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Conducting Polymer / Clay Composites: Preparation and Characterization

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The conducting polypyyrole-montmorillonite clay (PPy/MMT) composites were prepared using 2 : 1 mole ratio of $FeCl_3$ / pyrrole with various percentages of MMT clay in aqueous medium. The prepared samples were subjected to structural, thermal and morphological characterizations and d.c. conductivity measurement. The conductivity increased from 3.090×10^{-2} S/cm to 1.370×10^{-1} S/cm with the increase in the percentage of clay from 0.2 % to 1.0 %. The surface morphology of the prepared composite is denser and more compact. The X-ray diffraction result for PPY/MMT showed the intercalation of PPy polymer between the clay layers. The FT-IR result shows the successful incorporation of montmorillonite clay in the prepared PPy/MMT clay composite.

Keywords: conducting polymer, polypyrrole, montmorillonite clay.

INTRODUCTION

Polypyrrole is an intrinsic conducting polymer which can be made to have conductivites up to 1000 $S \cdot cm^{-1}$ rendering its versatile applications in batteries, electronic devices, functional electrodes, electrochromic devices, optical switching devices, sensors and so on [1 – 5]. In recent years, polypyrrole is popular in research and has been the focus of many studies over other conducting polymers because of its high chemical and air stability and ease of preparation. Oxidizing pyrrole to polypyrrole can be achieved either by electrochemical method or chemical method [6 – 8].

One advantage of polypyrrole concerns the low oxidation potential of pyrrole. The typical polypyrrole, which is insoluble and infusible, exhibits poor processability and lacks essential mechanical properties. Efforts to overcome these drawbacks have led to numerous researches on the synthesis of polypyrrole by both electrochemical and chemical routes. Among them, a significant strategy to approach both high electrical conductivity and desirable mechanical properties is preparing blends or composites of polypyrrole polymer with other insulating polymers having desirable mechanical properties [9 – 11]. Nanodimensional composites of polypyrrole with colloidal silica [12], tin oxide [13] and zirconium oxide [14] have been studied extensively. Clay minerals have been adapted to the field of nanocomposites because of their small particle size and intercalation property, especially in the application of reinforcement materials with polymers [15].

In this present communication, we report the synthesis of polypyrrole-montmorillonite clay composite by chemical method in aqueous medium and their structural, thermal and morphological characterizations.

EXPERIMENTAL

In this study, the monomer pyrrole (supplied by Fluka) was distilled prior to use. $FeCl_3 \cdot 6H_2O$ (supplied by APS Ajax Finechem) was used as the oxidant while montmorillonite clay (supplied by Fluka) was used as the clay material. Distilled water was used as the solvent. For the synthesis of polypyrrole/montmorillonite clay nanocomposites in aqueous medium, the montmorillonite clay dispersion in aqueous medium was first prepared by adding known weight of nanodimensional montmorillonite clay into known volume of distilled water under constant stirring. After 1 hour, $FeCl_3 \cdot 6H_2O$ was added to the dispersion in such a way that it would attain the required concentration. Pyrrole (known volume) was then added into the dispersion under constant stirring at room temperature (25 ºC). The relative proportions of $FeCl_3$/pyrrole were varied with mole ratio ranging from 0.5 to 4.0. The total volume of the reaction mixture was kept at 50 ml. The gradual change of colour from light black to deep greenish-black indicated the formation of polypyrrole. The reaction mixture was then kept under room temperature for 24 hours. The resulting deep greenish-black mass was filtered and then it was thoroughly washed with distilled water until it was completely free from $FeCl_3$. This process was repeated several times to remove all adhering substances. Finally, the product was washed with water again and then it was dried at 90 °C for 24 h to yield a very fine deep greenish-black powder. A Hand Press (Model: SPECAC) instrument for pellets preparation was used. The powder obtained was made pellets by using stainless steel mold applying 10 ton/cm^2 pressure under vacuum for 10 minutes.

