



Synthesis and characterization of polyaniline/poly (o-toluidine)/MMT-clay nanocomposite by mechanochemical method

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ABSTRACT

Polyaniline/ poly(o-toluidine) /MMT-clay nanocomposites can be prepared by mechanochemical method in which, interaction of precursor anilinium ion into the clay lattices accomplished by mechanical grinding of Na-MMT in presence of anilinium hydrochloride at room temperature using mortar and a pestle for about 30 minutes and subsequent grinding with oxidizing agent, ammoniumperoxysulphate. The appearance of green colour indicates the formation of polyaniline/ poly (o-toluidine)/ MMT-clay nanocomposites. The morphology and structural characteristics of the polyaniline clay nanocomposites were investigated using FTIR, XRD, Cyclic voltammogram and SEM.

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Introduction

Polyaniline is one of the most studied conducting polymers because of their high stability, enhanced conductivity and processability [1]. They are widely used in different areas of research including electronics, solar cells, batteries, electromagnetic shielding devices, anti-corrosive coating and sensors [2]. The most important applications of these types of polymers were used in microwave adsorbing materials [3]. It has been proved that the bulk electronic properties of PANI can be modified by templates assisted synthesis of polyaniline clay nanocomposites [4-5].

A multi-layer assembly of clay plates in presence of conjugate polymer system can be used to regulate the tunneling of charge carriers and the electron transfer properties [6]. Recently a mechanochemical technique has been proposed for the synthesis of polymer/clay nanocomposites in which the monomer intercalation and polymerization can be accomplished by mechanical grinding in mortar and a pestle [7-9]. This technique is considered to be a green chemistry way of production of bulk polymer/clay nanocomposites. In the present investigation we have synthesized polyaniline/poly o-toluidine montmorillonite clay nanocomposites by mechanochemical method using aniline and o-toluidine.

The montmorillonite preferentially absorbs the higher mass fractions. X-ray diffraction and FT-IR data confirms the presence of the conductive form of polymer in the clay layers. The morphology of polymer/clay nanocomposites were studied by SEM analysis.

Experimental Section

Chemicals

Aniline, o-toluidine and (NH₄)₂S₂O₈ were obtained Merck, India. Aniline was distilled under reduced pressure and stored at 5°C.

Clay sample was obtained from Aldrich, USA. All other chemicals were purchased from commercial sources.

Instrumentation

FT-IR

FT-IR Spectra were recorded by Perkin – Elmer Spectrometer (FT-1K, 16PC) USING KBr Pallets. All spectra were recorded against the background spectrum KBr.

X-Ray Diffractometer

X-Ray Diffractometer were recorded BRUKER make model D8 Advance, using Ni filter and 2.2 KW Cu anode, Ceramic X-ray tube source.

Cyclic voltammetric studies

Cyclic voltammogram were recorded using CHI instruments, USA (Model.616A). A three electrode cell step up with a single compartment arrangement was used. A gold electrode with 2 mm diameter rod was used as working electrode and platinum foil and Ag wire were acted as counter electrode and reference electrode respectively. The powdered polyaniline samples were dispersed in NMP solution and then applied to electrode surface for the electrochemical studies.

SEM analysis

SEM images were recorded in FEI Quanta 200 environmental scanning electron microscope (ESEM) with EDAX & EDS system.

