Polypyrrole–montmorillonite clay composites: An organic semiconductor

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Abstract

The conducting polypyrrole–montmorillonite clay (Ppy–MMT) composites were prepared by chemical polymerization. The prepared composites were subjected to structural, thermal and morphological characterizations and dc conductivity measurement. The dc conductivity of Ppy–MMT composites measured at room temperature was found to decrease from 2.25 to 0.31 S/cm with an increase in the percentage of montmorillonite (MMT) from 1\% to 7\%. The surface morphology of the prepared composites is denser and more compact compared to pure montmorillonite as can be evidenced from SEM micrographs. The formation of Ppy–MMT composites was supported by Fourier transform infrared (FTIR) spectra of the composites.

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1. Introduction

Conducting polypyrrole (Ppy) polymer has been extensively researched due to its varied potential applications in batteries \cite{1}, super-capacitors \cite{2}, and microwaves shielding and corrosion protection because of its environmental stability to oxygen and water, high conductivity and ease of synthesis \cite{3–6}. The positively charged Ppy, the electron holes available from longer polymer chains and the coplanarity between interchains are favorable for a higher conductivity performance \cite{7}. One advantage of Ppy concerns the low oxidation potential of pyrrole \cite{8}. The typical Ppy, which is insoluble and infusible, exhibits poor possibility and lacks essential mechanical properties. Efforts to overcome these drawbacks have led to numerous researches on the synthesis of Ppy by both electrochemical and chemical routes \cite{9–12}.

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. Among various clay materials, montmorillonite (MMT) clay, whose lamellae are constructed from an octahedral alumina sheet and sandwiched between two tetrahedral silica sheets, exhibits a net negative charge on lamellae surface, and causes it to absorb cations such as Na\textsuperscript{+} or Ca\textsuperscript{2+} \cite{13}.
The interlayer spacing becomes large enough to be penetrated by relative charge size micelles with swelling of the clay in water.

In this study, we synthesized and characterized the composites of conducting Ppy polymer and MMT clay through the chemical method in aqueous medium. We report the composites based on results of dc conductivity, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA).

2. Experimental

In this study, the monomer pyrrole (supplied by Fluka) was distilled prior to use. FeCl₃·6H₂O (supplied by APS Ajax Finechem) was used as an oxidant, while MMT clay (supplied by Fluka) was used as a clay mineral. Distilled water was used as the solvent (50 mL). For the synthesis of PPy–MMT clay composites in aqueous medium, a calculated amount of MMT (1% to 7% v/w) was added to an aqueous solution of 0.4 M of FeCl₃·6H₂O under continuous stirring. To this mixture, 0.1 M of pyrrole was added directly. The mixture was continuously stirred for 6 h at room temperature (25°C). The addition of pyrrole monomer to the MMT was accompanied by a gradual color change from light gray to greenish-blue to black, indicating the formation of Ppy [14]. Finally, the black mass (composite) present in the system was filtered and washed thoroughly with distilled water until it was completely free from FeCl₃. The black powder of the composite was then dried in the oven for 6 h at 45°C.

3. Characterization of the composites

The dc conductivity of the composites was measured at room temperature using a four-point probe. The composites were pelletized before measuring the conductivity. The conductivity meter was calibrated by using a standard silicon wafer (Standard Reference Material no. 2545, supplied by the National Institute of Standard and Technology, USA). The infrared spectra of various Ppy–MMT composites were taken on a Perkin-Elmer FTIR spectrophotometer. The thermal stability of the samples was measured by TGA (TA instrument Mettler Toledo SW 7.01). Surface morphology of the samples was studied by SEM (model Philip).

4. Results and discussion

The dc conductivity of the composites was measured by using the following equation: \( \sigma = \frac{(I \ln 2)}{(V \pi t)} \), where \( \sigma \) = conductivity, \( I \) = current in amperes, \( V \) = voltage in volts and \( t \) = thickness of the pellets. As shown in Table 1, the conductivity values of the composites decreased from 2.25 to 0.35 S/cm with the increase in the percentage of MMT clay. Since the conductivity measured by the four-point probe was done on the surface, the decrease in conductivity indicates that the MMT clay is distributed on the surface of the composite keeping the conducting Ppy in the galleries of the clay. The conductivity of the composites varied with the Ppy loading in the MMT. This may be due to the increase in more electron holes available along the longer polymer chain and the creation of more co-planarity between the interchain. Increasing the amount of MMT clay, the tetrahedral structure of

<table>
<thead>
<tr>
<th>Percentage of MMT used</th>
<th>Conductivity of Ppy–MMT composites (S/cm)</th>
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<tbody>
<tr>
<td>1</td>
<td>2.25</td>
</tr>
<tr>
<td>2</td>
<td>2.07</td>
</tr>
<tr>
<td>3</td>
<td>0.95</td>
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<tr>
<td>4</td>
<td>0.64</td>
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<tr>
<td>5</td>
<td>0.60</td>
</tr>
<tr>
<td>6</td>
<td>0.54</td>
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<td>7</td>
<td>0.38</td>
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Fig. 1. FTIR spectra for pure MMT, pure Ppy and Ppy–MMT composites.
MMT is likely to stop the elongation of the Ppy polymer chain, resulting in the limited electron transfer between the interchain, which in turn affected the conductivity of the composites. Thus, significant changes in the structure occur due to the intercalation of Ppy in the MMT clay galleries [15].

