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Solid phase mechanochemical synthesis of polyaniline-montmorillonite nanocomposite using grinded montmorillonite as oxidant

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Polyaniline-montmorillonite nanocomposite was prepared through mechanochemical processing using grinded montmorillonite (MMT) as oxidant. The method is based on mechanochemical reaction between grinded MMT and anilinium chloride (AnCl) powder wherein grinded MMT is used both as initiator of polymerization and as reinforcement for the nanocomposite material. The proportion of anilinium to MMT has been varied. The analysis of UV visible, FTIR spectroscopy, XRD and SEM techniques proved the polymerization of anilinium cations to the emeraldine form of polyaniline. Both Fe^{3+} cations localized at MMT octahedral layers and atmospheric oxygen act as oxidant for anilinium cations polymerization. This method allows the formation of polyaniline (PANI) with branched fibrous morphology. The AC conductivity and dielectric properties of the corresponding nanocomposite were measured using impedance analyzer. Electrical and dielectric properties have been studied using spectroscopy impedance. The ac conduction shows a regime of constant dc conductivity at low frequencies and a crossover to a frequency-dependent regime of the type $A\omega^S$ at high frequencies. The Dc conductivity is in the range of 1.66 10^{-3} S/cm.

1. Introduction

During the last three decades, PANI became the one of the most extensively studied conducting polymers because of its simple synthesis, low cost, high conductivity and excellent environmental stability [1]. PANI has found a wide applicability as Dye-sensitized solar cells [2], anticorrosive coating [3], and dye-sensitized solar cell [4]. MMT is the 2:1 layered silicate, composed of superposed lamellae, which bear a diffuse negative charge due to different substitutions in the crystal lattice of lamellae. This negative charge is compensated by adsorption of cations such as Na^{+}, Ca^{2+}, Mg^{2+}. The combination of conducting polymers with MMT opens a way to nanocomposite materials showing novel properties. The most widely used methods to prepare PANI-MMT nanocomposites are based on solution intercalation polymerization techniques [5]. These methods have the following problems: i) they require a dispersion phase of MMT is in water or organic pollutant solvent and (ii) it has a problem related to environmental in the case of using organic solvent as dispersant agent for clay. The process of polymerization in the solid state seems a promising alternative. The latter is a mechanochemical reaction that occurs between powders in the solid state.

On the other hand, persulfate of ammonium has been widely used as oxidant for aniline polymerization since it is suitable for mass production of polyaniline, however this oxidant is stoichiometrically consumed during the reaction which requires large amount of product. In addition, the reaction generates large amount of acidic by-products resulting in difficult separation of PANI from the reaction mixtures. Consequently, some studies have investigated the use of other oxidants such as iron(III)chloride/ozone [6] or Fe^{3+} intercalated in MMT as interlayer cations [7,8]. The use of iron as oxidant is justified by the fact that a small amount of iron(III) is required for aniline polymerization and by-product is only water. In addition, it has been shown that branched polyaniline nanofibrous is obtained when using $FeCl_3 \cdot 6H_2O$ as oxidant without adding any other surfactant or organic acid [9]. It is thought that Fe(III) plays an important role in the formation of polyaniline nanostructures [9,10].

Iron (in the form of ferric and/or ferrous ions) occupies the octahedral sheet of MMT layer. The molar ratio of $Fe^{2+}$to Fe^{3+} is related to redox conditions of the environment at the time of the formation of the mineral. Since MMT contains structural Fe^{3+}, which is known by its high oxidative reactivity in soil [11], we had the motivation to test the possibility of formation of polyaniline-

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MMT nanocomposite using structural octahedral Fe^{3+} as oxidant without the need to use external pollutant oxidant. However, taking into account the small amount of structural Fe^{3+} in the clay, an amelioration of oxidative property of MMT is necessary. To achieve this objective, the activation of MMT by grinding was adopted since grinding enables the conversion of structured Fe^{2+} to Fe^{3+} by atmospheric oxygen [12]. In fact, the idea of using mechanochemically activated clay minerals as initiator for monomer polymerization is not novel. Kargin and Plate were the first to report that some monomers could be polymerized using mechanically activated metallic oxides and clay minerals [13]. However, this reaction is limited to some monomers, especially those known by the easiness of their polymerization such as ethylene [14] and no attempt has been made for conducting polymers.

In this study, PANI-MMT nanocomposite was synthesized by a facile and environmentally friendly method for the first time wherein grinded MMT is used both as oxidant for aniline polymerization and as reinforcement for the nanocomposite material at the same time.

2. Experimental

2.1. Materials and reagents

The crude clay mineral was obtained from the region of Zaghouan in North-eastern Tunisia. Purification and recuperation of clay mineral fraction has been carried out using standard protocol [15]. The crude sample contains quartz and calcite as major impurities. This sample has been the subject of several studies in our laboratory [8,16,17]. 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. By means of lithium test it was found that it constituted essentially of MMT. The chemical composition of the MMT, determined by Atomic Absorption Spectrometer (AAS Vario), was found to be as follows: 50.1% SiO_2, 3.95% MgO, 17.4% Al_2O_3, 0.2% K_2O, 0.08% CaO, 1.5% Na_2O, 6.3% (Fe_2O_{3+}FeO) and 20.4% as loss on ignition. The cation exchange capacity (CEC) of the montmorillonite (determined by Cu(II) ethylenediamine complex is about 100 Meq/100 g. The sample has a BET specific surface area (Quantachrome, Autosorb I) of about 80 m^2/g. AnCl was purchased from Aldrich.

2.2. The protocol of preparation of PANI-MMT nanocomposite

The protocol of preparation of PANI-MMT nanocomposite is as follow: 0.5 of MMT has been grinded using Retsch mortar grinder for 30 min then AnCl has been added and the mixture has been grinded for 120 min. Finally the grinded mixture is allowed to stand at ambient air until the change of color to dark green. The molar ratio of structural iron to AnCl (R) has been varied from 0.01 to 0.12.

2.3. Characterization techniques

The structure was examined by X-ray diffraction using a Panalytical diffractometer X-ray diffractometer using Cu radiation. The IR spectra were collected with a Nicolet spectrophotometer model 560 spectrophotometer using a scanning range from 400 to 4000 cm^{-1}. Samples were prepared as KBr pellet. The electronic structure of the nanocomposite was determined from UV–vis absorption spectrum in dimethylformamide (DFM) solution on a PERKIN ELMER(modelLAMBDA 20) spectrophotometer. The SEM images were obtained by a JSM-5400 scanning electron microscope (JEOL). A fine gold coat has been deposited on the samples under vacuum in a JFC-1100 sputter coater (JEOL). The electrical conductivity of different samples were prepared as pellet form under a pressure of 5 Mg/cm^2 and coated on both sides with silver paint using a Hewlett Packard model 4192 A impedance analyzer.

3. Results and discussion

3.1. Characterization of the nanocomposite

3.1.1. Evolution of color during ageing

As can be seen from Fig. 1, the grinding and the ageing of AnCl with mechanochemical activated MMT have for effect the change of the color from brown green to dark green. As shown in Table1, for R corresponding to 0.01, 0.04, 0.08, 0.11 and 0.12, the process

Fig. 1. Evolution of color with grinding and ageing of the grinded mixture of aniline chloride with grinded MMT (The molar ratio of (structural iron /AnCl)=0.12). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)