UDK 678.7:66.017
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 46(6)643(2012)

SYNTHESIS OF NANO-COMPOSITE POLY (4-4-DIAMINO DIPHENYL SULFON) WITH VARIOUS METALS

SINTEZA NANOPOLIKOMPOZITA (4-4-DIAMINO DIFENIL SULFONA) Z RAZLIČNIMI KOVINAMI

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Prejem rokopisa – received: 2012-06-07; sprejem za objavo – accepted for publication: 2012-06-27

We report on an in-situ synthetic method for the preparation of poly(4-4-diamino diphenyl sulfon) [poly(DDS)] nanoparticle-composite materials with different metals (copper, nickel and silver) that have been successfully developed and characterized. In this study, DDS with cupric sulfate, nickel sulfate and silver nitrate was used as the precursor; during the reaction DDS oxidized and formed poly(DDS), while, on the other hand, cupric sulfate, nickel sulfate and silver nitrate became reduced and formed copper, nickel and silver nanoparticles. The microstructure of the poly(DDS) metals was studied by scanning electron microscopy (SEM). IR and UV–vis spectra were used to determine the structure of the polymer. In order to investigate the size and morphology of the polymer, X-ray diffraction and scanning electron microscopy techniques were applied.

Keywords: 4-4-diamino diphenyl sulfon, metal nanoparticles, SEM, in-situ polymerization

Poročamo o uspešnem razvoju in karakterizaciji in situ sintetične metode za pripravo poli (4-4-diamino difenil sulfon) ali [poli(DDS)] kompozitnih materialov z različnimi kovinskimi (bakrenimi, nikljevimi in srebrovimi) nanodelci. V tej študiji je bil uporabljen kot prekurzor DDS z bakrovim sulfatom, nikljevim sulfatom in srebrovim nitratom; med reakcijo je bil DDS oksidiran in je tvoril poli(DDS), medtem ko so se bakrov sulfat, nikljev sulfat in srebrov nitrat reducirali in nastali so nanodelci bakra, niklja in srebra. Mikrostrukturo poli(DDS)-kovine smo preučevali z vrstično elektronsko mikroskopijo (SEM). IR in UV(vidni)-spekter sta bila uporabljena za določanje strukture polimera. Rentgenska difrakcija in vrstična elektronska mikroskopija sta bili uporabljeni za preučevanje velikosti in morfologije polimera.

Ključne besede: 4-4-diamino difenil sulfon, kovinski nanodelci, SEM, in situ polimerizacija

1 INTRODUCTION

Conjugated polymers have attracted enormous attention in both science and technology as semiconductors and electro active materials for the applications such as batteries, molecular electronic devices, light emitting diodes (LED), etc.[1,2] Electroluminescence has emerged as a promising application of liquid crystal display (LCD) devices involving semiconducting polymers.[3–5] Inorganic nanoparticles of different sizes and shapes can be combined with conducting polymers to form composite materials. The incorporation of inorganic nanoparticles in conducting polymers can provide an enhanced performance for both the "host" and the "guest" that can lead to interesting physical properties and important potential applications such as electrodes of batteries, display devices, immunodiagnostic assay, etc. To exploit the full potential of the technological application of a composite material, it is important to characterize the nature of the association between its different components. Although the incorporation of gold, copper, platinum and palladium nanoparticles in the conducting polymers has been reported by using chemical or electrochemical techniques, the synthesis of conducting polymer-metal nanoparticle composite materials having a nano fiber-like morphology has not yet been undertaken.[6–19] Many investigations regarding the development of the techniques for incorporating the nanoparticles into a polymer matrix have been published[20]. In most of the cases, such combinations require blending or mixing of the components, and usually involve the polymer in a solution or in a melt form.[20] There have been several attempts to achieve nanoparticle polymer composites. Overall, we note four different approaches used to date. The first technique consists of an in-situ preparation of the nanoparticles in a polymer matrix. This is affected by the reduction of the metal salts dissolved in the polymer matrix.[21–23] The second technique involves polymerizing the matrix around the nanoparticles.[24] The blending of the pre-formed nanoparticles into a pre-synthesized polymer can be considered as the third technique for the preparation of a nanoparticle polymer composite material.[25] The fourth process involves an in-situ synthesis of a composite material, with the metal nanoparticles being formed from an ionic precursor and the polymer being produced from the monomer. The major advantage of this method lies in the provision of a better particle-polymer interaction.[12]

