



Morphological, Mechanical, Electrical and Optical Properties of Poly (Aniline)/Montmorillonite Nanocomposites

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Abstract In this research programme in situ Polymerization technique was used for the preparation of Polyaniline (PANI)/ MMT nanocomposites where the aniline monomer is allowed to polymerize in presence of HCl. Then Nanocomposites were characterized by various techniques like FT-IR, X-ray diffraction, TGA and TEM. The Electrical conductivity of the nanocomposites were also measured. FTIR analysis provided an evidence for the formation of nanocomposites. X-ray diffraction analysis confirmed that the clay was almost exfoliated in between the polymer matrix. A delayed onset of thermal degradation by as much as 70 °C in case of PANI / MMT indicates that the incorporation of MMT increased the thermal stability of the composites.

Keywords Polyaniline, MMT, Conducting polymer

Introduction

Electronic devices working on low energy is the most challenging field of research for the scientists throughout the world, because today world is facing problems associated with energy [1-5]. A transistor is used to open or close the circuit or can also be used as an amplifier [6-8]. So it is important to manufacture transistors that work on low voltage with low switching time and low threshold [8]. The important part of a transistor is dielectric layer which determines the operation voltage and threshold voltage [9]. Switching time influenced by the mobility of the semiconductor and channel length [10]. So now a days conductive polymer composites have become one of the most important research subject because of its wide range of applications [11]. In some cases because of conjugated chain structure some polymers are highly conductive by nature [12]. In order to synthesize the polymer nanocomposites organomodified clay are the first choice because their charged layers can easily be exchanged by cationic surfactants and helps in the formation of intercalation [13]. The conductivity of Polyaniline(PANI) is well known [14]. There are large number of articles available confirming the conductivity nature of PANI [15-17]. In this paper, we present the synthesis and characterization of PANI blended with MMT using in-situ polymerization method and tested its conductivity.

Materials and methods

Materials

MMT was procured from Southern Clay, USA. All other chemicals like aniline (ANI), Ammonium persulfate (APS), hydrochloric acid, acetic acid etc. were used as received.

Preparation of Polyaniline (PANI)/MMT Nanocomposites

For the preparation of PANI/MMT nanocomposites we have used the in situ polymerization technique where aniline was allowed to polymerize in acidic medium (HCl). Firstly the moisture was removed from the clay MMT by drying it at 75 to 80 °C for 24 hours in hot air oven. Then it was added to 1 M HCl solution and sonicated for 30 min. Then the monomer PANI was added to the sonicated solution and the mixture was further sonicated for 30 minutes more. This leads the replacement of inorganic ions present between the lamella of clay by molecules of aniline. Then 1 M HCl solution along with ammonium persulfate (which acts like an oxidizing agent) was added dropwise to the above mixture of sonicated solution (containing PANI and MMT) under constant stirring. The polymerization of aniline was carried out at lower temperatures i.e. between 0 to -4



°C, for 6h. Then the product was filtered through porous glass funnel. The final product was appeared as a green coloured powder and was washed with distilled water and dried at 50°C for 24 h in a hot air oven.

Characterization of Nanocomposites

Fourier transmission infrared spectroscopy (FTIR)

The Fourier Transmission Infrared Spectra (FT-IR) for PANI/ MMT were obtained through a Perkin Elmer Spectrum RX1 FT-IR spectrometer.

X-ray Diffraction (XRD)

The change in gallery height of the blend was investigated by WAXD experiments, which were carried out using an X-ray diffractometer (BEDE D-3 system) with CuK α radiation at a generator voltage of 40 kV and a generator current of 100 MA. Samples were scanned from $2\theta=1-100^\circ$ at a scanning rate of $2^\circ/\text{min}$.

Transmission Electron Microscopy (TEM)

The PANI/MMT samples were directly placed on the copper grids for TEM observation. Then the structure and morphology of the nanocomposites were visualized.

Thermogravimetric Analysis (TGA)

Perkin Elmer thermo-gravimetric analyzer was used to analyse the TGA of the samples. The test samples (about 3 mg) were allowed to be heated at 50 °C to 800 °C at a heating rate of 20 °C/min.