The electrical conductivity was measured at room temperature using a standard Four Point Probe technique. The probes were placed on surface of the pellet. The thickness of the pellets was measured by using a micrometer. Calculation of the conductivity is as stated below:

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$\sigma = I \ln 2/V \pi t$,

where σ = conductivity, I = current in Ampere, V = voltage in Volts and t = thickness of the pellet in cm.

X-ray diffraction measurements were performed using a Philip PW-1390 model. The infrared spectrum of the samples were recorded in the wave-number range from 400 – 4000 cm^{-1} using a Perkin Elmer FT-IR Spectrophotometer. The scanning electron microscope (model LEO 1455 VP) was used to get the micrographs of the samples.

RESULTS AND DISCUSSION

The conductivity of the pellets of the samples obtained from using 0.2 %, 0.4 %, 0.6 %, 0.8 % and 1.0 % of MMT clay with 2:1 mole ratio of $FeCl_3$ to pyrrole was measured. Figure 1 shows the variation of conductivity with increasing percentage of clay. It was observed from the conductivity measurement that PPy/MMT clay composite showed the highest conductivity value of 1.370×10^{-1} S/cm using 1.0 % MMT clay.

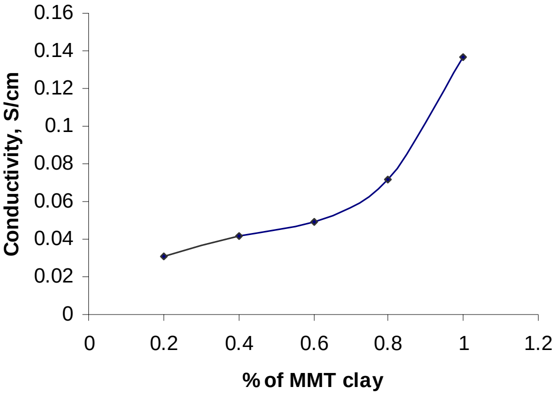

Fig. 1. Values of conductivity for different percentages of MMT clay in the composite using 2:1 mole ratio of $FeCl_3$ to pyrrole

Insertion of the PPy into the layer of clay was also examined by XRD, which confirmed that the PPy chain was aligned with the layers of clay. Figure 2 shows X-ray diffraction pattern for (A) pure MMT clay, (B) pure PPY, (C) PPY/MMT 0.2 % clay, (D) PPY/MMT 0.4 % clay, (E) PPY/MMT 0.6 % clay, (F) PPY/MMT 0.8 % clay and (G) PPY/MMT 1.0 % clay, respectively. All the spectra show polycrystalline structure due to the presence of sharp peaks except for Figure 2 (B) where there is none except a broad peak. The broad maxima in the 2θ were obtained in the range of 22.0° to 26.0° for pure polypyrrole (Figure 2 (B)) which suggests the structure of pure polypyrrole to be amorphous. The crystalline peak at 6.43° (2θ value) of the MMT samples was shifted toward a lower angle which suggests the intercalation of PPY material between the clay layers during nanocomposite synthesis. For PPy without clay, there are no such peaks in that 2θ range. The sharp crystalline peak for pure MMT clay at 2θ value of 28° can be seen in all the PPY/MMT clay composites but with low intensities. It was found gradually increasing with the increase in clay percentage in the composite. The values of *d*-spacing for MMT clay, pure PPY and PPY/MMT clay composite are shown in Table 1.

Table 1. The calculated interplaner d Bragg's spacing for pure MMT clay, pure PPY and PPY/MMT composite

Sample	*d*-spacing (Å)
Pure MMT clay	13.7346
Pure PPy	3.9842
PPY/MMT composite	16.651

