# Synthesis of Polyaniline-Montmorillonite Nanocomposites Using $H_2O_2$ as the Oxidant
## (Sintesis Komposit Nanopolianilia-Montmorilonit Menggunakan $H_2O_2$ sebagai Pengoksida)

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ABSTRACT

*Polyaniline montmorillonite nanocomposite was prepared using $H_2O_2$ as the oxidant. The catalytic environment of montmorillonite favours polymerization. Intercalation and composite formation was proven from various techniques such as XRD, FTIR, DRS and thermal analysis. XRD patterns give the dimension of the intercalated PANI, from the shift of 2θ values, which is in the nano range. FTIR showed that PANI composite formation occured without affecting the basic clay layer structure. Thus the successful development of an alternative cheap route for polyaniline–montmorillonite nanocomposite was well established.*

*Keywords: Chemical synthesis; montmorillonite; polyaniline nanocomposite*

ABSTRAK

*Komposit nanopolianilin-montmorilonit telah disediakan dengan menggunakan $H_2O_2$ sebagai pengoksida. Montmorilonit bersifat pemangkin yang dapat membantu pempolimeran. Kemasukan dan pembentukan komposit telah dibuktikan melalui berbagai ujian seperti XRD, FTIR, DRS and analisis terma. Corak ujian XRD membuktikan adanya kemasukan PANI yang dapat dilihat melalui perubahan nilai 2θ, yang merupakan julat nano. Ujian FTIR menunjukkan pembentukan komposit PANI terjadi tanpa mengganggu struktur asas lapisan tanah liat. Kajian ini telah menghasilkan kaedah alternatif untuk menghasilkan komposit nano polianilia–montmorilonit dengan kos yang rendah.*

*Kata kunci: Komposit nanopolianilia; montmorilonit; sintesis kimia*

## INTRODUCTION

Conducting polyanilines have increasing scientific and technological interest in the synthesis of a broad variety of promising new materials due to their unique electrical, optical and optoelectrical properties as well as the ease of preparation and environmental stability (Gustafsson et al. 1992; Sailor et al. 1990). The formation of polyaniline (PANI) composites with inorganic materials provides new synergistic properties that cannot be attained from individual materials (Goller et al. 1998; Riede et al. 2000). Thermal stability, mechanical strength (Kim et al. 2002), gas barrier properties, fire retardant properties (Gilman et al. 2000) and processability can be enhanced by the synthesis of the composites.

Inorganic materials such as montmorillonite clays (MMT) have been adopted to the field of nanocomposites because of its small particle size (<10 μm), ready availability and well-known propensity for intercalation (Kim et al. 1999). Clay/polymer nanocomposites offer tremendous improvement in a wide range of physical properties. This method is currently emphasized commercially and has received great attention in recent years (Gao 2004). The MMT clay whose lamella is constructed from an octahedral alumina sheet sandwiched between two tetrahedral silica sheets, exhibits a net negative charge on the surface layers due to substitution of some $Al^{3+}$ by $Mg^{2+}$. Cations such as $Na^+$ or $Ca^{2+}$ are present between layers to compensate the net negative charge (Whittingham 1982).

In the present study, the anilinium ions exchange the interlamellar cations and thus polymerization occurs within the layers. The confined environment of the clay forced the PANI to form a single chain with extended chain conformation (Wu et al. 2000) and high degree of polymer order, which have profound effects on polymer structure, properties and electrical conduction mechanisms (Goddart et al. 2003). The ability to have a tunable conductivity by doping make PANI an ideal material for the applications in batteries, microelectronics (Sirringhaus et al. 1998), displays (Pages et al. 2001), antistatic coatings (Duke & Gibson 1982), electromagnetic shielding materials (Koul et al. 2000), sensors and actuators (Sukeerthi & Contractor 1999). From the industrial point of view the fabrication of a thermally processable conducting polymer would be preferable. Composite formation improves the mechanical properties of PANI and the electrical conductivity can be tailored for a given application. They have attractive mechanical and other properties of the inorganic materials. For the application as electrostatic dissipation (ESD) the

conductivity levels required are approximately in the range of $10^{-5}$–$10^{-9}$ Scm$^{-1}$. Here we report PANI/ MMT composites synthesized through a simple, inexpensive route, whose conductivity falls in the range for the application as ESD. PANI is prepared either chemically or electrochemically by oxidation of aniline under acidic conditions and some photochemical methods are also used. There are a number of reports that adopt $(NH_4)_2S_2O_8$ as the oxidant (Chen & Yang 2003; Kim et al. 2001a, 2001b; Lee & Char 2002; Lim et al. 2002; Orata & Segor 2000; Wu et al. 2000). In the present work $H_2O_2$ (30% aqueous solution) was used as the oxidant on the structural as well as conducting properties of the PANI/MMT composites.

