Preparation of intercalated polyaniline/clay nanocomposite and its exfoliation exhibiting dendritic structure

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Abstract. Intercalated composite of polyaniline and clay has been reported. The composite was prepared by *in situ* polymerization of aniline within the layers of 'illite' clay. The composite was characterized for its structural, spectral, and microscopic properties. At higher level of loading the layered structure of composite breaks forming exfoliated composite, revealing well-defined nanosized dendritic morphology of polyaniline.

Keywords. Polyaniline; illite; nanocomposite; exfoliated composite.

1. Introduction

Inorganic–organic nanostructured materials have become a field of intensive interest for scientists and industrialists due to their multifaceted properties (Gomez-Romero 2001). Recently, a new class of advanced materials based on conducting polymer–clay nanocomposites has added a novel dimension to this field (Skotheim *et al* 1998; Chandrasekhar 1999; Gangopadhyay and De 2000). These materials have given manifold high-tech applications on electrorheological fluids, anti-corrosion materials, molecular wires, sensor devices, smart windows, electochemical devices etc (Pinnavaia and Beall 2001).

Clays are natural substances having interesting properties due to their geometries, surface area and electrostatic charge. Incorporation of guest electroactive polymers such as polyaniline (PANI), polypyrrole (PPy) etc. into host clay particles has attracted great attention because of their better processibilty with colloidal stability, mechanical strength and novel electrical, catalytic properties (Alexandre and Dubois 2000). Intercalation and delamination methods have been used extensively to explain the nanomorphologies of composites (Kanatzidis *et al* 1987; Carrado and Xu 1998).

Intercalation of electronically conducting polymer in clays is widely studied by various scientists. Kanatzidis *et al* (1987) have reported first time a procedure termed '*in situ* intercalative polymerization' for preparing PPy–FeOCl nanocomposites. The interlayer adsorption of aniline into Cu^{2+} and Fe^{2+} montmorillonites from aqueous solutions was studied by Cloos and coworkers (Moreale *et al* 1985; Cloos *et al* 1979). Mehrotra and Giannelis have reported the intercalative polymerization of aniline using a Cu^{2+} exchanged synthetic hectorite but these nanocomposites are insulating form of PANI. The conducting form was obtained by exposing these composites to HCl vapors (Mahrota and Giannelis 1991). In another general method PANI was formed in the interlayer space of smectites by an ion-exchange process (Chang *et al* 1992). Synthesis of same compounds was reported by electrochemical procedure also (Ioune and Yoneyama 1987). The conductivity of PANI-clay composite prepared from anilinium–montmorillonite was found lower than the nanocomposites reported by Mahrota and Giannelis which was assumed due to high anisotropic conductivity in these materials. Carado and Xu have proposed another approach to synthesize PANI-hectorite nanocomposites by *in situ* hydrothermal crystallization (Carrado and Xu 1998). Recently, a solvent-free synthesis of polyaniline-clay nanocomposite is reported by mechanochemical intercalation method (Yoshimoto *et al* 2004). The electrorheological property of polyaniline-montmorillonite clay has been investigated extensively (Choi *et al* 2001; Lua and Zhao 2002). Apart from PANI-clay nanocomposites, many other systems have also been synthesized based on intercalation method (Mortland and Pinnavaia 1971). Besides intercalated composites, delaminated clay layers resulting into exfoliated structure have also attracted interest due to enhanced interaction of polymer–clay (Narayanan *et al* 2010). Exfoliated nanocomposites are more interesting because entire surface of clay layers could be used by polymer. Recently, some works have been reported regarding the enhancement of conductivity (Gök *et al* 2007; Bekri-Abbes and Srasra 2010) and anti-corrosive (Olad and Rashidzadeh 2008;

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Olad and Naseri 2009) properties in pani/clay composite. They showed that conductivity of pani/montmorillonite is higher than pure polyaniline due to polymerization of aniline in the clay interlayer with an extended chain conformation which effect the decreasing of π defects and the polymer bridges.

Our current work focuses on the enhancement of structural properties of PANI. We selected clay of river Ganga as host material due to its small particle size and easy availability. Aniline monomer acted as guest material. The composite was synthesized by *in situ* chemical polymerization method.

2. Experimental

Aniline (qualigen AR) was distilled prior to use. The clay was collected at a depth of two feet on the bank of river Ganga and a distance of five feet from the running water. The clay and PANI composites were made in 5, 10, 20, 40, 60, 80 PANI wt%. The monomer solution was made by adding 0·25, 0·50, 1·00, 2·00, 3·00 and 4·00 ml (separately) of pristine aniline (specific gravity 1·02) to 100 ml of 0·5 M HCl. Required amount of washed and dried clay (4·75, 4·50, 4·0, 3·0, 2·0 and 1·0 g respectively) was added to the aniline hydrochloride solution and stirred continuously for 3–4 h in ice-bath. Oxidizing agent $(NH_4)_2S_2O_8$ (0·2 M) (qualigen) was added slowly to start the polymerization. After completion of polymerization the colour of solution turned green. The solution was stirred on magnetic stirrer for 3–4 h. The mixture was left overnight at about 4–6°C. Next day, the suspension was poured off and the compact sediment of composite was redispersed in 0·2 M HCl. After the sedimentation of clay, the supernatant liquid was again poured off. The product was washed with 0·2 M HCl followed by distilled water repeatedly. The filtered powder was dried in oven at 50°C and characterized.