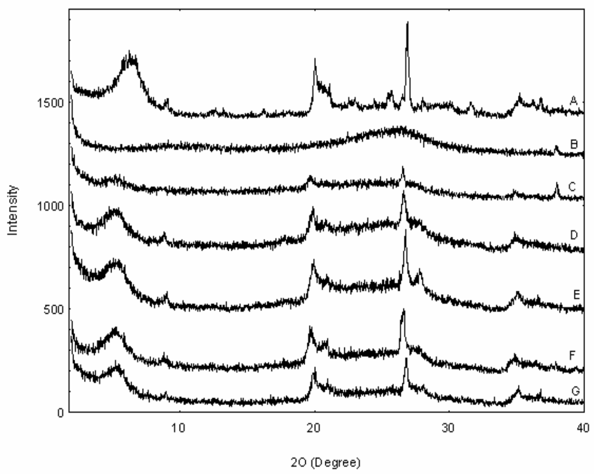

Fig. 2. X-ray diffraction patterns for: (A) pure MMT clay, (B) pure PPY, (C) 0.2 % w/v clay, (D) 0.4 % w/v clay, (E) 0.6 % w/v clay, (F) 0.8 % w/v clay and (G) 1.0 % w/v clay respectively

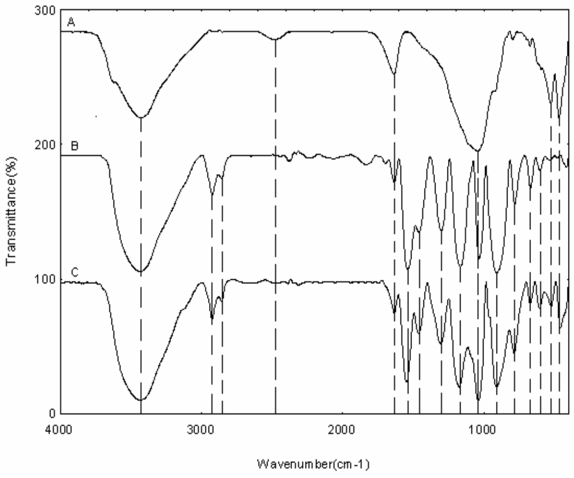

Fig. 3. FTIR spectra for (A) pure MMT, (B) pure PPY, (C) PPY/MMT

FTIR ANALYSIS

The FT-IR absorption spectra for MMT clay, chemically synthesis PPY without clay and chemically synthesis PPY/MMT clay composite are shown in Figure 3. The FTIR spectra of the PPY/MMT clay composite reveal the peaks associated with pure PPY and the principal clay peaks. The strong absorption at 3424 cm^{-1}, 2474 cm^{-1}, 1638 cm^{-1} and 1048 cm^{-1} are characteristic peaks of MMT clay. The spectra also show the characteristic polypyrrole absorption at 3436 cm^{-1}, 2924 cm^{-1}, 1538 cm^{-1}, 1300 cm^{-1}, 1166 cm^{-1}, 1032 cm^{-1}, 908 cm^{-1} and 782 cm^{-1}. There is not much difference for PPY/MMT spectra compared to PPY spectra. The infrared absorption spectra peaks of MMT clay, PPY and PPY/MMT are shown in Table 2.

Table 2. The infrared absorption spectra of MMT clay, pure PPY and PPY/MMT

Sample	Frequency (cm^{-1})			
	V_{N-H}	V_{C-H}	$V_{C=C}$	V_{C-N}
MMT clay	3424	1048	1638	
Pure PPy	3436	1032	1538	1460
PPy/MMT	3434	1040	1548	1462

SCANNING ELECTRON MICROSCOPY (SEM)

Scanning electron micrographs (SEM) revealed some interesting morphological differences between the pure MMT clay and PPY-MMT clay composites.

