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Research paper

In-situ synthesis of polyaniline coated montmorillonite (Mt) clay using Fe^{+3} intercalated Mt as oxidizing agent

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ABSTRACT

Polyaniline (PAni) coated over montmorillonite clay (Mt) layers is reported through in-situ oxidative polymerization. A new approach of synthesis has been adopted in which oxidizing agent ($FeCl_3 \cdot 6H_2O$) is first intercalated into organically modified montmorillonite clay (OMt) in THF solvent and this ferric ions intercalated clay layers are thereafter re-dispersed into aqueous solution of monomer for polymerization. Choice of THF and aqueous medium is governed by ease of intercalation of Fe^{+3} into OMt and subsequent diffusion of monomer into interlayer spaces during polymerization respectively. The intercalation of polymer within the interlayer spaces has been studied and confirmed using various techniques.

1. Introduction

Conductive or semi-conductive polymeric composites find a wide range of application in electronic or electrical applications like electrostatic charge dissipation (ESD), touch control switches, electromagnetic interference (EMI) shielding and pressure sensor (Faez et al., 2002; McQueen et al., 2004; Moreira et al., 2006; Soares et al., 2006). Metal powders are usually used as conducting filler in insulating polymer matrixes for making these kinds of composites. But incorporation of metal powders increases the cost, weight and degradability of the composites (Chung, 2002). Thus, a lot of research has been focused on the usage of conducting polymers as conducting fillers in insulating polymer matrixes. Polyaniline, among all the conducting polymers has attracted significant interest for the same due to its superior properties, ease of synthesis and potential applications especially in electronic sector (Saxena and Santhanam, 2003; Sendai et al., 2009; Shibao et al., 2007).

However, PAni cannot be used as filler directly due to its poor mechanical strength and thermal stability. But, if it is adhered to a strong substrate and that is used as filler in polymer matrix, some improvement in mechanical, thermal and electrical properties are expected (Neoh et al., 2000; Soundararajaha et al., 2009). There are several literature reports which quote synthesis of conducting fillers by coating PAni over conventional fillers like clay, silica, silicates, carbon black, and poly (methyl methacrylate) (Cho et al., 2003; Gupta and Prakash, 2009; Lee et al., 2005; Srivastava et al., 2009). Amongst these, PAni/Montmorillonite clay composites have attracted significant interest due to easy availability of clay and comparatively superior mechanical, thermal and barrier properties (Maiti and Yadav, 2008; Ray and Okamoto, 2003; Singh et al., 2010).

Montmorillonite clay is a layered inorganic material, composed of silicate layers 1 nm thick and 200–300 nm in the lateral dimension. Thus, the large surface area is expected to enhance mechanical and thermal properties of the polymer. However, the enhancement of these properties also depends to a large extent on interactions between the polymer and the silicate layers, and also on the nanostructure formed upon composite formation.

PAni/Montmorillonite clay systems can be synthesized using various routes like electrochemical polymerization, mechanochemical intercalation, in-situ oxidative polymerization. However, it was found that in comparison to chemical oxidation, electrochemical oxidation takes a longer time due to inactive clay particles (Hoang and Holze, 2006). In mechanochemical intercalation method, the mixtures of sodium montmorillonite clay and anilinium chloride were mechanochemically ground with a mortar and a pestle at room temperature and a sufficient amount of oxidizing agent was added and the mixture was further ground for about 72 h to get the composite (Yoshimoto et al., 2004). However, majority of literature dealing with these systems report the synthesis through in-situ intercalative oxidation technique in which the monomer is intercalated into the clay layers by exploiting the cation

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exchangeability of montmorillonite. The clay layers intercalated with monomer are thereafter dispersed in the oxidizing agent for further polymerization of monomers (Lee et al., 2000; Nascimento et al., 2002).

However, in-situ intercalative polymerization was carried out by intercalating the oxidizing agent within the interlayer spaces of clay and there by dispersing the oxidizing agent intercalated clay layers in the monomer solution has not been reported so far. In this work, we report the synthesis of PAni coated clay layers by intercalating ferric ions in OMt and thereby dispersing them into the aniline solution in acidic medium.

2. Experiment

2.1. Materials used

Aniline (99.5%, Merck Chemicals Ltd.) was used after vacuum distillation. Montmorillonite clay organically modified with dimethyl dialkyl amine supplied by Sigma Aldrich, USA. Tetrahydrofuran, 99.9% supplied by Spectrochem, India; Ferric Chloride, 98%, Merck Chemicals Limited, India; and Hydrochloric acid, Chemlabs, India; were used as supplied.

2.2. Instruments

Electrochemical characterizations were carried out using electrochemical workstation (model CHI7041C), CH-Instrument Inc., TX, USA. Electrochemical experiments were performed in a single-compartment cell using three electrodes assembly with graphite paste as the working electrode, Pt plate as auxiliary electrode and Ag/AgCl as reference electrode. Polymer was incorporated with graphite paste and cyclic voltammetry was carried out in 0.1 M HCl for scan rate 0.02 V/s vs. Ag/AgCl. Spectrophotometer (Lambda 25 of Perkin Elmer, Germany) was used for spectral analysis. XRD measurements were carried out using 18 kW rotating anode (Cu K_α wave length 1.543 Å) based Rigku, Japan powder diffractometer operating in the Bragg–Brentano geometry and fitted with a graphite monochromator in the diffracted beam with 3 deg/min scan rate. Scanning electron microscopic images were carried out by spreading the samples over carbon tape using Quanta MK2 microscope operated at 25 kV in ESEM mode. Transmission electron microscopy was performed using HRTEM, model Tecnai 30 G2 S-Twin electron microscope, operated at 300 kV accelerating voltage. Thermogravimetric analysis (TGA) measurements were performed on a NETZSCH, STA 409 PC analyzer with a heating rate of 10 °C/min.