Results and discussion

FT-IR analysis

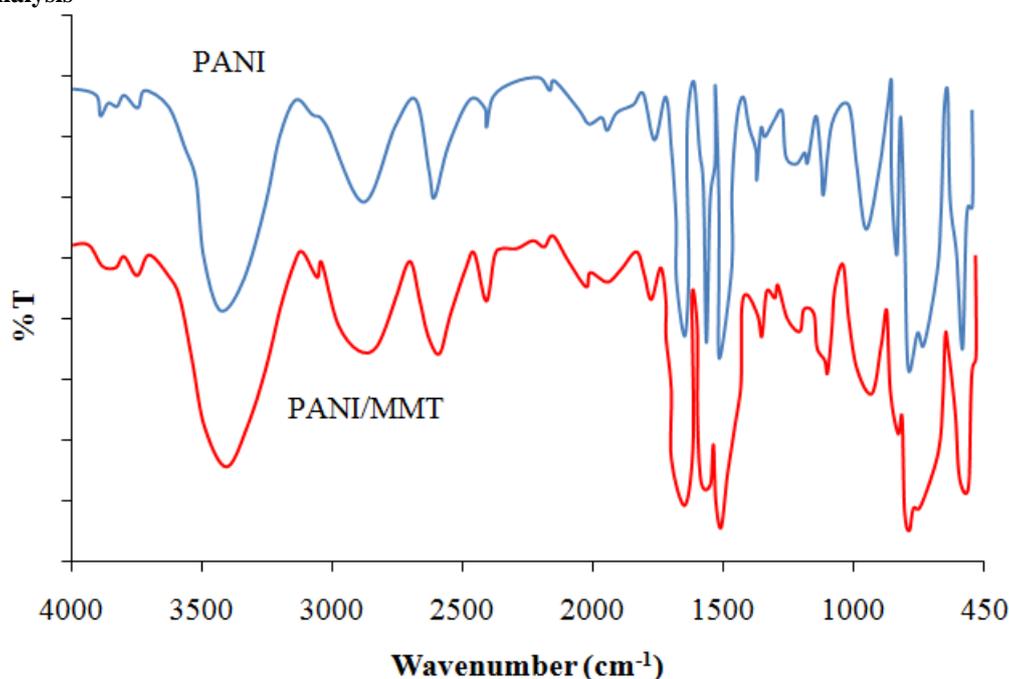


Figure 1: FTIR spectra of Polyaniline and Polyaniline/MMT nanocomposites

In Figure 1 the FTIR spectra for PANI shows two bands at 1575 and 1440 cm^{-1} which correspond to the C=C stretching of aromatic ring groups quinoids (Q) and benzenoid (B) respectively. The same values are also reported by other workers earlier. Bands for C-N-H bond stretching were observed at 1290 cm^{-1} . There is another band in the region at 1134 cm^{-1} which is a confirmation band for the formation of polarons. We found all the bands almost in the same region in both cases, i.e. PANI and PANI/MMT. Hence it can be concluded that MMT does not affect the formation of conducting polymer.

X-Ray diffraction

The X-Ray diffraction patterns of PANI, PANI/MMT, and MMT were shown in Figure 2. The characteristic peak for MMT is observed at $2\theta = 7.5^\circ$ and 19.68° . PANI and PANI/MMT show almost similar diffractograms in the 2θ regions. An additional peak appears at $2\theta = 6.3^\circ$ in the case of PANI/MMT and hence can be concluded that the peak is a result of the presence of MMT in the polymer matrix. Comparing with the peaks of MMT, PANI/MMT shows the peak with smaller intensity and slight shift towards the smaller angle, i.e. from 7.5° to 6.3° , confirming the formation of intercalation between the clay and the polymer.



