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Synthesis and Characterization of Polyaniline-Na^+-Montmorillonite Nanocomposite by Microemulsion Polymerization

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Novel nanocomposite materials of conducting polyaniline (PANI) and Na^+-montmorillonite (MMT) were synthesized via a microemulsion polymerization. Microemulsions are macroscopically homogenous mixtures consisting of oil, water and surfactant. By investigating the X-ray diffraction analysis, we found that the d-spacing of the PANI/MMT nanocomposites became wider than that of pristine Na^+-montmorillonite, showing that the PANI was successfully intercalated into the Na^+-montmorillonite layers. FT-IR spectra of the nanocomposites also confirmed characteristic peaks of both PANI and MMT. SEM images of the PANI/MMT nanocomposite indicated that the polymerization occurs mainly between the clay layers. The room temperature dc conductivity of nanocomposites was studied.

Keywords: montmorillonite; microemulsion; nanocomposite; polyaniline

INTRODUCTION

Polyaniline (PANI) is known to be one of the most promising conducting materials for commercial applications, due to its high electrical conductivity, relatively low cost, ease of synthesis, together with their higher stability in air when compared to other conducting polymers such as polypyrrole, poly(*p*-phenylene vinylene) and so on [1–3]. Recently, electrorheological (ER) fluids have been also recognized as one of potential practical applications of PANI materials [4–6] in which the ER fluid is a

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colloidal dispersion whose rheological properties are changed by an imposed electrical field. Concurrently, an attention has been drawn to organic/inorganic nano-scaled composites as one of the most important classes of synthetic materials [7]. Among these, polymer/clay nanocomposite, with the intercalated structure of conducting polymers into the interlayer spaces of layered inorganic host materials such as mica-type silicates and metal oxides, has a topic of great interest during recent years [8,9]. In this study, we synthesized nanocomposite particles of PANI intercalated between MMT layer by using a microemulsion. Microemulsions are clear, isotropic liquid mixtures of oil, water and surfactant and co-surfactant. Oil-in-water (O/W) microemulsions consist of oil droplets (a few nanometers) dispersed in water with aid of surfactant (sodium dodecyl sulfate, SDS) and cosurfactant (1-pentanol). Incorporation of amphipathic $(CH_2)_5OH$ into the adsorbed layer of SDS around the droplet greatly reduces the electrostatic repulsion force between two SDS molecules, minimized the oil-water interfacial tension and decrease the persistence length of the interfacial layer [10]. The results of XRD, SEM, FT-IR [11] and resistivity meter measurements for the systems are reported.

EXPERIMENTAL

The clay used was Na^+-montmorillonite (Southern Clay Product), with its cation-exchange capacity (CEC) of 92.6 meq/100 g clay. As the guest material, aniline monomer (99% pure) was used. Hydrochloric acid (HCl) as a dopant and ammonium persulfate ((NH4)2S2O8, APS) as an oxidant initiator were adopted as received without further treatment. The synthesis of the PANI-MMT nanocomposite was carried out by the microemulsion polymerization. Intially, Na^+-montmorillonite in aqueous medium was prepared and dispersed by using an ultrasonic generator at 60°C. Pentanol was added when sodium dodecyl sulfate dispersed in di-water well, and aniline monomer was added to the solution. After that, we used homogenizer, by which way the microemulsion solution was formed. Afterward, this homogeneous solution was mixed with the dispersed Na^+-montmorillonite. The obtained materials were dispersed in 1 M aqueous HCl, with the aid of vigorous stirring at 0°C. The initiator, APS which was dissolved in 1 M aqueous HCl, was dropped into the above mentioned suspension. The dark green precipitate was filtered, washed with deionized water and methanol, and then dried under vacuum at 60°C for 24 h. The product was finally pulverized into a fine power. The insertion of XRD pattern of the PANI between the layers of clay was confirmed from a Rikaku X-ray diffractometer, and an FT-IR spectrum (a Perkin

Elmer System, spectrum 2000) of PANI-MMT nanocomposite was taken. The morphology of composites was observed under the condition of 3k magnification and 10 kV. Resistivity meter (MCP-T610, Mitsubishi Chemical Co., Japan) gave dc conductivity of nanocomposites at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the XRD results for the Na^+-montmorillonite, pure PANI, and PANI-MMT nanocomposite. The variation of the d-spacing (001) of the clay interlayer of the materials, which was calculated from the observed peaks by using the Bragg equation: $\lambda = 2d \sin\theta$ ($\lambda = 0.154$ nm). The d-spacing in the direction of pristine MMT is about 1.18 nm. After polymerization, the diffraction peak of the PANI/MMT nanocomposite was shifted to a lower angle. The d-spacing of nanocomposite was more increased up to 1.32 nm. This result demonstrated the insertion of PANI between the clay layers. FT-IR spectra of the PANI/MMT nanocomposite is shown in Figure 2, together with pristine MMT. The band at 1570 cm^{-1} is assigned to the C=N stretching mode, and those at 1305, 1245 cm^{-1} are associated with the C–N stretching modes. These peaks are ascribed to the formation of PANI. The strong peaks of 1041, 915 cm^{-1} and the peak at 840 cm^{-1} were estimated to be the characteristic vibrations of