## EXPERIMENTAL TECHNIQUES

Anilinium hydrochloride prepared from aniline (MERCK) and HCl (RANBAXY Fine chemicals Ltd, 35.5%) was thoroughly mixed with aqueous suspension of Na$^+$ exchanged montmorillonite KSF clay in a ratio of 50 mmol aniline/g clay (Aldrich) for 8 hours. The mixture was then kept at 0-5°C and $H_2O_2$ (MERCK, 30% aqueous solution) was added as the oxidant. It was stirred well for 10 h and was kept for 24 h, filtered, washed several times with acetone and ethanol to separate oligomers. The washing for the removal of excess monomer and oligomers formed are done by extraction in a soxhlet apparatus. A dark green PANI/MMT composite thus obtained was then air dried. The filtrate containing the oligomers was dried and was analyzed for the exchangeable cations (EDAX measurements using Stereoscan 440 Cambridge, UK analyser).

The as-synthesized composite was characterized using XRD (Rigaku X-ray diffractometer with Ni filtered Cu-Kα radiation (λ=1.5414A°)), FTIR (KBr pellet method on ABB BOMEM (MB Series) spectrometer), DRS (recorded at room temperature between 200 and 800 nm using MgO as standard in the Ocean Optics AD 2000 instrument with CC detector) and conductivity measurements (room temperature dc conductivity using a two probe method).

## RESULTS AND DISCUSSION

The polymerization occurs inside the clay layers where the exchangeable cations were replaced by anilinium ions. The cation exchange was proven from the analysis of the filtrate containing oligomers that shows the presence of the elements Na, Ca, K and Fe. Anilinium hydrochloride when mixed with Na$^+$-MMT shows a colour change towards green, which proposes that the chemical composition of MMT has a catalytic effect on the polymerization (Jia et al. 2002). The oxidant $H_2O_2$ then completes the formation of PANI/ MMT composite. Though the common oxidant used for the polymerization is $(NH_4)_2S_2O_8$, presence of the catalytically active MMT favours efficient polymerization within the layers even with $H_2O_2$ which is not effective for the polymerization of aniline otherwise. The polymerization process within the clay galleries is expected to be slow

owing to the confinement imparted by the clay layer structure (Kim et al. 2001a).

Figure 1 compares the XRD patterns of PANI/MMT and MMT samples. The crystalline peak at a 2θ value of ~8.9° in MMT corresponds to the periodicity in the direction of (100) plane of the clay sample (Kim et al. 2001b).
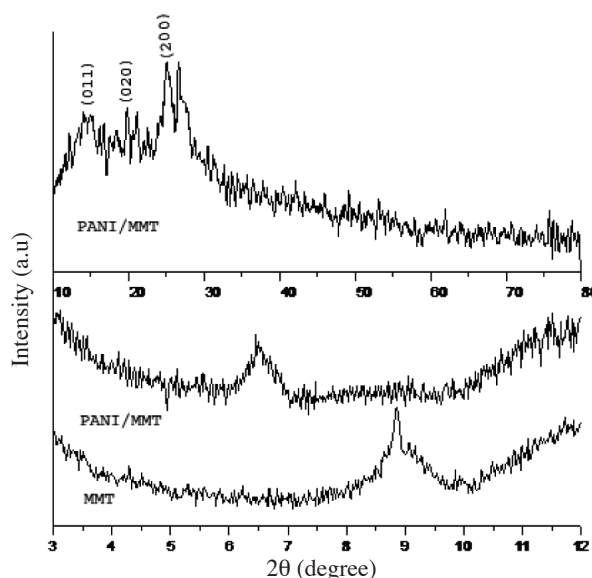


