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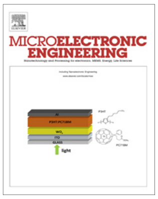

Preparation and characterization of graphite composites of polyaniline

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ABSTRACT

In this work, synthesis and characterization of composite materials based on graphite (GH) and boric acid doped polyaniline (PANI) was studied. PANI + GH composites were prepared via a simple in situ polymerization of aniline in graphite dispersion. The resulting composites of the PANI + GH were characterized by using spectroscopic, morphologic and physical methods. Ac conductivity and electronic properties of PANI doped 2%, 5% and 10% GHs have been investigated by impedance spectroscopy within the frequency interval of 10 kHz–15 MHz. The frequency dependence of ac conductivity (σ_{AC}) of PANI and PANI + GH composites have been investigated by means of frequency exponent "*s*" parameter in the low and high frequency regions.

1. Introduction

Due to a great variety of applications in many fields, such as sensors, electrochromism, electroluminescence and energy storage systems, conducting polymers have become the subjects of increased research interest [1,2]. Electrically conducting conjugated polymers such as polyparaphenylene, polythiophene (PTh), polyaniline, polypyrrole, and polyacetylene have received considerable attention from researchers because of their curious electronic, magnetic, and optical properties [3–5]. Polyaniline (PANI) was one of most studied because of its easy and economic preparation, good environmental stability, and its conductivity that occurs upon doping [6,7]. However, pure PANI is a non-conducting polymer, in addition, for most doped PANI, the conductivity is typically less than 100 S/cm, and usage of PANI in electronic devices is not yet realistic because charge carriers mobilities are too low to be useful [8]. Conducting polymer composites has attracted much attention mainly because of their numerous applications that can be used as antistatic material, electromagnetic shielding material, conductive film, conductive coatings, and phase-transfer catalysis material [9–11]. Graphite is pure carbon in a crystal form much like that of mica-sheets of strongly linked atoms, with very weak bonds between the sheets. Graphite, which is naturally abundant and low cost, has been widely used as electronically conducting filler in preparing conducting polymer composites [12]. In the literature, developing conducting polymer nanocomposites with inorganic materials such as clay, mesoporous materials, MWNTs and inorganic particles are a novel way to construct organic–inorganic hybrid systems and provide new synergistic properties that cannot be attained from individual materials, including easier control of the conductivity and improvement of the mechanical or thermal stability [13].

In this study, PANI/polyaniline and polyaniline + graphite/PANI + GH composites were prepared by using oxidative polymerization of aniline and GH in the presence of different weight percentage of 2%, 5% and 10%. Composites of GH and PANI are prepared and characterized by using electrical properties. Also, obtained PANI and PANI + GH composites were investigated by Fourier Transform Infrared (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM), and conductivity measurements with Impedance Spectroscopy (IS).

2. Experimental part

2.1. Materials

Aniline (99%, Aldrich), ammonium persulfate (Fluka), graphite (Aldrich), boric acid (Fluka).

2.2. Preparations and characterization of polyaniline + graphite composites

Synthesis of boric acid doped PANI was performed according to the literature [14]. A nanocomposite of colloidal graphene oxide (CGO) and PANI was fabricated by Hummers method and physical

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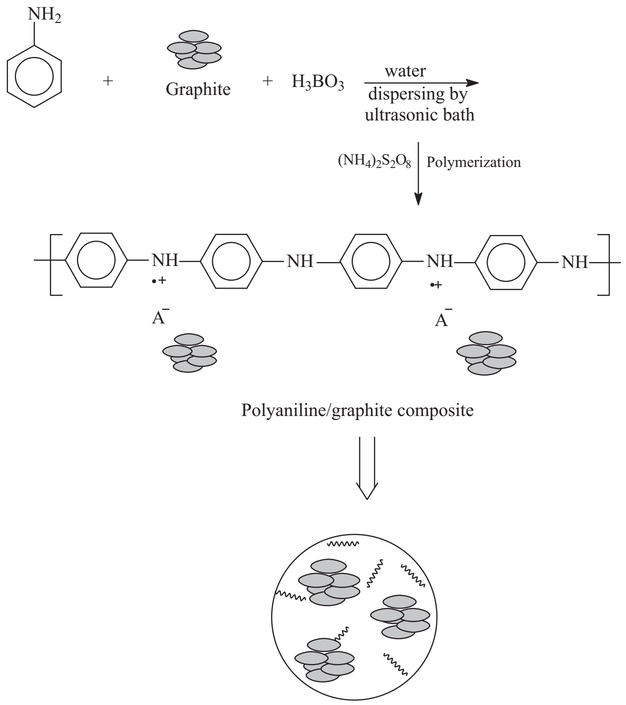

Scheme 1. Preparation of the polyaniline/graphite composite.

properties were characterized by X-ray diffraction (XRD) in the literature [15]. In this study, GH and PANI were prepared by using oxidative polymerization of aniline in the presence of different weight percentage of GH (2%, 5% and 10%) are shown in Scheme 1. Different weight percentage of GH (2%, 5% and 10%) in 20 mL of water were placed into ultrasonic bath at room temperature and sonicated for 5 h. Then 1 g of aniline and 1 M of boric acid were dissolved in 50 mL of water. This mixture was added into GH mixture. This solution was placed in an ice-bath and a 30 mL aqueous solution containing 2.42 g of ammonium persulfate was added drop wise (15–20 min interval) at 0 °C. The reaction mixture was kept for 24 h at room temperature. The reaction mixture was filtered, washed with excess of water, and finally with ethanol. The sample was dried at room temperature under vacuum until constant weight was reached.