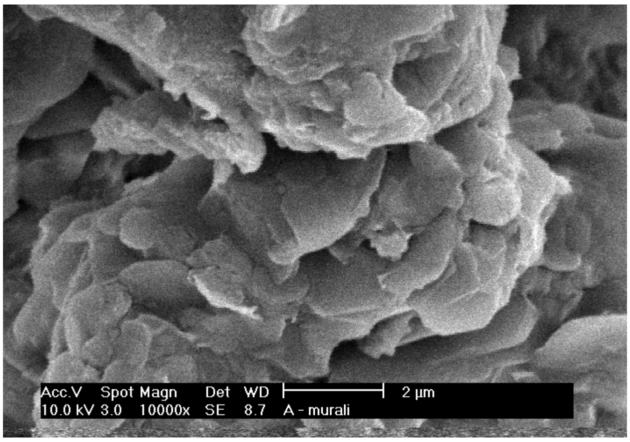

Fig. 4 (a). Scanning electron micrograph of pure MMT clay at magnification 10000 times

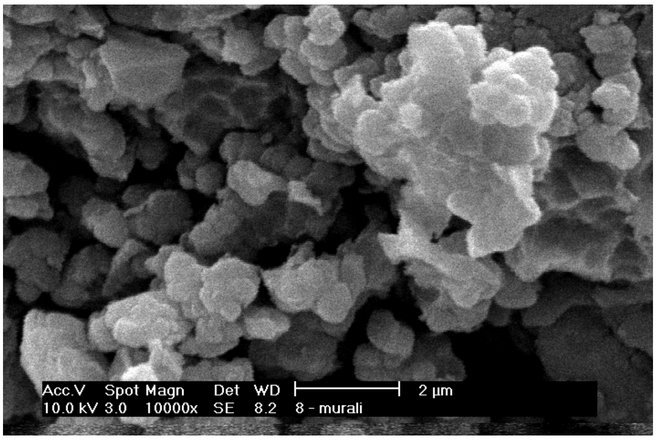

Fig. 4 (b). Scanning electron micrograph of PPY/MMT clay (0.4 % clay) at magnification 10000×

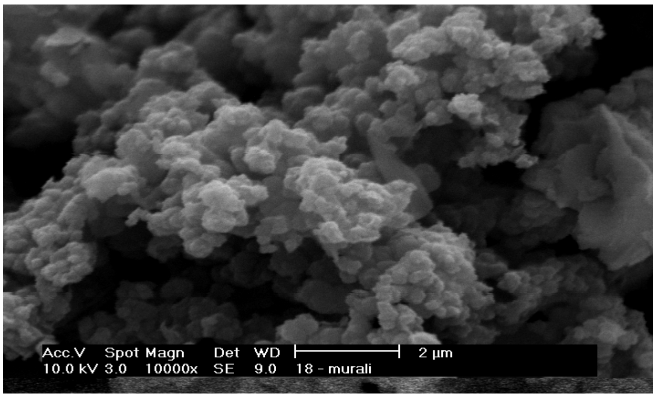

Fig. 4 (c). Scanning electron micrograph of PPY/MMT clay (0.8% w/v clay) at magnification 10000 times

The surface of pure montmorrilonite clay was flaky as shown in Figure 4 (a). The SEM of the films synthesised from pyrrole + $FeCl_3$ + MMT clay are shown in Figure 4 (b – c) which were of different granule sizes. The micrograph shown in Figure 4 (c) exhibits more ordered and dense structure (smaller sizes with high density of granules per unit area) comparing to Figure 3 (b) (bigger sizes with less density per unit area). It shows that the increase in clay percentage in the preparation solution will increase the compactness of the films albeit more dense.

It shows that the improvement in the conductivity of the PPY/MMT clay composite could be attributed to more ordered and dense structure enhancing inter-chain electron hopping.

CONCLUSIONS

MMT clay-based composites of PPY were successfully obtained by polymerizing pyrrole in the presence of $FeCl_3$-impregnated MMT clay in aqueous medium. The conductivities of PPY/MMT composites increased with the increase in MMT clay loading in the composite. The X-ray diffraction results demonstrate the intercalation of conducting PPY materials between the MMT clay layers and support the formation of PPY-MMT clay compsites. The FTIR study shows the successful incorporation of polypyrrole in the clay structure. The morphological study from the SEM analysis shows the denser and more compact morphology of PPy/MMT clay composite with the increase in MMT clay which is responsible for enhancing the conductivity.

Acknowledgment

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