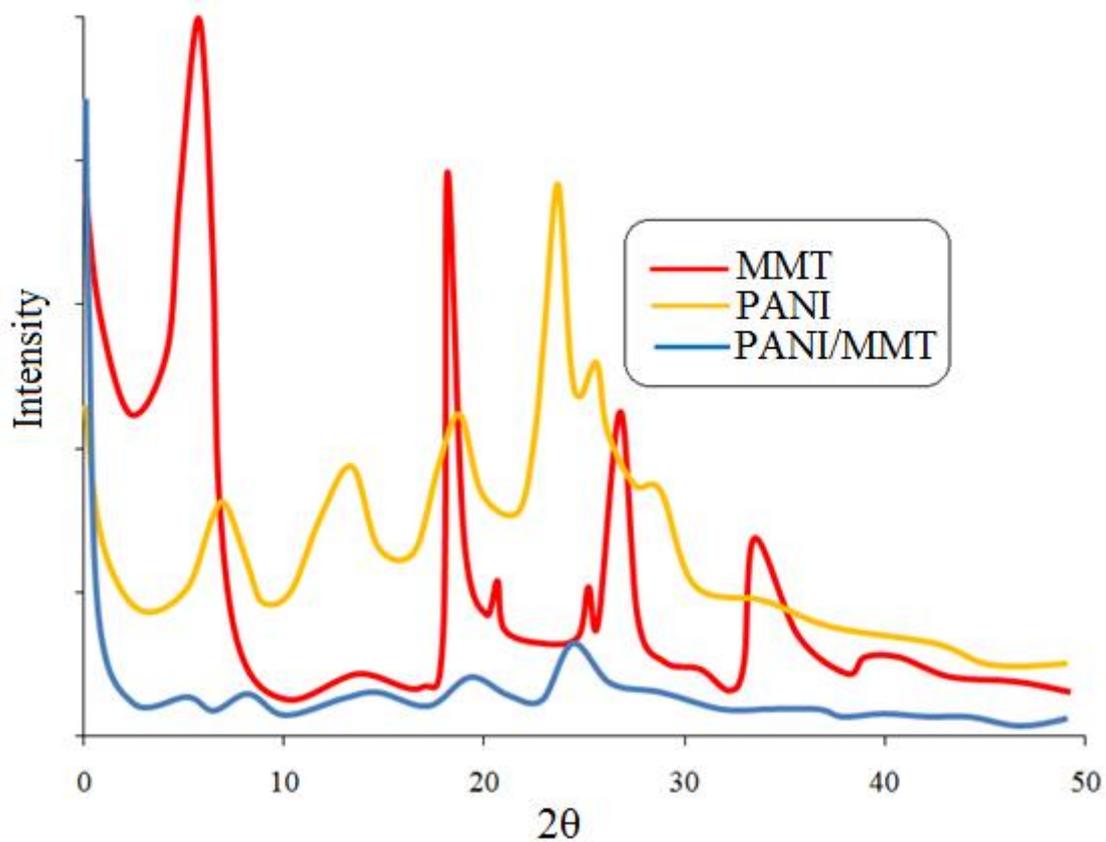


Figure 2: X-Ray diffraction of MMT, PANI and PANI-MMT

Transmission electron microscopy (TEM)

From the transmission electron microscopic study (Figure3) of PANI/MMT it can be clearly seen that the polymer layers around the clay lamellae. So from the TEM image also it is found that intercalation between the clay MMT and polymer PANI has been occurred.

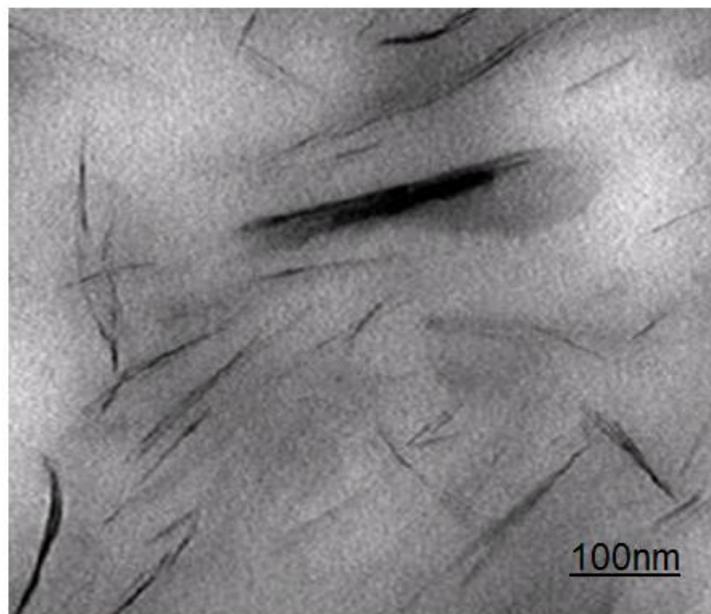


Figure3: TEM of PANI/MMT

Thermogravimetric analysis (TGA)

