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Chemically reduced versus photo-reduced clay-Ag-polypyrrole ternary nanocomposites: Comparing thermal, optical, electrical and electromagnetic shielding properties

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ABSTRACT

Polypyrrole (PPy) is a well-known polymeric material, which is widely used for producing electroconductive substrates. Despite its good electrical performances, it has been shown that PPy composites exhibit better conductivity and electromagnetic shielding properties than pure PPy. Based on these advantages, we aimed to synthesize clay-Ag-polypyrrole nanocomposites using two different methods of chemical deposition and photo-reduction. We evaluated the chemical, physical, morphological, thermal, electrical and electromagnetic interference shielding properties of nanocomposites using spectroscopic and microscopic methods. Spectroscopic results showed chemical interactions among clay, Ag and polypyrrole due to coordination within the nanocomposite structure. Our results demonstrated that the photo-reduced clay-Ag-polypyrrole nanocomposite has higher thermal stability, better electrical conductivity and electromagnetic shielding effectiveness among all samples tested.

1. Introduction

Polypyrrole (PPy) is an electrically conductive organic polymer with multifunctional applications in biosensors [1], gas sensors [2], wires [3], microactuators [4], coatings [5], solid electrolytic capacitors [6], electrochromic displays, packaging, polymeric batteries, electronic devices and functional membranes, etc. [7].

Major research projects have been conducted in the past years for improving the thermal properties and electrical conductivity of PPy through mixing with nanoclay or silver in order to synthesizing a binary nanocomposite. Some research groups produced PPy–montmorillonite nanocomposites by emulsion polymerization using dodecylbenzenesulfonic acid (DBSA) as emulsifier and dopant. They observed that the added clay is capable of improving the thermal stability and sensory properties of PPy against methanol, ethanol, hexane and benzene vapors [8–11]. It has been shown that PPy-clay nanocomposite can be obtained via a solvent casting method using 2-ethylhexyl sulfosuccinate as dopant [12]. Letaïef studied the influences of iron in clay layers on the conductivity of PPy-clay nanocomposites. They found that iron induces a mixed ionic–electronic conductivity in PPy/clay nanocomposites, whereas electronic conductivity predominates in PPy-organoclay nanocomposites [13]. Montmorillonite can also be mixed with 15% mass loading of PPy by *in-situ* polymerization using DBSA as dopant and $FeCl_3$ as oxidant. Organo-modified montmorillonite showed a much higher electrical conductivity than non-modified montmorillonite after blending with PPy due to the hydrophobic properties of long alkyl chains [9,14]. Shakoor et al. [15,16] synthesized PPy-aluminum pillared montmorillonite composites by *in-situ* polymerization of pyrrole in aqueous dispersion of modified montmorillonite and $FeCl_3$. They observed a significant increase in the DC conductivity of the PPy due to the presence of aluminum pillared clay. This group also used a similar method for producing PPy/Na^+–montmorillonite nanocomposites [17]. Conductive PPy/kaolinite composites can also be made by *in situ* chemical polymerization of pyrrole in an aqueous dispersion of kaolinite using $FeCl_3$ as oxidant [18,19].

Another field of interest to polymer chemists is improving the electrical conductivity of PPy by mixing with silver nanoparticles. Pintér et al. [20] synthesized PPy-Silver nanocomposites by using $FeCl_3$ and/or $Fe(NO_3)_3$ oxidants in presence of silver salt solutions. According to their observation, pyrrole can be polymerized based on the redox-type interaction, which leads to the formation of

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metallic silver in the polymer matrix. Two research groups introduced a novel approach for producing PPy-silver nanocomposites via an interfacial polymerization in a water/chloroform interface using Ag(I) or Fe(III) as oxidizing agent. The main advantage of their method is achieving a controllable procedure with slow reaction rate, which is in contrast with the conventional aqueous phase polymerization methods [21–23]. PPy-silver nanocomposites can also be successfully produced *via in situ* chemical oxidation polymerization of pyrrole in the presence of mercapto-carboxylic acid [24], CTAB/SDS [25], poly(vinyl alcohol) [26] and polyvinylpyrrolidone [27,28].

Various morphologies of PPy-Silver nanocomposites can be obtained through different synthesizing methods, including nanofiber [21], nanospheres [29,30], nanosnakes [31], nanotubes and oval-like rods [32]. More recently, photo-induced polymerization of pyrrole with the aid of silver ions as electron acceptor/‘dopant’ and a photo-initiator is established. Ultraviolet light has been demonstrated to be an efficient and cost-effectively energy for reduction of silver ions, and provide an improvement of the reaction rate and distribution of silver nanoparticles within the PPy matrix.

According to earlier reports in the literature, many research works focused on the synthesis of PPy-nanoclay or PPy-silver nanocomposites [20–32], but only one study has reported the synthesis of a PPy-nanoclay-silver ternary nanocomposite [33]. Jlassi et al. [33] revealed that pyrrole is photopolymerizable in the presence of silver nitrate as a photo-sensitizer and nanoclay as the anchoring substrate. They also found the nanocomposite to be a strong catalytic agent for the reduction of methylene blue by $NaBH_4$. However, they did not evaluate the optical, electrical and electromagnetic shielding properties of the resultant nanocomposites.

