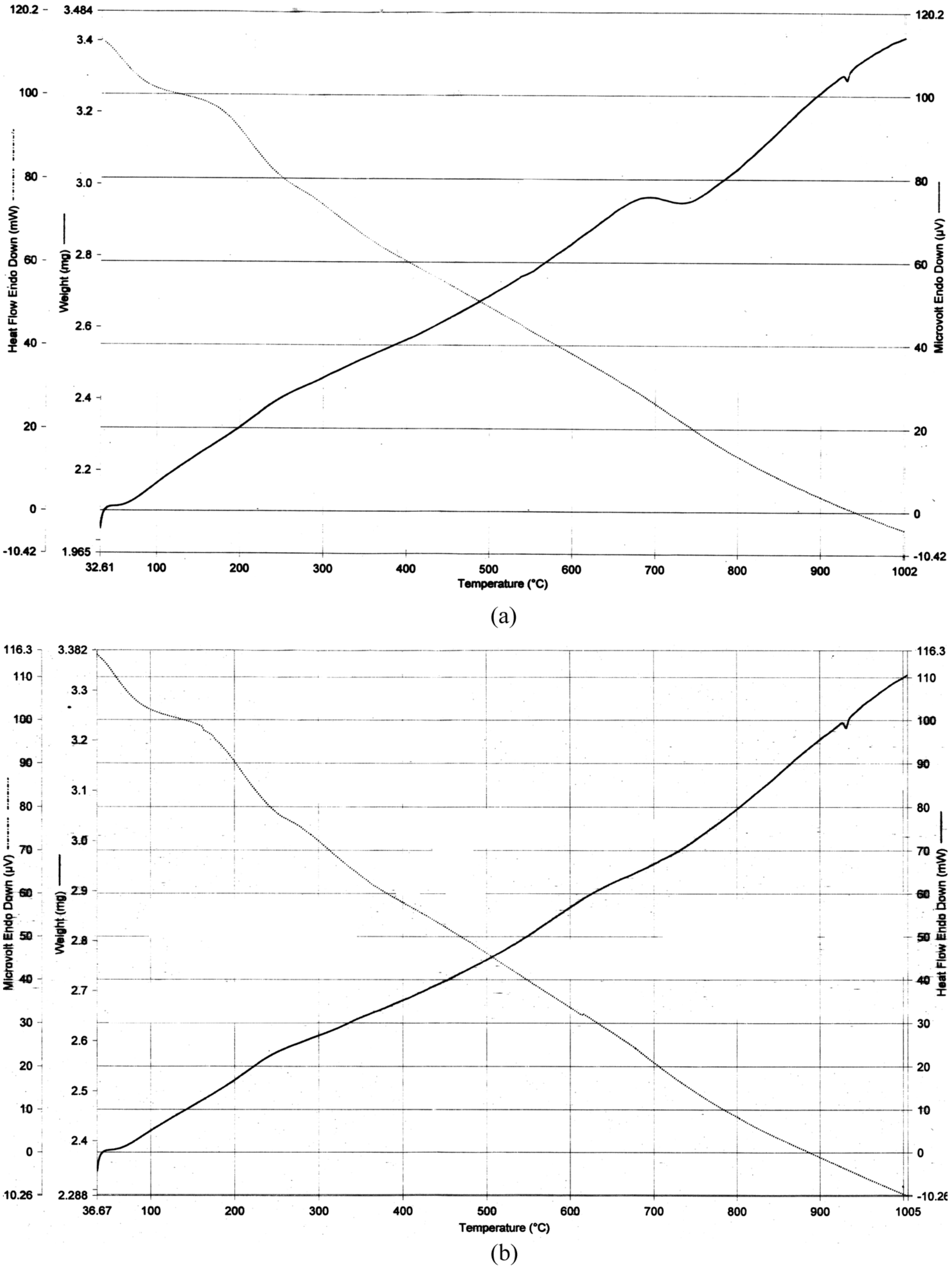


Figure 3: XRD Patten of Ppy-Ag_1.



(a)

(b)

Figure 4: (a) Thermogravimetric curves of Ppy-Ag_1 composite, showing the data in both the TG (dashed) and the DTA (lined) forms; (b) Thermogravimetric curves obtained with a Ppy-Ag_2 composite, showing the data in both the TG (dashed) and the DTA (lined) forms.