In order to know the thermal behaviour of the polymer thermo gravimetric analysis technique has been used. The TGA graph of MMT and PANI/MMT is shown in Figure4. From the figure it can be seen that at about 85



°C a first degradation of both the samples appeared which is due to the loss of water molecules present in the polymer. There is a second thermal event at 180 °C in case of PANI/MMT which is may be due to the degradation oligomers. Because of the structural rearrangement of the polymer a third thermal event starts at 300 °C. The fourth and final thermal event for PANI/MMT starts at around 480°C. This is due to the degradation of the polymerchains. From the TGA result it can concluded that the PANI/MMT nanocomposite is best suited if used below its degradation onset temperature i.e. 200 °C.

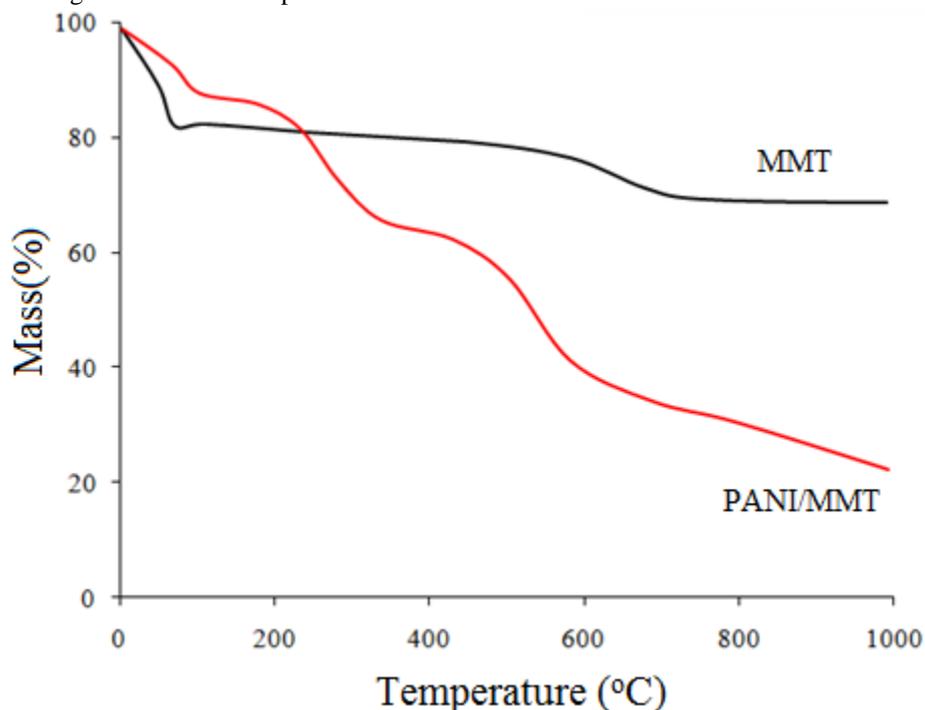


Figure 4: TGA graphs of MMT and PANI/MMT

Electrical conductivity

Four point method [18] was adopted to measure the electrical conductivity of PANI and PANI/MMT. The electrical conductivity of the PANI and PANI/MMT were measured as 83 S cm^{-1} and 62 S cm^{-1} respectively. From the result it is found that the addition of MMT to PANI decrease the conductivity nature of PANI probably because of the presence of insulating charges. But the electrical conductivity value for PANI/MMT is still higher enough and can be consider as very good conductor of electricity.

Conclusion

From all the characterization data it was confirmed that by using the oxidizing agent APS in presence of HCl the PANI/MMT nanocomposites were successfully synthesized. This technique of synthesis is also called as in-situ polymerization. From XRD and TEM results it is also found that MMT particles are well dispersed within the polymer matrix forming the intercalated structure. Interestingly It was also found that the conductivity of PANI slightly decreased by the addition of nanoclay MMT because of the insulating nature of the clay. But still PANI/MMT nanocomposites show excellent electrical conductivity.

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