The present study thus introduces a comparative study on synthesizing novel ternary nanocomposites of PPy-nanoclay-silver through chemical and UV reduction methods. Such an investigation has not been previously reported elsewhere. We also studied the optical, morphological, electrical and electromagnetic shielding characteristics of the materials obtained through different analytical techniques. Our inorganic/organic hybrid nanocomposite is a very promising compound with multifunctional abilities for civil and industrial applications.

2. Experimental

2.1. Materials

Bentonite nanoclay, Kunipia-F supplied by Kunimine Industries Co. Ltd. (Japan) was used for this research. Silver nitrate, pyrrole monomer and Iron(III) chloride hexahydrate were supplied by Merck (Germany). P-Toluenesulfonic acid (Sigma-Aldrich, USA) was used to synthesize the clay-Ag-PPy ternary nanocomposites.

2.2. Sample preparation

A 2 wt% suspension of clay nanoparticles was heated to 60 °C for 30 min in 100 ml of deionized water. Then 50 ml of silver nitrate solution (1 M-$AgNO_3$) was added to the suspension and it was exposed to an ultraviolet lamp (15 W-UV) for 24 h with concurrent dispersion on a magnetic stirrer. The samples were then rinsed several times with distilled water and centrifuged for 30 min to remove the unreacted silver ions (Ag^+). Finally, the solid residue was heated at 80 °C for 24 h resulting to produce a clay-Ag nanocomposite powder.

The clay-Ag nanocomposite was mixed with pyrrole to produce a clay-Ag-PPy hybrid nanocomposite by the chemical reduction method. This process was carried out by doping p-toluene sulfonic acid (PTSA) and $FeCl_3{\cdot}6H_2O$ as an oxidant agent in the clay-Ag suspension. The molar ratio of PTSA:Pyrrole: $FeCl_3{\cdot}6H_2O$ monomer was kept at 1:4:6 and the reduction proceeded for 4 h at 4 °C in a fridge. The solution was then centrifuged and rinsed with ethanol and distilled water. Finally, the precipitates were dried at 60 C for 24 h.

The clay-Ag-PPy nanocomposite was also prepared by a photo-reduction method. To do this, p-toluene sulfonic acid (PTSA) and $FeCl_3{\cdot}6H_2O$ was doped in the clay-Ag suspension. The molar ratio of PTSA: Pyrrole: clay-Ag was set at 4:1:1 and the reaction proceeded for 4 h under 15 W-UV lamps. The final product was achieved after rinsing and drying.

2.3. Characterization

The functional groups of the samples were analyzed by Fourier Transform Infrared Spectroscopy (FTIR, BOMEM, MB100) with a resolution of 8 cm^{-1} in the range 500–3800 cm^{-1}.

X-ray diffraction (XRD) patterns were monitored by using a XRD diffractometer (PHILIPS-X’PERT MPD). The instrument was equipped with Cu-Kα X-ray radiation (40 kV, 30 mA) at the rate of 0.02/s over the range of $2\theta = 10°–90°$. Phase identification was achieved by use of the XPert High Score Plus software.

The thermal analysis of the samples was also performed using a PerkinElmer thermoanalyzer (Pyris diamond SII). 4 mg of each sample was analyzed under N_2 at a heating rate of 10 °C/min from 60 °C to 520 °C.

For morphological characterization, a scanning electron microscope (SEM, MADELL, KYKY-EM3200) with an accelerating voltage of 26 kV was used to obtain the images from the samples. Transmission electron microscopy (TEM) was performed using a Ziess EM10 microscope, operating at an acceleration voltage of 100 kV. In this regard, the nanocomposite powders were ground and dispersed in ethanol at room temperature for acquiring images.

Elemental analyses of the samples were evaluated via an energy dispersive X-ray spectroscopy instrument (EDS, ISI ABT, SR-50) at 21 kV.

The reflectance spectra of the samples were investigated by using a Texflash Spectrophotometer (Data Color, Switzerland). Color coordinates of the samples were assessed in ‘include’ mode with a geometry of 0/d under the condition of 10° observer and D65 illuminant.

Electrical conductivity of the samples were compared using a four-probe method with a digital Nanovoltmeter (Keithley, 2182A) combined with the Series 2400 SourceMeter® instrument providing DC voltage measurements. The composite powders were compacted into disk pellets of 10 mm in diameter under a pressure of 6 kgN/cm^2. The conductivity values were calculated at room temperature using the following formula:

$$\rho = Rdw/l \qquad (1)$$

where ρ is surface resistivity, R is resistance, d is the sample thickness, w is width of each electrode, and l is the distance between electrodes. In the following investigation, the distance between the copper electrodes (l) was set at 6 mm and the width of each electrode (w) was 10 mm. The value of conductivity (S/cm) can be calculated by the inverse of surface resistivity (ohms/square) as in Eq. (2):

$$\sigma = 1/\rho \qquad (2)$$

where σ indicates conductivity and ρ is surface resistivity as calculated in Eq. (1).

A Network analyzer (HP 8410C), reflection & transmission test unit (HP 8743B) operating from 4600 to 7800 MHz were employed