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Solid-state synthesis and electrical properties of polyaniline/Cu-montmorillonite nanocomposite

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ABSTRACT

In this paper, the solid-state synthesis of polyaniline/Cu-montmorillonite nanocomposite is reported. Mixture of anilinium chlorure and Cu exchanged montmorillonite was grinded at room temperature while we vary the molar rate of aniline to interlayer Cu^{2+} cations (R) from 0.5 to 6. The properties of the hybrid compounds are characterized by X-ray diffraction, thermogravimetric analysis, SEM, FTIR and impedance spectroscopy. The results showed that the structure and the conductivity of PANI in hybrid materials depend on R. The ac conduction showed a regime of constant dc conductivity at low frequencies and a crossover to a frequency-dependent regime of the type A ω^s at high frequencies.

1. Introduction

In recent years, nanocomposite hybrid compounds have been the subject of considerable investigation [1–3]. The inorganic lattices provide confined spaces which can force the polymer molecules into organized arrays, thereby modifying their bulk properties. Polyaniline (PANI) has become one of the most important electroactive polymeric materials [4]. Depending on the synthesis conditions, it can be obtained in several forms and different structures. PANI has been inserted into several inorganic hosts by different methods. One approach uses hosts with sufficient oxidative power to intercalate and polymerize aniline in situ. FeOCl [5,6] and V_2O_5 xerogel [7–9] are examples of such hosts. This type of compounds is comparatively rare, because most host materials are either nonoxidizing or weakly oxidizing. Therefore, to polymerize monomers inside host materials with insufficient oxidative power, external oxidants must be used [10–12]. Another method to insert conjugated polymers in host materials is to directly modify the oxidative power of the host by incorporation of oxidants. Zeolite having oxidant ions, such as Cu(II) or Fe(III), has been used to encapsulate polyaniline in their cavities [13].

Montmorillonite clay is 2:1 layer silicates containing interlayer galleries that result in many interesting and novel chemical properties. Aromatic organic compounds such as aniline readily polymerize in the interlayer region of smectite clays that contain Cu^{2+} cations [14,15].

The route commonly used in the literature for the preparation of their nanocomposite with polyaniline consist of intercalation Cu^{2+} oxidant cations into clay through cation exchange reaction and then the monomer is dissolved in a organic solvent and intercalated in montmorillonite clays [13–15].

This technique has the following problems:

(i) It requires the step in which clay minerals are dispersed in water, swollen to form a suspension required for the liquid–liquid reaction.
(ii) It has a problem related to environmental pollution as for the treatment of waste water and industrial waste caused from the step in which the swollen is separated by decantation.
(iii) In the liquid–liquid reaction, an organic guest substance is intercalated in the interlayer spaces of host clay, after the crystalline structure of the host bentonite is broken once. Accordingly, irregular stacking is caused in the composite of organic bentonite and the product has low crystallinity.

A process of intercalation, which is not used very frequently, is the so-called solid–solid reaction. The latter is a mechanochemical adsorption that occurs between powders in the solid state [16]. A mechanochemical reaction has been mainly employed in the study of metals and alloys and seldom attempted in organic fields. However, it has obvious advantages, such as being a simple process, having high capacity and relatively low cost. Furthermore, a mechanochemical reaction is the environmentally benign one, with a small amount of solvent or without any solvent. It has been

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reported that solid-state intercalations are useful ways to introduce organic guest species into the interlayer spaces of clays [15–22]. In addition, we have reported the solid-state intercalation of 2-mercaptopyridine into Na, Al and Co-montmorillonite [23] and the solid-state polymerization of aniline into Na-montmorillonite initiated by ammonium persulfate as oxidant [24]. Therefore, this technology is effective and can be expected to be used widely for various kinds of guest ions or molecules to develop nanocomposites.

The aim of this publication is to report the synthesis and characterization of polyaniline/Cu-montmorillonite nanocomposites performed at room temperature through oxidation of aniline by interlayer Cu^{2+} cations in solid state. The structure of PANI/Cu-MMT nanocomposite obtained by this method is compared to free PANI prepared by mechanochemical route.

2. Experimental details

2.1. Reagents and materials

Clay material was obtained from the region of Zaghouan, from the East West of Tunisia. Purified clay was obtained by sedimentation, centrifugation and drying. The resulting clay fraction is a fine-particle structure with particles less than 2 μm in size with a cation exchange capacity of 90 milliequivalents 100 g^{-1}. The presence of smectite was confirmed by the d_{001} spacing of the sample after air drying, calcination at 600 °C for 2 h and glycol treatment. And by means of specific tests (test of lithium), it was found that it constitutes essentially of montmorillonite. The copper montmorillonite (Cu-MMT) was prepared by stirring 10% MMT suspension with 1.0 M $Cu(NO_3)_2$ at room temperature for 48 h. The resulting Cu-MMT was washed with distilled water and then centrifuged and dried. All materials are purchased as analytical grade chemicals, including, chlorure of aniline and $Cu(NO_3)_2$.