Reports have been published on the synthesis of the Cu–polyaniline composite material by using a sonochemical synthetic route in which copper (II) acetate and aniline were irradiated with a high-intensity ultrasonic horn under 1.5 bar of argon at 10 °C for 3 h.[12] A copper–polyaniline composite has also been prepared by reducing copper nitrate with sodium borohydride and then mixing the resultant sol with aniline and ammonium per sulfate.[13] Substituted polyaniline, i.e., poly(o-toluidine) and copper nanoparticles have also been produced on preformed poly(o-toluidine) by exploiting the various oxidation states of the polymer.[14]

In this study, the composites of poly(DDS) doped with copper, nickel and silver were prepared separately by an in-situ chemical synthetic route. The distinguishing feature of this route is a simultaneous formation of nano-sized copper, nickel and silver with poly (DDS) in a single redox reaction.

2 EXPERIMENTAL SECTION

2.1 Materials

Unless otherwise indicated, all the chemicals used were of an analytical grade and were used as received. The DDS and methanol were purchased from Merck, while cupric sulfate, nickel sulfate and silver nitrate came from Alderich. The stock solutions of cupric sulfate, nickel sulfate and silver nitrate (10^{-1}, 10^{-1}, 2×10^{-1}) mol dm^{-3} were prepared in distilled water.

2.2 Synthesis of the composite material

In a typical reaction, 0.8 g of DDS was dissolved in 25 mL of magnetically stirred methanol in a 50-mL conical flask. After complete dissolution, 100-mL dilute cupric-sulfate solution (10^{-1} mol dm^{-3}) was added dropwise. During this addition, a green-colored turbidity developed. After the addition of the entire cupric sulfate, the precipitated material collected at the bottom of the flask. This showed for the two solutions of nickel sulfate and silver nitrate that white and milky colored colloidal solutions could be observed.

2.3 Instrumentation and methods

Scanning electron microscopy (SEM) images were taken using a VEGA HV (high potential) 1500 V at various magnifications. An ultra-thin windowed energy-dispersive X-ray spectrometer (EDS) attached to the SEM was used to determine the chemical composition of the samples. The remaining solution was filtered and a small portion of the remaining solid mass was dissolved in methanol and used for an UV-vis spectrophotometry analysis. The UV–visible absorption spectrum was obtained ex-situ at room temperature in the wavelength range of 300–1100 nm using a microprocessor-controlled double-beam UV-visible spectrophotometer (Hitachi, Model U2000). The next portion of the solid was dried under vacuum and used for an IR spectral analysis. The FTIR transmission spectrum of polypyrrole coating was recorded in a horizontally attenuated total reflectance mode in the spectral range 3500–550 cm^{-1} using a Bruker spectrometer, Vector Series 22, Germany.

X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-3A X-ray diffractometer using Cu-Ka radiation (k = 0.154 nm) operating at 50 kV. The experiments were performed in the angular range 2θ = 10–50°.

The electrical conductivities of the blends were measured by using a Keithley 6517A electrometer, a multimeter Minipa ET2907 and a homemade four-probe device with a medium distance between the probes of (0.171 ± 0.03) cm. The measurements were performed on a disk film with a thickness of 0.5 mm.

3 RESULTS AND DISCUSSION

The SEM studies, **Figure 1**, reveal the morphology of the composite material. The image shows a thin layer having a thickness in the range of 70–90 nm.

Figure 2 shows EDS spectra derived from placing the electron beam directly on a nanoparticle in the polymer. This and the other analyses confirmed that