Preparation of polyaniline/ poly o-Toluidine clay nanocomposites

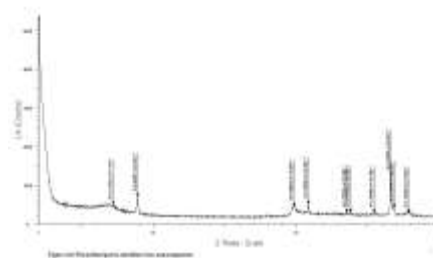
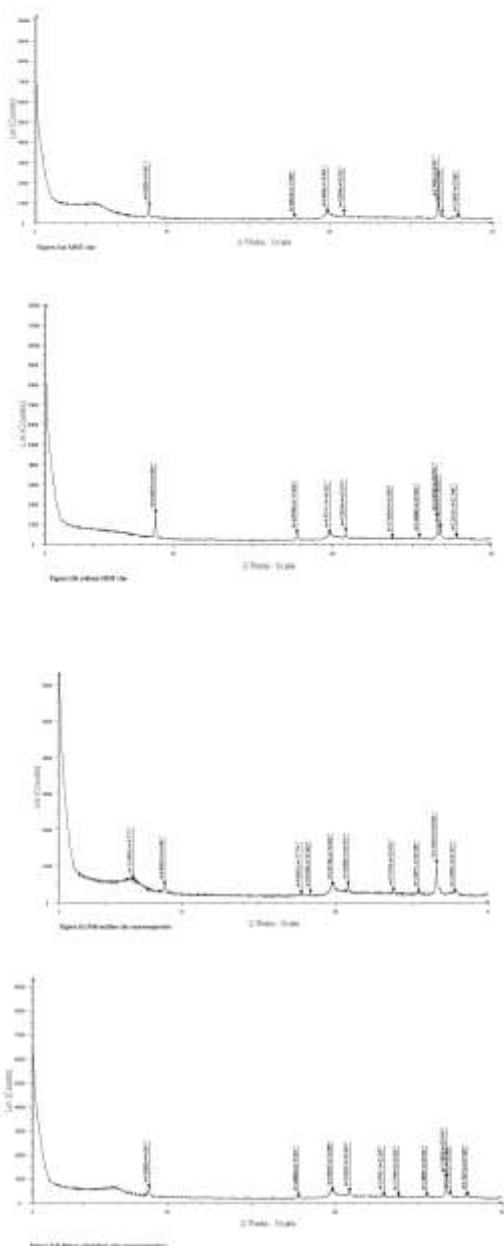
The co-polymer clay nanocomposites were prepared in the following way. A mixture of sodium MMT (1.0g) suspended with a few drops of water and a required amount of aniline-HCl and o-toluidine- HCl were added and the reaction mixture was mechanically grounded in a mortar and a pestle at room temperature for 10min. The grinding processes was continued further followed by the addition of a sufficient amount of (NH₂)₂S₂O₈ (the molar ratio of (NH₂)₂S₂O₈ to monomer was 1.5). The reaction mixture was allowed to stand for 72 hours and the appearance of the dark green powder indicates the formation of polyaniline/ poly o-toluidine / clay nanocomposites which

was isolated by extensive washing with deionised water and followed by washed with 1M HCl. The final product was dried under vacuum.

Result and Discussion

XRD Studies

The XRD patterns of the pure clay and polymer clay nanocomposites are shown, Figure. 1(a) presents the XRD trace for the as received MMT and Figure. 1(b) presents the Na⁺ MMT. The XRD patterns of the polyaniline, poly(o-toluidine) and polyaniline/poly(o-toluidine) clay nanocomposites are shown in Figure.1(c,d,e). The XRD Patterns of the products after washing with distilled water showed a decrease in the basal spacing due to desorption of the intercalated anilinium ion[10]. The basal spacing of the product prepared by a conventional solution method was less than mechanochemical method. The diffraction peaks at the products after polymerization were decreased due to orderly arrangement of polymer inside the clay lattice as shown in the Figure.1(e), indicating the synthesis of PANI/ poly o-toluidine clay nanocomposites in the clay layers.



FT- IR Analysis

The FTIR spectra confirm the presence of the conductive form of PANI in the clay layers. Figure.2a shows the FTIR spectrum of sodium treated MMT clay. The bands at 1600 and 1570 cm⁻¹ consist of benzenoid and quinoid form of polyaniline backbone and also these bands implies that the charge neutralization with the counter ion present in the polyaniline chain. The peaks at 1305 and 1245 cm⁻¹ are associated with the C-N stretching mode[11-12]. The strong peak at 1041 cm⁻¹ and the peaks at 915 and 840 cm⁻¹ are the characteristic vibrations of MMT. The higher frequency side a peak at 3250cm⁻¹ is assigned for the N-H stretching vibration (Figure.2b). The additional peaks were observed in the higher frequency side for the methyl group stretching peaks.

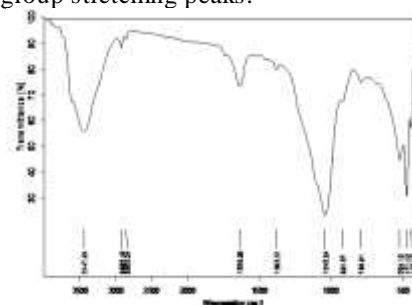
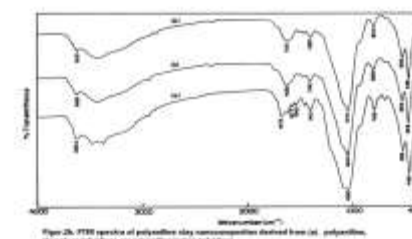


Figure. 2(a) Na⁺ MMT clay

Electrochemical Studies

Electrochemical studies of poly aniline /poly (o-toluidine) clay nanocomposites synthesised by mechanochemical method has been tested using cyclic voltammetry studies (Figure.3) shows the cyclic voltammetric behavior of PANI/MMT, poly (o-toluidine)-MMT and PANI / poly(o-toluidine)/MMT clay nanocomposites in 1.0M H₂SO₄. Two sets of redox wave was observed for the polyaniline (emeraldine salt form) synthesized by the conventional method in acid medium. A shoulder peak was observed in between the set of redox peak centered at 0.4V vs Ag wire in the anodic side and a peak at 0.3V vs Ag wire indicate the quinone formation during polymerization. The first peak is due to the benzenoid form of polyaniline and a redox pair at 0.65V and 0.5V vs Ag wire indicate the quinoid form of polyaniline backbone. The redox behavior is as similar as reported results [14-15]. The redox pairs were not clearly observed in the case of polyaniline/ poly (o-toluidine) clay nanocomposite under same condition.