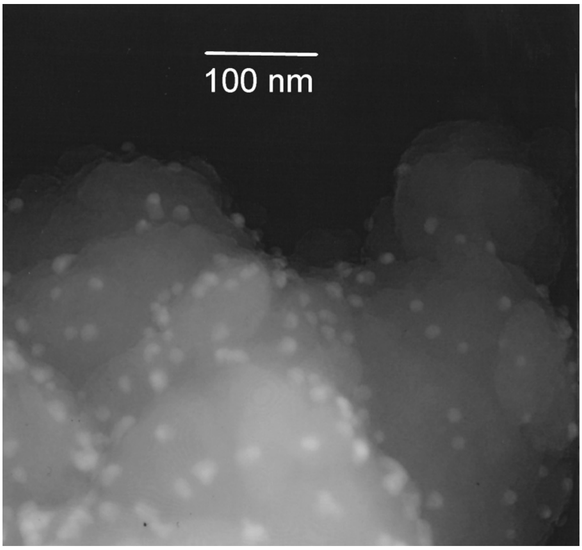


Figure 5: TEM images of Ppy-Ag_1.

X-Ray Diffraction Studies

Figure 3 shows typical X-ray diffraction patterns of Ppy-Ag nanocomposites. We can see that the Ppy-AgNC with the two molar ratio concentrations (Ppy-Ag_1 and Ppy-Ag_2) have similar peaks for Ppy-Ag_1 (in representative sample, Figure 3). The four main peaks at $2\theta = 38.5°$, $44.5°$, $64.5°$ and $77.5°$ correspond to (111), (200) (220) and (311), matching with the JCPDS pattern of silver nanoparticles (JCPDS-03-0921), indicating that the composite contains Ag nanoparticles. The value of $2\theta = 38.5°$, which is identical with the Ag (111) excitation, indicates the presence of metallic silver.

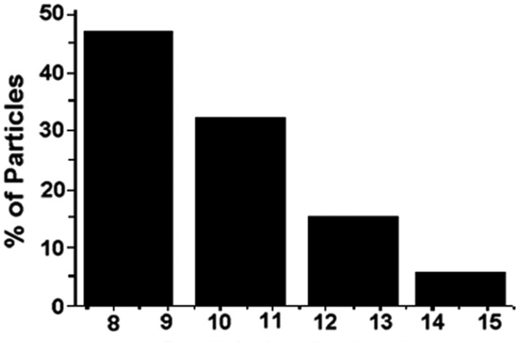


Figure 6: Particle size distribution histogram of Ppy-Ag_1 determined from TEM image.

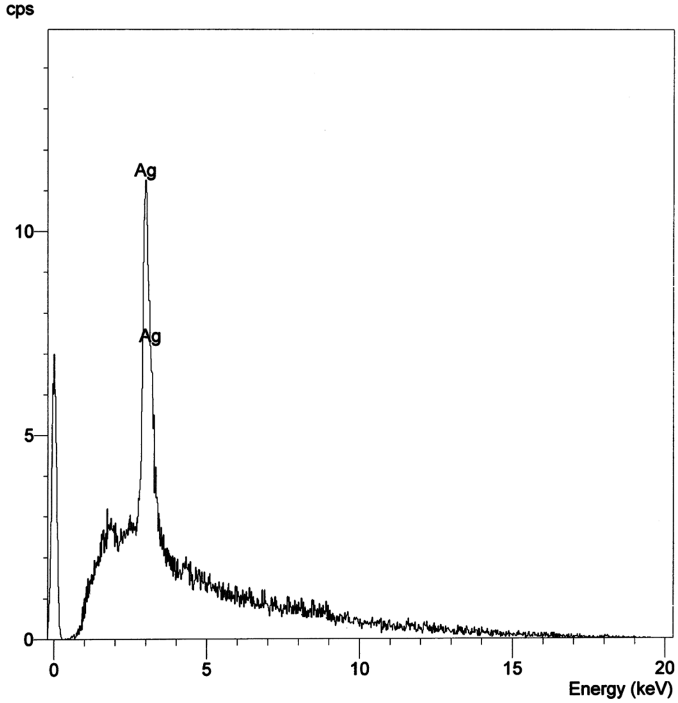


Figure 7: EDAX of Ppy-Ag_1 nanocomposite.

Thermal Behavior

The thermal behavior of Ppy-Ag_1 (Figure 4(a)) shows that the loss of low molecular weight volatiles is observed at an earlier stage (100°C) and the decomposition pattern thereafter is gradual and continuous in a single step. It is interesting to note that the char left out after decomposition was found to be 32 wt% losses. As the sample under investigation is an Ag composite, the residue would contain some Ag complex, formed on polymerization of the Ppy composite. The drastic decrease in thermal stability of this compound and the weight percentage of the residue left clearly indicates that the silver has acted as a catalyst aiding the thermal decomposition behavior [33] at the initial stages of the decomposition of the polymer, and at the later stage Ag reacts with the by-products of the polymer formed during the polymerization. This interesting phenomenon can also be observed for Ppy-Ag_2 composite, which had different decomposition behavior from the beginning (Figure 4b). Possible understanding of this phenomenon requires a detailed study involving the knowledge of heat and energy changes occurring at every step of the reaction. This study is in progress (at this stage, looking into the thermal traces it may be suggested that silver acts as a catalyst for decomposition). DTA trace in Figure 4a Ppy-Ag_1 shows one endothermic peak at around