FIGURE 1. XRD patterns of PANI/MMT and MMT

Intercalation of PANI between the clay layers is evident from the shift of the peak towards a 2θ value of 6.46°. The *d*-spacing of MMT, which is approximately at 9.8 Å, increased to a value of 13.7 Å. (Guinier 1994) which confirms that the intercalated PANI is in the order of nanoscale size (<10Å). In PANI/MMT, two broad peaks were observed centered at 2θ values 21° and 25° which are ascribed to the periodicity parallel and perpendicular to the polymer chain respectively (Pouget et al. 1991). Diffraction at 15° and 26° was also present in agreement with those already reported (Sui et al. 2004). The crystalline peaks appear at around 2θ = 15°, 21° and 25° corresponds to (0 1 1), (0 2 0) and (2 0 0) crystal planes of PANI in its emeraldine salt form, respectively

FTIR spectra of the PANI/MMT and MMT show characteristic vibration of both clay as well as the polymer (Figure 2). The peaks due to the benzenoid ring of PANI are present at 1480 cm$^{-1}$, 1444 cm$^{-1}$ and 821 cm$^{-1}$. Peaks at 1570 cm$^{-1}$ and 1140 cm$^{-1}$ correspond to quinoid ring (Xia & Wang 2002).

The Si-O-Si stretching frequency of the clay matrix (1040 cm$^{-1}$) present in the montmorillonite merged with the peak at 1140cm$^{-1}$ in the composite and this peak appears as a broad one. This is an indication of the strong interaction between clay as well as PANI in the composite. A band around 870 cm$^{-1}$ is due to stretching vibration of Al$^{IV}$ tetrahedral (Booij et al. 1996) and is present both in the composite as well as in the montmorillonite. This confirms
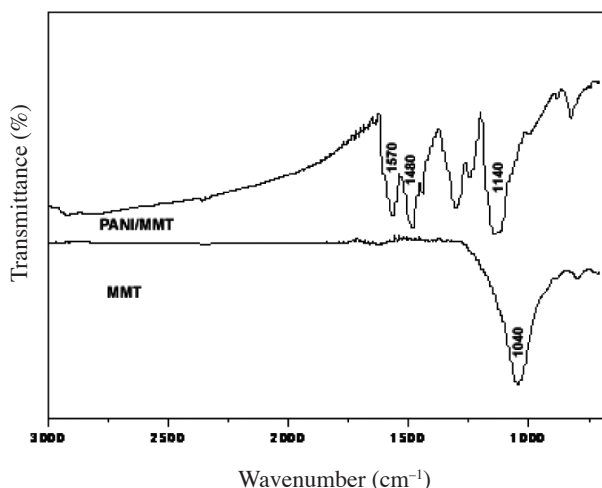
FIGURE 2. FTIR spectra of the PANI/MMT and MMT

the retention of basic clay structure after composite formation (Shewring et al. 1995). The peaks at 1240 cm$^{-1}$ and 1300 cm$^{-1}$ originate from the C-N stretching vibrations associated with the oxidation or protonation (doped) states in PANI (Quillard et al. 1994).

Figure 3 shows the diffuse reflectance spectra of PANI/MMT and MMT. PANI/MMT shows peaks due to $\pi$-$\pi$* (325-360 nm), polaron-$\pi$* (400-430 nm) and $\pi$-polaron (780-826) transitions (broadened due to free-carrier tail (Alan & Arthur 1995)), in the higher wavelength region) (Stafstrom et al. 1987). The results suggest that the prepared PANI is in the doped state.
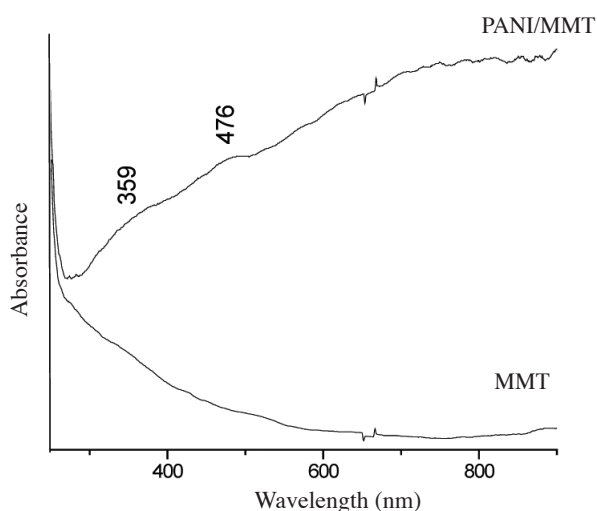
dispersed in energy. This explains the presence broad bands where polaron transitions are present (Wu et al. 2000).