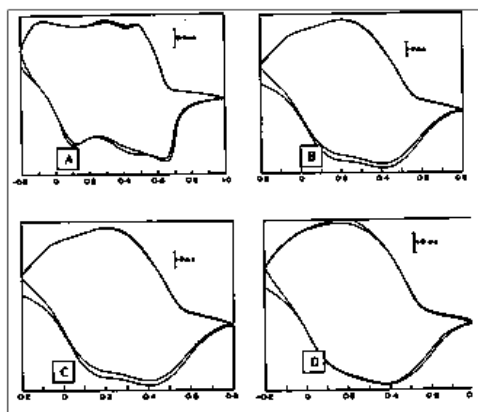


Figure.3 Cyclic voltammogram of pure polyaniline (A), poly(o-toluidine)-clay nanocomposites (B), poly(o-aniline)-clay nanocomposites (C), and polyaniline/poly(o-toluidine)clay nanocomposites (D) in 1.0 M H₂SO₄ medium with scan rate of 100mV/s.

Scanning Electron Microscopy (SEM)

The SEM images (Figure.a,b,c) were recorded for the pure polyaniline & poly(o-toluidine) and polyaniline / poly(o-toluidine) copolymer clay nanocomposites. We have compared the surface morphology for the polyaniline/ poly(o-toluidine) intercalated clay nanocomposites, which was synthesized by mechanochemical method. It is concluded that the Polymer confined within clay lattices show fibril in nature [13].

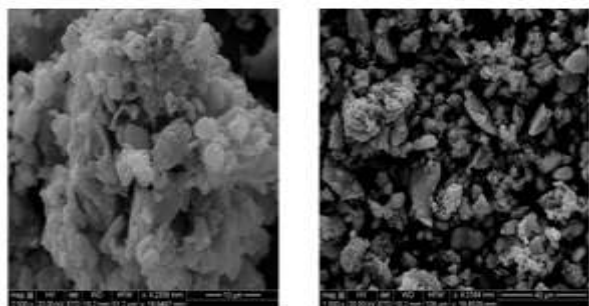


Figure.4 (a) Polyaniline clay nanocomposites

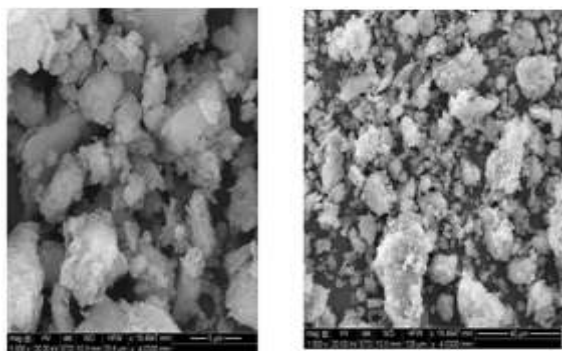


Fig.4 (b) Poly(o-toluidine) clay nanocomposites

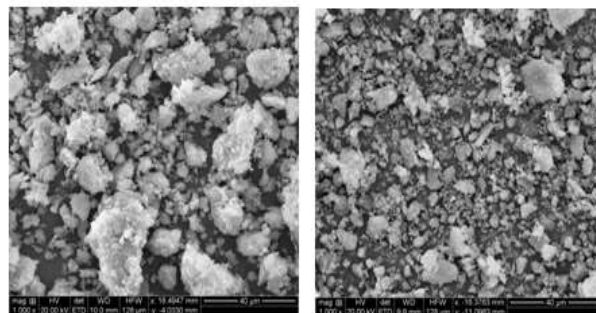


Fig.4 (c) Polyaniline/poly(o-toluidine) clay nanocomposites

Conclusion

Aniline and o-toluidine co-polymer clay nanocomposites have been synthesized in acidic media by mechanochemical intercalation polymerisation. The polyaniline/poly(o-toluidine) MMT clay nanocomposites were characterized by FTIR, SEM, XRD and cyclic voltammetry techniques. The decrease in the basal spacing after polymerization indicates that the synthesized polymer chains would be arranged in a parallel confirmation in the interlamellar regions of clay. SEM images concluded that the polymer confine with in clay lattices show fibril in nature.

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