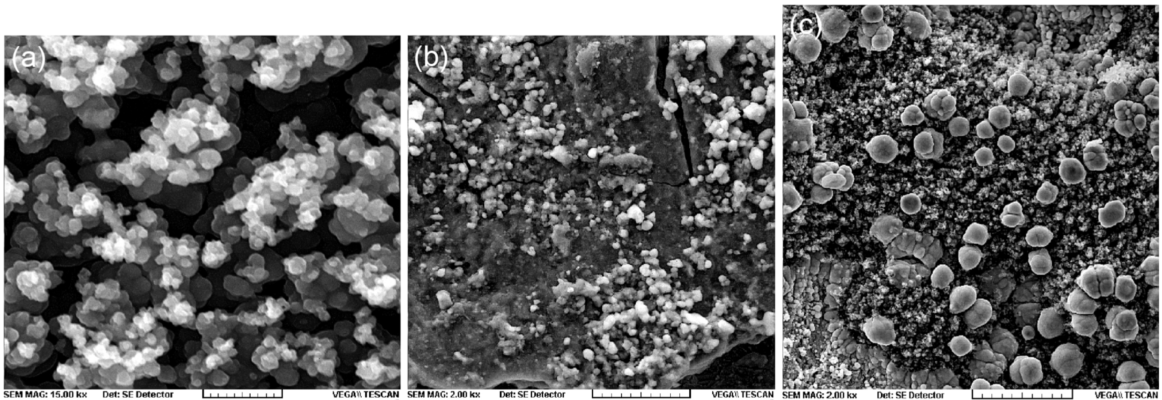

Figure 1: SEM image of the: a) poly(DDS)-Cu, b) poly(DDS)-Ni, c) poly(DDS)-Ag composite materials
Slika 1: SEM-posnetek: a) poli(DDS)-Cu, b) poli(DDS)-Ni, c) poli(DDS)-Ag kompozita

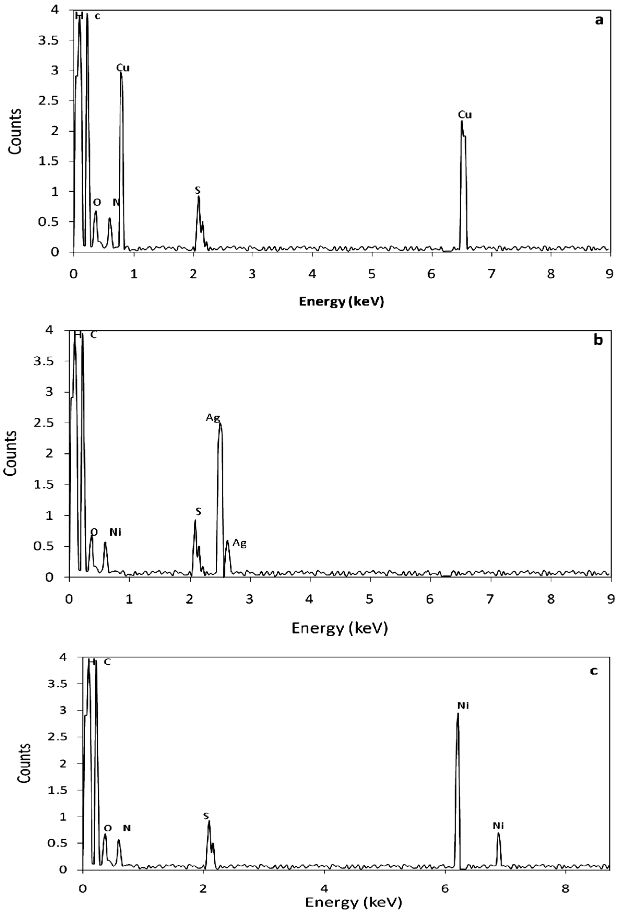

Figure 2: Typical EDS analysis of a nanoparticle: a) poly(DDS)-Cu, b) poly(DDS)-Ag, c) poly(DDS)-Ni composite materials

Slika 2: Značilna EDS-analiza nanodelcev: a) poli(DDS)-Cu, b) poli(DDS)-Ag, c) poli(DDS)-Ni kompozitnega materiala

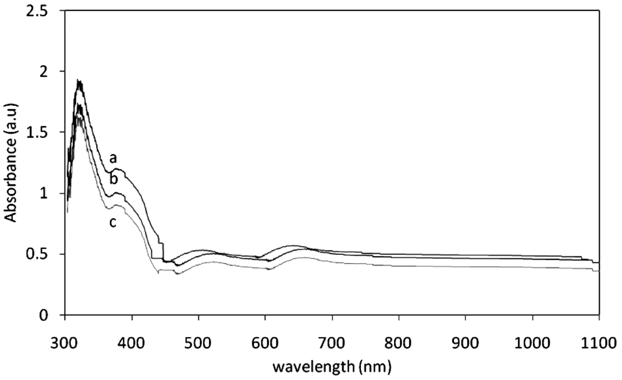

Figure 3: UV-vis spectrum of the metal-polymer composite material: a) polymer-Cu, b) polymer-Ni, c) polymer-Ag

Slika 3: UV(vidni)-spekter kovina-polimer kompozitnega materiala: a) polimer-Cu, b) polimer-Ni, c) polimer-Ag

copper, nickel and silver were only found to be associated with the nanoparticles.