The dc conductivity of PANI/MMT composite measured through a two-probe method is $2.1 \times 10^{-5}$ S cm$^{-1}$, which is in the range required for the application as ESD, by varying the dopant concentration and by the introduction of other dopants conductivity can be tuned to the required level. Nanocomposites of clay with polyaniline using $(NH_4)_2S_2O_8$ prepared via the same method shows conductivity in the range $10^{-6}$ only which proves (Chang et al. 1992) the superiority of present method.

In order to reconfirm whether polyaniline was formed within the clay layers, TGA/DTG (Thermogravimetric/ Derivative curves are shown in Figure 4) analysis of the clay as well as composite is done. In MMT, the huge weight loss in the 50-150°C regions was due to the removal of the physically adsorbed water molecules present. However at higher temperature the weight loss was more gradual without any well-defined inflection point. These losses can be assigned to the removal of chemisorbed water. The weight loss corresponding to the dehydroxylation of the clay sheet was found to occur in temperature range of 425-650°C. From the DTG of MMT the weight loss around 620°C was clearly seen as a dip (minimum) which is attributed to the dehydroxylation of silicate structure (Moreau et al. 1999). In PANI/MMT three stages of weight loss were seen and was clear as three minima in DTG. The weight loss below 100°C was due to loss of moisture, the dopant HCl loss occurs in the range 200 - 300°C and the polymer backbone chain breakage occurs in the range 400 - 600°C.
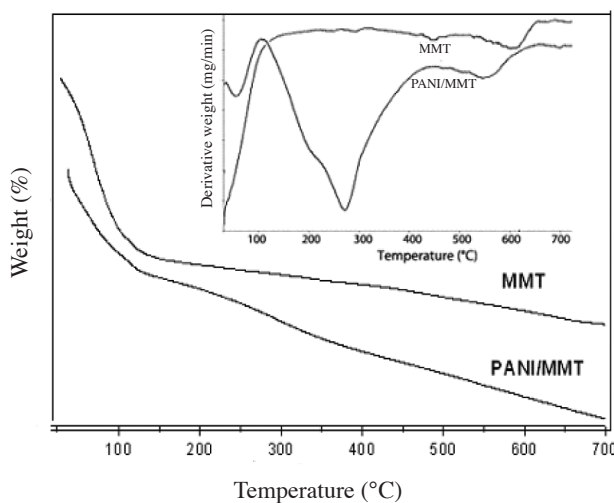


FIGURE 3. Diffuse reflectance spectra of PANI/MMT and MMT



FIGURE 4. TGA/DTG curves of PANI/MMT and MMT

Broadening is consistent with the delocalization of electrons in the polaron band promoted by an extended conformation of the polymer chains. Inside the clay layers which are apart in the nanometer scale, the interaction of different polymer chains are eliminated and the chain contraction is limited. This strengthens the interaction between the polarons, and the polaron bands become more

From DTG the minimum for polymer backbone chain breakage occurs at 551.7°C, and was greater than that reported for pure PANI (ES). From reports PANI (ES) and simple PANI (ES)/MMT mixture shows the minimum at 530.6°C (Lee & Char 2002). This shift of degradation towards higher temperature (of about 21.1°C) is expected because within the layers there is attractive coulomb

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interaction between the positive nitrogen of PANI layer and the negatively charged surface of the clay layer. Thus the nanocomposite formation and the thermal stability of the polymer inside the matrix are evident.

## CONCLUSIONS

PANI/MMT composite was prepared using $H_2O_2$ as the oxidant, which avoids the oxidative degradation of the polymer compared with the $(NH_4)_2S_2O_8$ oxidation and various analytical techniques prove the formation of PANI/MMT composite. FTIR and DRS analysis suggests that PANI was in the emeraldine form whereas XRD analysis supports intercalation. The conductivity obtained in the present study is suitable for the application as ESD and can be improved using various dopant concentrations. The high thermal stability was evident from TGA/DTG curves. Thus we offer an alternative, simple and economic cheap route for the preparation of PANI/MMT composite with tunable conductivity.

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