The PANI doped GHs samples were characterized with impedance spectroscopy to determine their electrical parameters. FT-IR measurements were recorded in the range of 400–4000 cm^{-1} (KBr pellets) using a Perkin Elmer FT-IR Spectrometer. FEI Quanta 250 FEG scanning electron microscopy (FE-SEM) was used to observe the morphology of the PANI doped GHs composites. A HP 4194A Impedance Analyzer was employed for the IS measurements. The root mean square (RMS) amplitude of the signal was set to ~500 mV and the impedance parameters were measured at frequencies between 10 kHz and 15 MHz. Alternative current (AC) electric properties were analyzed from the impedance and dielectric values.

3. Results and discussion

PANI + GH composites were prepared by using oxidative polymerization of aniline in the presence of different weight percentage of GH (2%, 5% and 10%). Spectroscopic characterizations of the composites of the PANI + GH were investigated of the GH 10% by FT-IR (Fig. 1).

Spectroscopic characterizations of the composites were performed by FT-IR. The main characteristic bands of doped PANI are assigned as follows: the bands at 1580 and 1495 cm^{-1} are attributable to C=N and C=C stretching mode for the quinoid and benzenoid rings. The band at about 1141 cm^{-1} is assigned to a plane bending vibration of C—H (mode of N=Q=N, Q=N + H–B and B–N + H–B), which is formed during protonation.

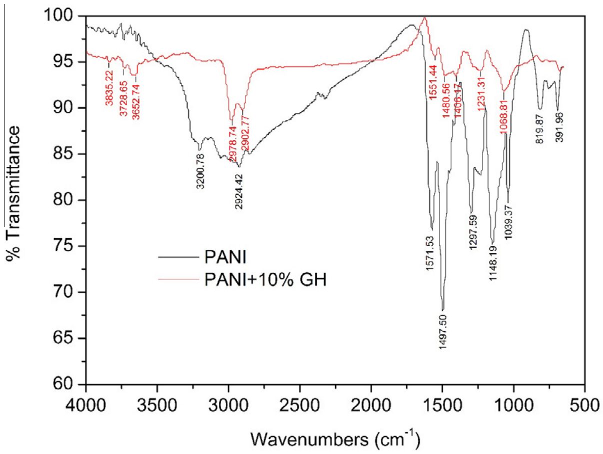

Fig. 1. FT-IR spectra of boric acid doped PANI and PANI + 10% GH composite.

Curve in Fig. 1 indicates that the main characteristic bands of doped PANI and GH all appear in FT-IR spectra of polyaniline/graphite composite. However, the incorporation of graphite particles leads to the shift of some bands of PANI. The bands at 1551 and 1231 cm^{-1}, corresponding to the stretching mode of C=N and C–N, all shifted to lower wavenumbers.

The SEM images of the PANI (Fig. 2a), the graphite (Fig. 2b) and synthesized PANI + GH are shown in (Fig. 2c and d). The particle size of PANI is about ~200 nm. The composites show a uniform distribution of small particles in graphite and PANI matrix (Fig. 2c and d); the graphite dispersed in PANI matrix and the PANI also embedded in the graphite are clearly observed. Furthermore, increasing quantity of the graphite powders are distributed quite uniformly within the PANI matrix.

Also, Fig. 2(c and d) demonstrates a well coating of the graphite and particle size of composites larger than pure PANI.

Impedance properties were used to measure the response of the PANI + GH to the root mean square (rms) amplitude of the device response over the range of frequencies. The complex impedance describes for the sample, $Z^*(\omega) = Z' + jz'' = R + jX$. where ω is the angular frequency, $Z^*(\omega)$ is the complex impedance, $Z'(\omega)$ is the real part, $Z''(\omega)$ is the imaginary part of the impedance the response to an alternating signal.

Fig. 3 shows the frequency evolution of the real part of the impedance $Z'(\omega)$ in log–log graph for PANI and different weight percentage of PANI doped 2%, 5% and 10% GH in the frequency range of 10 kHz–15 MHz. The real part of the impedance/$Z'(\omega)$ for PANI loaded GHs have nearly linear decrease with the frequency. The real part of the impedance values decrease within the all frequency range and different weight percentage of PANI doped 2%, 5% and 10% GH. At the low frequency region, the largest value of the real part of the impedance has been recorded for 10% GH + PANI while its smallest value has been observed for 2% GH + PANI.

The frequency evolution of the imaginary part of the impedance/$Z''(\omega)$ values for PANI with different GH concentrations has been showed in Fig. 4(a–c). The $Z''(\omega)$ for PANI doped 2%, 5% and 10% GH have linear decrease with the increasing frequency. The critical frequencies for PANI doped 2%, 5% and 10% GH have been determined 9043852.8 Hz (in Fig. 4a), 552280.92 Hz (in Fig. 4b), and 309,130 Hz (in Fig. 4c) Hz, respectively. The critical frequency