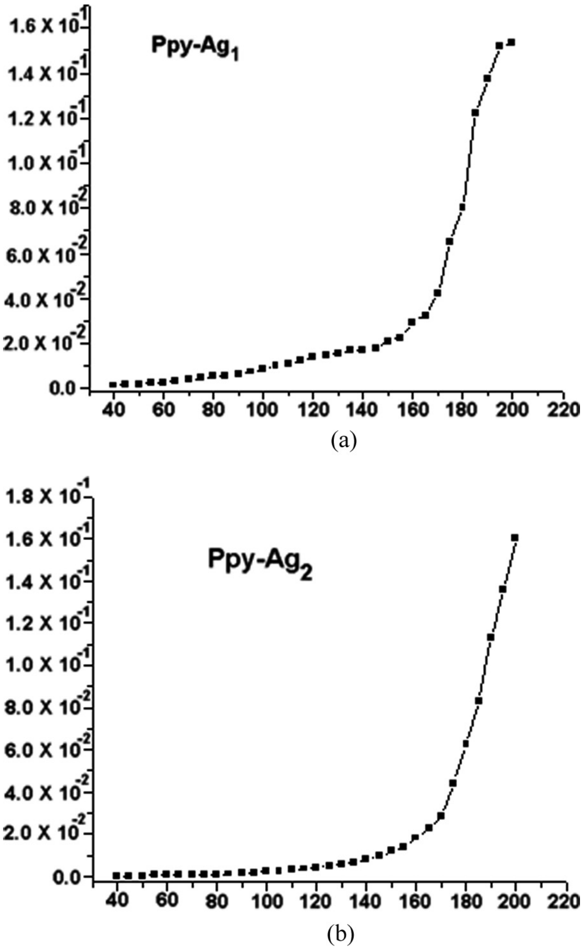


Figure 8: (a) Conductivity measurement of Ppy-Ag$_1$; (b) Conductivity measurement of Ppy-Ag$_2$.

690°C, which is assigned due to the decomposition of polymer composites. The DTA trace for Ppy-Ag$_2$ is quite complex, not indicating a proper decomposition (Figure 4b).

Transmission Electron Microscopy

Figure 5 shows the transmission electron micrographs (TEM) for the size distribution in the Ppy-Ag composite. The results show that the size of the largest particles is 8–12 nm (histogram Figure 6). The simultaneous growth of the Ppy chain along with the reduction of Ag$^+$ results first in the isolation of the nucleation centers and further to the growth of spherical nanoparticles that remain attached in the Ppy matrix. On this basis, we may state that this Ppy-Ag composite contains the inorganic component in the nanosize range, and the size distribution of the nanocomposite is rather uniform.

Energy-Dispersive X-Ray Microanalysis

The energy-dispersive X-ray microanalysis (EDAX) (Figure 7) has clearly indicated the presence of theoretical silver percentage. Figure 7 shows the EDAX of the representative Ppy-Ag nanocomposites (Ppy-Ag_1).

Electrical Conductivity

The conductivity of virgin polymer is already reported in our earlier work [19]. Figure 8(a–b) shows the conductivity of representative samples for Ppy-Ag_1 and Ppy-Ag_2 composites, which are increased by doping to the order of 10^{-3} to 10^{-1} S/cm.

CONCLUSIONS

On the basis of the results, we may state that silver containing nanocomposite polymer materials can be successfully prepared by using a rather simple interfacial polymerization method. The chemical state of the incorporating silver depends first of all on the nature of the anion, present in the polymerization solution. In this case, the composite is a metal-conducting polymer nanocomposite, as proved by the XRD spectra data evidenced in the metallic form of the silver, which could be easily interpreted by assuming a redox reaction between the polymer and the silver ions. On the basis of this experimental fact, we may come to the conclusion that silver directly interacts with nonoxidized segments within the polymer. On the basis of this experimental fact, we may come to the conclusion that silver directly interacts within the polymer, since the conductance of the polypyrrole prior to impregnation is 10^{-3} S/cm. UV-visible spectroscopy also supports the proposed formation of the Ppy-Ag nanocomposites. This has many advantages in catalysis, biosensors, energy storage systems, nanodevices and other ever-expanding technological applications. These results may be applied in the preparation and application of conducting polymer-silver composites as new electrodes (Ag, Au and Pd), where the catalytic activity of the nanosize metal component wired electrically through the conducting matrix can be utilized. This method can be used as a guide during the preparation of further metal-incorporating conducting polymer composites with tunable properties.

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