2.2. Synthesis of polyaniline/Cu-MMT nanocomposite

Polyaniline/Cu-MMT nanocomposite was synthesized at room temperature by the following procedures. The mixtures of the hosts (Cu-MMT) and the guest species (chlorure of anilinium: Cl-An) were grinded manually using an agate mortar and pestle at room temperature until the color of the mixture turned to dark green. The molar rate of aniline species to the interlayer Cu cations was varied from 0.5 to 6. Hereafter, the products prepared from the mixtures of Cl-An and Cu-MMT with different proportions are denoted as Cu-MMT/PANI (*R*), where *R* indicates the molar rate of Cl-An to interlayer Cu cations.

2.3. Instruments

The interlayer spaces of hybrid compounds were checked by XRD technique on a Panalytical diffractometer using Cu radiation. The IR spectra were obtained with a Nicolet spectrophotometer (model 560) with a scanning range between 400 and 4000 cm^{-1}. The samples were prepared as tablets diluted in KBr while we kept constant the sample/KBr ratio and the total weight of sample. Surface morphology analysis was made with a Philips Fei Quanta 200 Scanning Electron Microscope. The electronic structure of hybrid compounds was determined from UV–vis absorption spectra in dimethylformamide solution on a PERKIN-ELMER (model LAMBDA 20) spectrophotometer. Specific surface area and the total pore volume were measured using an automatic adsorption instrument (Autosorb I). Conductivity measurements are carried out with a Hewlett Packard 4192A impedance analyser. The samples were prepared with pellet form under the pressure of 10 tonnes/cm^2 and they are coated on two opposite sides with silver paint.

3. Results and discussions

3.1. Characterization

The grinding of Cl-An with Cu-MMT results in a gradual change of color mixture from grey (initial color of Cu-MMT) to brown and finally to dark green. For molar rates of Cl-An to interlayer Cu^{2+} cations (*R*) ranging from 1 to 6 the process takes respectively 20, 10, 8, and 6 min to obtain a dark green color. It is well known that this color is characteristic of the protonated emeraldine form of polyaniline. Thus, by observing just the color, we can estimate that for these values of *R*, aniline species have been polymerized into protonated emeraldine salt. On the other hand, for *R* corresponding to 0.5, the final color of the mixture is only pale green and it did not darken even after 40 min of fine dry grinding. Ilic and co-workers have studied the polymerization of aniline in aqueous dispersion of Cu-MMT, the authors have shown that below a critical concentration of aniline of about 2.6 mmol L^{-1} a pale green complex is formed between aniline and copper and above this concentration aniline monomers are polymerized [15].

For comparison, we have synthesised PANI by solid–solid reaction using ammonium persulfate (APS) as oxidant according to the procedure given by Huang et al. [25]. Chlorure of anilinium and $(NH_4)_2S_2O_8$ with variable molar rates were grinded in an agate mortar until the color changed to dark green. The polymerization was lasted for 24 h at room temperature. Afterward, the dark green product was washed with distilled water until a colorless wash solution without oligomers was obtained. We have found that in this case the change of color is faster than that in the interlayer of clay. The difference is certainly due to diffusion phenomena. Martin et al. have claimed that in solid–solid reaction, diffusion plays an important role. Reagents are transported through diffusion towards an interface which separates the reactants and the product [26]. The low diffusion of aniline in the case of PANI/Cu-MMT nanocomposite compared to polyaniline is essentially due to copper cations which are not free and they are localized in the clay interlayer.

In addition, we have noticed that the gradual change of color using persulfate of ammonium as oxidant is different from that with Cu-MMT. For free PANI, the color of mixture turned progressively to blue and finally to dark green. These color changes have been explained in the literature [27,28] on the basis of the formation of pernigraniline salt as intermediate, which is the protonated fully oxidized form of PANI with blue color. However, for PANI/Cu-MMT nanocomposite the appearance of intermediate brown color proves that the mechanism of polymerization is different from that using ammonium persulfate.

In fact, the mechanism of aniline polymerization is dependent on the nature of used oxidant. For persulfate ions, which are commonly used as oxidizing agent, the mechanism involves the formation of aniline radical cation, then coupling of radical cations and chain propagation. The initially formed polymer is the fully oxidized pernigraniline salt form of polyaniline. When all oxidant is consumed, the remaining aniline reduces the pernigraniline to form the final product, the green emeraldine salt. The color changes during the reaction to reflect the described steps; the blue color is due to the formation of protonated pernigraniline and in final step green emeraldine salt is formed. Polyaniline can also be prepared inside inorganic porous materials with oxidizing power such as the vanadium pentoxide xerogel [7–9]. Intercalative polymerization of aniline is controlled by redox reaction which modifies the electronic structure of host material V_2O_5 both by expanding the interlayer distance and changing the electronic configuration of V_5^+ ions. During the polymerization process V_5^+ transfers to V_4^+ which yields mixed valence behaviour of Vanadyl atoms. Toshima et al. [29] have reported the polymerization of aniline by stirring the solution of aniline and copper(II) salts in acetonitrile and water. It was proven