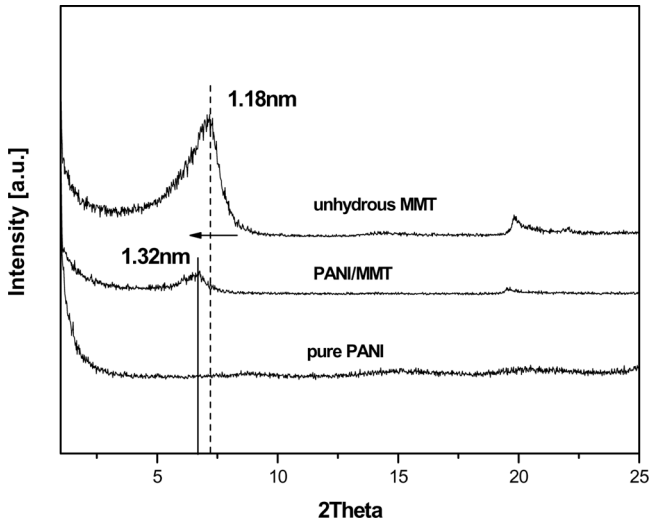

FIGURE 1 XRD analysis of Na^+-MMT, PANI, and PANI/MMT nanocomposite.

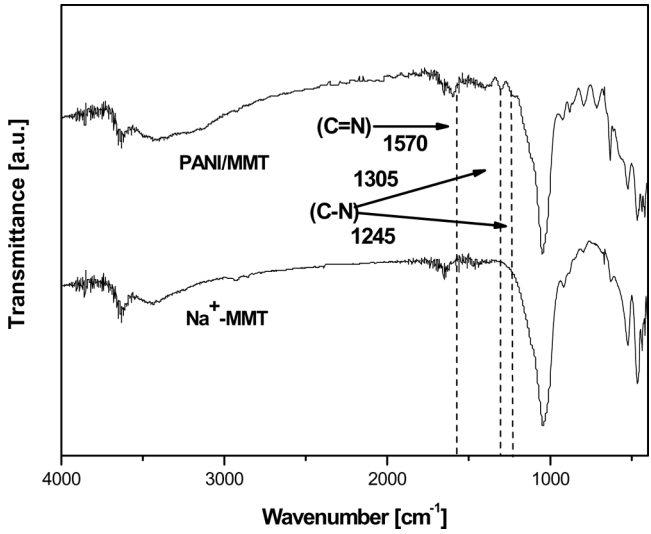

FIGURE 2 FT-IR spectra of Na^+-MMT and PANI/MMT nanocomposite.

MMT. SEM measurements were carried out to confirm the morphology of PANI/MMT nanocomposite. Figure 3 shows morphology of samples. From the SEM micrographs, pure PANI has a granular

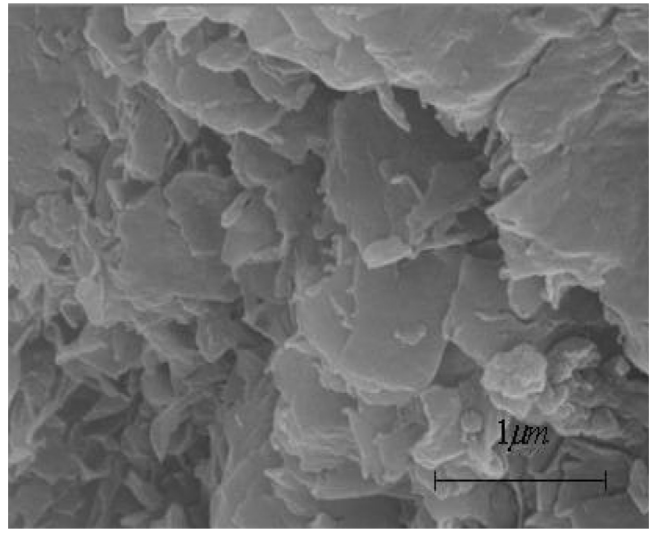

FIGURE 3 SEM image of PANI/MMT nanocomposite.

texture and pristine MMT has a flaky texture reflecting its layered structure. It is possible to notice that the morphology of PANI/MMT nanocomposite was similar to that of pristine MMT, demonstrating that the polymerization occurs mainly between the clay layers. The room temperature dc conductivities of nanocomposite were also measured. The sample of the PANI/MMT nanocomposite has electrical conductivity of 6.8×10^{-6} S/cm, two orders higher than that from the emulsion polymerized nanocomposite [12]. In contrast to ordinary emulsions, microemulsions form upon simple mixing of the components and do not require high shear conditions, thus also showing larger interlayer distance. On the other hand, as a continuation of our work, their ER performance will be studied near feature [12].

CONCLUSION

Polyaniline and Na^+-MMT nanocomposite were successfully synthesized by microemulsion polymerization, and then characterized. In this hybrid nanocomposite, polyaniline was inserted between the clay layers. The structure property relationship of these nanocomposites was investigated by a combination of XRD, FT-IR, SEM, and dc conductivity measurement.

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