The UV–vis spectrum, **Figure 3**, of the composite material shows three characteristic absorption bands at (320, 400 and 500) nm along with a shoulder at 600 nm. The absorption peak at 320 nm occurred due to the π–π* transition of the benzenoid rings. The peak at 420 nm results from the polaron/bipolaron transition. A broad band with intense overlapping features was found between 450 nm and 700 nm. Strong absorption peaks at 500 nm and 600 nm were observed when a very slow scanning condition was applied. The band at 600–650 nm corresponds to the transition from a localized benzenoid, highest occupied molecular orbital, to a quinoid, lowest unoccupied molecular orbital,[26] i.e., a benzenoid-to-quinoid excitonic transition.[27] The blue shift can be attributed to the lowering of the extent of conjugation caused by the steric repulsion between –CH3 and the adjacent phenyl ring hydrogen.[28] In the present work, the UV-vis spectra revealed an intermediate absorption peak at ≈500 nm along with a shoulder at 600 nm. This can be explained, respectively, in terms of the benzenoid-to-quinoid excitonic transition and the influence of –CH3 groups in the poly DDS backbone, while the presence of a shoulder at ≈600 nm can be explained as the plasma oscillation of the copper surface.[29]

The IR spectrum, **Figure 4a**, reveals the presence of different species, which are involved in the fabrication of the composite polymer. The bands at (3470, 3350 and 3215) cm^{-1} correspond to the N-H stretching vibration, whereas the bands at (3050, 2970 and 2850) cm^{-1} result from the aromatic C-H stretching vibration. The peak at 1600 cm^{-1} is due to the stretching deformation of the quinone ring. The 1280 cm^{-1} band is assigned to the C-N stretching in a secondary aromatic amine, whereas the peaks at 1080 cm^{-1} and 1150 cm^{-1} represent the aromatic C-H in-plane bending modes. The out-of-plane deformation of C-H in the 1.4-disubstituted benzene ring is located at 835 cm^{-1}.

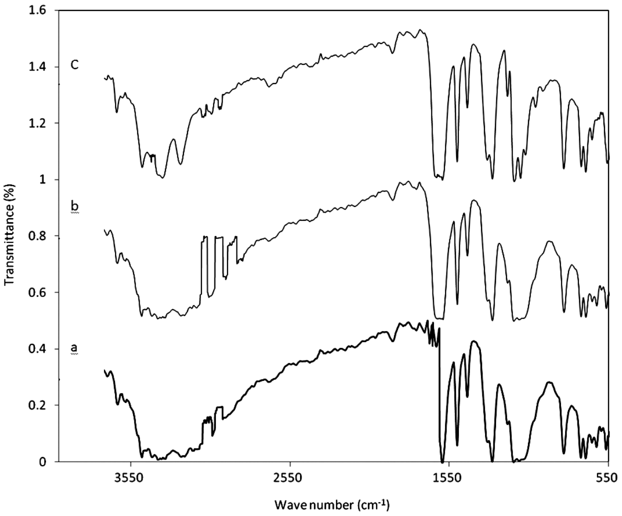

Figure 4: IR spectrum of the composite material: a) polymer-Ag, b) polymer-Cu, c) polymer-Ni

Slika 4: IR-spekter kompozitnega materiala: a) polimer-Ag, b) polimer-Cu, c) polimer-Ni

In the IR spectrum, **Figure 4b**, the bands at the higher wavenumber region correspond to the N–H stretching (3470–3220 cm^{-1}) and the aromatic C–H stretching vibration (3080–2960 cm^{-1}). The group N=Q=N, where Q represents a quinone ring, absorbs the IR radiation at 1600 cm^{-1} and N–B–N (B represents a benzenoid ring) absorbs it at 1510 cm^{-1}. The band at 1290 cm^{-1} is assigned to the C–N stretching of the secondary aromatic amine whereas the band at 1270 cm^{-1} is related to the protonated C–N group. The absorption bands at 1 130 cm^{-1} and 1070 cm^{-1} are due to the aromatic C–H in-plane bending modes. The out-of-plane deformations of C–H in the 1.4-substituted benzene ring result in the band at 825 cm^{-1}.