FTIR spectroscopy reveals the functional groups of Ppy and MMT in the Ppy–MMT composites. Fig. 1 shows the FTIR spectrum of Ppy. A broad peak at 3437 cm\(^{-1}\) is the characteristic of the N–H stretching mode. The peak at 1539 cm\(^{-1}\) is for C=\(\equiv\) C stretching of pyrrole. A small peak at 1454 cm\(^{-1}\) is due to C–N stretching of pyrrole. The peak at 1168 cm\(^{-1}\) is observed for C–C stretching of pyrrole. The C–H stretching and N–H bending of pyrrole can be observed at 1046 cm\(^{-1}\). The peak at 780 cm\(^{-1}\) is for C–H bending. The peak observed at 672 cm\(^{-1}\) refers to the C–H stretching of pyrrole. The characteristic peaks for MMT are also shown in Fig. 1. The broad peak observed at 3381 cm\(^{-1}\) is for O–H stretching of MMT. The next peaks at 2951, 2460 and 1637 cm\(^{-1}\) are due to C–H vibration. The peak observed at 910 cm\(^{-1}\) is due to Si–O stretching. The peaks found at 596 and 531 cm\(^{-1}\) are due to Al–O stretching. The peak at 470 cm\(^{-1}\) is due to Si–O bending.

The FTIR spectrum for Ppy–MMT composite is also shown in Fig. 1. The broad peak observed at 3428 cm\(^{-1}\) is the characteristic for O–H vibration of MMT and pyrrole. The peaks 1632 and 1482 cm\(^{-1}\)

![Fig. 2. TGA analyses for (a) Ppy, (b) MMT and (c) Ppy–MMT composites.](image-url)
are due to C–H vibration of MMT. The peak at 1482 cm\(^{-1}\) is referred to the C\(=\text{C}\) vibration of pyrrole. The peak at 1454 cm\(^{-1}\) is referred to the C–N vibration of pyrrole. C–C vibration of pyrrole can be observed at 1309 and 1182 cm\(^{-1}\). C–H stretching and N–H stretching of pyrrole can be observed at 1037 cm\(^{-1}\). The peak at 906 cm\(^{-1}\) refers to Si–O stretching of MMT. C–H stretching of pyrrole can be observed at 780 and 681 cm\(^{-1}\). The peaks at 615 and 517 cm\(^{-1}\) are due to Al–O stretching of MMT. The peak observed at 460 cm\(^{-1}\) is due to Si–O vibration of MMT.

The characteristic functional groups of both Ppy and MMT can be observed in the Ppy–MMT spectrum in Fig. 1. Thus, the FTIR spectrum of Ppy–MMT confirms the formation of the Ppy–MMT composite.

The thermal properties of the Ppy–MMT composite, Ppy and MMT are shown in Fig. 2. It shows that the degradation of pure Ppy starts at 156.31 °C and the percentage weight loss is 10.35%. The second degradation starts at 413.33 °C and weight loss is 13.86%. This degradation process is referred to the organic compound in the pure Ppy. The degradation is completed at 612.04 °C. The TGA analysis for pure MMT shows the degradation at 199.68 °C with a weight loss of 2.87%. The second degradation step for MMT starts at 341.21 °C and the weight loss is 2.10%. The degradation process is complete at 612.87 °C, which is attributed to the thermal decomposition of the organic modifier of the clay.

TGA patterns obtained in the Ppy–MMT composite reveal a better thermal stability compared to
the pure Ppy. The dehydration step for Ppy–MMT starts at a temperature of 43.69 °C and the weight loss is 6.30%. The degradation of the composite begins at the temperature of 177.21 °C with a 5.60% percent weight loss. The second degradation starts at a temperature of 379.55 °C and the weight loss is 4.12%. The degradation of the composite is complete at 524.24 °C. The reasons could be attributed to a more ordered and dense structure of the Ppy–MMT composite and the interaction of Ppy within the clay structure, resulting in a shielding effect by clay layers in the thermal analysis.

The scanning electron micrographs reveal some interesting morphological differences among MMT, Ppy and Ppy–MMT composite. Particles of MMT (Fig. 3) have irregular plate-like shapes of hundreds of micrometers in two dimensions, length and width. The typical Ppy structure (Fig. 4) is micro-globules. As shown by SEM, the original structure of MMT changes with the rearrangement of the MMT structure caused by the presence of Ppy (Fig. 5). It shows that Ppy modified the flaky structure of MMT nanoparticles. The SEM morphology for the Ppy–MMT composite (Fig. 5) also exhibits that the particles appear to be more densely packed, with the manifestation of relatively smaller particles size. It also shows that the Ppy–MMT composite has a globular pattern with non-uniform particle distribution.

5. Conclusions

Ppy–MMT conducting polymer composites have been successfully prepared by polymerizing pyrrole in the presence of FeCl₃ · 6H₂O and MMT clay in aqueous medium. The results reveal a decreasing trend of the conductivity from 2.25 to 0.35 S/cm with the increase in percentage of MMT clay. The FTIR result shows the successful incorporation of MMT in the Ppy structure. The TGA analyses show the thermal degradation of the Ppy–MMT composite, which reveals that Ppy–MMT is thermally less stable than pure Ppy due to the composite formation of Ppy–MMT. The surface morphology shown by SEM reveals the denser and more compact morphology of the Ppy–MMT composite.

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References