2.3. Synthesis of iron intercalated interlayer space

OMt (50 mg) was dispersed in 4 ml of tetrahydrofuran and dispersion was thoroughly stirred and sonicated. Alongside, $FeCl_3$ solution was prepared by adding 200 mg of $FeCl_3 \cdot 6H_2O$ in 2 ml of THF. The as prepared solution was thereafter added to a dispersion of clay in THF. The mixture was thoroughly stirred, sonicated again and incubated at room temperature. A yellow precipitate was seen to form at the bottom of the flask due to Fe^{+3} intercalation with the clay. The amount of Fe^{+3} intercalated was calculated by measuring the change in intensity of peak (340 nm) corresponding to Fe^{+3} in UV–vis spectra before and after addition of the clay. Absorption spectra were recorded before and after addition of clay (50 mg) in Ferric Chloride (200 mg) solution in THF. The spectra of both are shown in Fig. 1. Drop in absorbance after mixing ferric chloride showed the intercalation of iron in clay galleries. The concentration of ferric chloride in the mixture was calculated using Lambert–Beers law. The yellow precipitate was thereafter filtered and washed with THF to remove leftover ferric ions in the precipitate. The washing was carried out till a colorless filtrate was observed.

2.4. In-situ polymerization of aniline

Aniline monomer was dissolved in 0.5 M HCl and Fe^{+3}–Mt precipitate was thereafter re-dispersed into monomer solution under constant stirring condition at room temperature. The mole ratio of aniline to the number of ferric ions intercalated was taken as 4:1. The reaction mixture was left over for 48 h at room temperature in a closed flask. A light green precipitate was formed which was then filtered and washed with water. Light green colored precipitate was thus obtained thereafter and dried for 12 h at 50 °C.

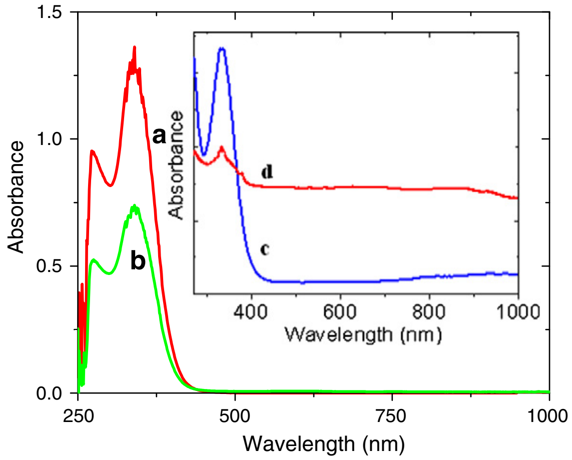

Fig. 1. a) Absorption spectra of 200 mg of $FeCl_3 \cdot 6H_2O$ in 6 ml of THF b) Absorption spectra of 200 mg of $FeCl_3 \cdot 6H_2O$ in 6 ml of THF with 50 mg of clay. Inset: c) Absorption spectra of PAni prepared using $FeCl_3 \cdot 6H_2O$ as oxidizing agent d) Absorption spectra of PAni–Mt.

3. Results and discussion

Intercalation of oxidizing agent into interlayer spaces is vital for this process. $FeCl_3 \cdot 6H_2O$ was used as an oxidizing agent so that the positively charged Fe^{+3} could be intercalated into the negatively charged clay layers. Alongside, a medium which could dissolve the oxidizing agent and also produce a stable dispersion with organically modified clay was required; so that, ion exchange between Fe^{+3} and intercalated organic molecules could be facilitated. Thus, THF was chosen as it produced a stable dispersion with OMt owing to the organophilic intercalated organic molecules present over interlayer spaces and also dissolved $FeCl_3$. Aqueous medium was preferred as compared to organic medium for polymerization for two reasons. Firstly, anilinium ions formed in acidic medium have a higher probability of getting intercalated into negatively charged clay layers. Secondly, Fe^{+3}–Mt are expected to have a better dispersion in aqueous medium due to hydration of Fe^{+3} ions which facilitate intercalation of monomer.

3.1. UV–visible spectroscopy

UV–visible spectroscopy was used to confirm the formation of polymer by using iron intercalated interlayer spaces as oxidizing agent. Fig. 1 (inset) shows the UV spectra of polymer by using $FeCl_3 \cdot 6H_2O$ as oxidizing agent (neat PAni without clay) and polymer formed by using iron intercalated clay layers as oxidizing agent (PAni–Mt). The presence of characteristic π–π^* peak of polyaniline at 335 nm later confirms polymer formation. Lower absorbance of peak at 335 nm in comparison to neat polymer can be associated to less % weight of PAni. Relatively higher absorbance in case of PAni prepared using iron intercalated Mt at wavelengths higher than 400 nm can be attributed to scattering caused by clay particles.

3.2. X-ray diffraction

Fig. 2 shows the X-ray diffraction spectra of OMt, iron intercalated Mt and PAni–Mt. The 2θ values for peak corresponding to 001 basal plane of OMt, iron intercalated Mt and PAni–Mt were found to be 6.94°, 7.28°, and 6.32° and inter layer using Braggs law were obtained