The IR spectrum, **Figure 4c**, of the precipitate showed two main peaks at 1505 and 1600 cm^{-1} corresponding to the stretching deformation mode of N–B–N (B represents the benzenoid ring) and N=Q=N (Q represents the quinoid ring) groups. The bands at (3475, 3360 and 3210) cm^{-1} represent the N–H stretching modes. The bands at (3120, 3030 and 2980) cm^{-1} are assigned to the aromatic C–H stretching modes. The band at 1270 cm^{-1} is assigned to the C–N stretching mode in the secondary aromatic amine. Two bands at 1100 cm^{-1} and 830 cm^{-1} correspond to an aromatic C–H in-plain bending mode.

The crystalline regions in the metal–polymer composite are shown by the presence of relatively sharp peaks. The amorphous regions are visible by the broad low-intensity peaks. The X-ray diffraction profile, **Figure 5**, of the metal–polymer composite indicates a substantial degree of crystallinity in the doped forms. The base form of the metal–polymer composite with various metals exhibited different types of crystallinity. The use of the Scherrer equation is the primary technique to determine the size or thickness of the polymer crystallites.[30,31]

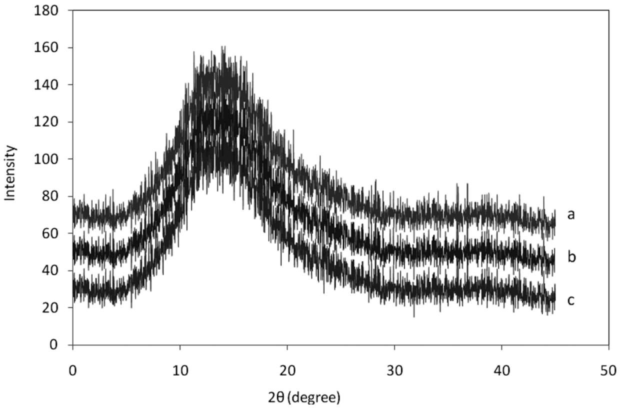

Figure 5: X-ray diffraction patterns of: a) polymer-Cu, b) polymer-Ni and c) polymer-Ag

Slika 5: Uklon rentgenskih žarkov na vzorcih: a) polimer-Cu, b) polimer-Ni, c) polimer-Ag

The crystallite size of the copolymer was determined by employing the XRD results and Scherrer formula (formula 1):

$$\text{Crystall Size} = \frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

where K is the shape factor of the average crystallite (the expected shape factor is 0.9), λ the wavelength (usually 0.154 nm), θ the peak position and β is the full width at half maximum. By employing the above method, the crystallite sizes of the metal-polymer composites were determined as (90, 80 and 70) nm confirming the presence of nano-structured metal–polymer composites with nickel, copper and silver, respectively (**Table 1**). This is the first report on the crystallite sizes of the composites of metals and 4-4-diamino diphenyl sulphone (DDS).

Table 1: XRD data of the samples prepared with different metals

Tabela 1: Rentgenski podatki za vzorce, pripravljene z različnimi kovinami

Sample	β/°	2θ/°	crystal size /nm
Ni-polymer	0.85	18	90
Cu-polymer	0.97	19	80
Ag-polymer	1.14	17	70

Table 2: Electrical conductivity of the polymer-metal composites

Tabela 2: Električna prevodnost kompozitov polimer-kovina

Sample	Conductivity/(S cm^{-1})
Cu-polymer	1.0×10^{-1}
Ni-polymer	2×10^{-3}
Ag-polymer	0.6×10^{-1}

Electrical properties of a modified metal–polymer composite are of primary interest. When the poly(DDS) base was treated with different metals, the conductivity increased to 1.0×10^{-1} S cm^{-1} with copper, but it is shown to be 2×10^{-3} S cm^{-1} and 0.6×10^{-1} S cm^{-1} for nickel and silver, respectively (**Table 2**).

4 CONCLUSION

Our results demonstrate a single-step synthetic route for the preparation of a metal–polymer composite material, where cupric sulfate, nickel sulfate and silver nitrate with 4-4-diamino diphenyl sulfon were utilized as the precursors. The surface morphology and grain size (70–90 nm) were established with the SEM experiments. The XRD studies confirmed the formation of the nano-sized copolymers. The copolymer formation and characteristics of the functional groups were confirmed through the FTIR spectrum. The conductivity of the poly (4-4-diamino diphenyl sulfon)-Ag composite material was found to be 0.6×10^{-1} S cm^{-1} by using the 4-point probe technique. The studies regarding the potential applications of this material and the larger-scale production of such composite materials are currently underway.

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