The energy dispersive X-ray analysis (EDAX) for elemental analysis was done using X-ray microanalyzer (Oxford Scientific). XRD were recorded on Bruker X-ray diffractometer D8 using CuK$_\alpha$ radiation. TEM photos were taken using JEOL 2010 HRTEM at 80 kV acceleration voltage; the samples for the TEM experiments were prepared by suspending dried samples in absolute ethanol. A drop of the sample suspension was allowed to dry on a copper grid (400 mesh, Electron Microscopy Sciences) coated with a carbon film. The a.c. electrical measurements were done on LCZ meter (Keithley Model-3330) at various frequencies at room temperature between two platinum contacts. The samples were compressed in form of pellet at 8 ton load. The specific conductance (conductivity) was calculated by normalizing the conductance with area (1·32 cm^2) and thickness (4–5 mm) of the pellet.

3. Results and discussion

3.1 Mineralogy

The energy dispersive X-ray analysis (EDAX) produced strong silicon (1·7398 KeV, Kα), oxygen (0·5249 KeV, Kα), and aluminum (1·4866 KeV, Kα) peaks, with some traces of potassium (3·3129 KeV, Kα), iron (0·7048 KeV, Lα KeV, Kα), titanium (0·4522 KeV, Lα KeV, Kα) and carbon (0·2774 KeV, Kα (figure 1). The chemical structure of illite form of clay is (K, H_3O) [Al_{2-x}(Mg. Fe)$_x$] ($Si_{4-x}Al_x$)O_{10}(OH)$_2$ with majority constituent SiO_2 (54·01%) and Al_2O_3 (17·02%) (Weaver 1973). The comparison of this information with our data demonstrates that the clay we used was in illite form. This was further confirmed by XRD study of the clay.

3.2 XRD studies

XRD spectra were recorded to determine the degree of swelling in clays and to monitor the formation and structure of these nanocomposites. Figure 2 shows wide as well as small angle XRD spectra of the composites. The wide angle spectra of clay show an intense peak at $2\theta = 26·72°$ (003 plane) (figure 2c), which is characteristic of 'illite' form of clay (Usuki *et al* 1993). As far as polyaniline is concerned, it is a semicrystalline material, which shows broad and less intense band in XRD spectra. The characteristic band is found at $2\theta = 25·4°$ (figure 2a) (Messersmith *et al* 1994). The peak is close to the peaks of illite and is not resolvable in the composite spectra due to superimposition (figure 2b). While the wide angle XRD is used to characterize the material, the low angle XRD is used to study the exfoliation mechanism of clay. The low angle spectra of pure clay (spectra 'a' in the inset of figure 2) show d001 peak at $2\theta = 9·28°$ (corresponding $d = 9·52$ Å). On intercalation (spectra 'b') the d001 2θ value moves to 7·72°, showing an increase in the
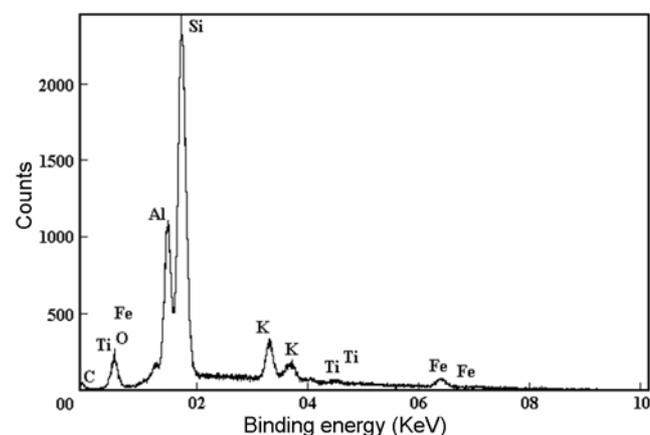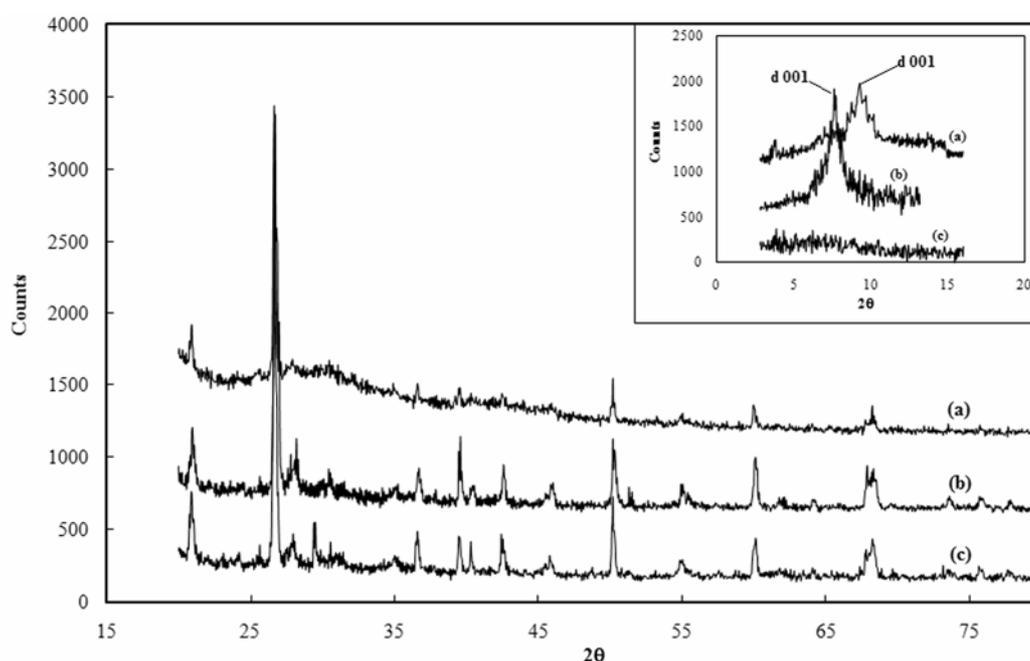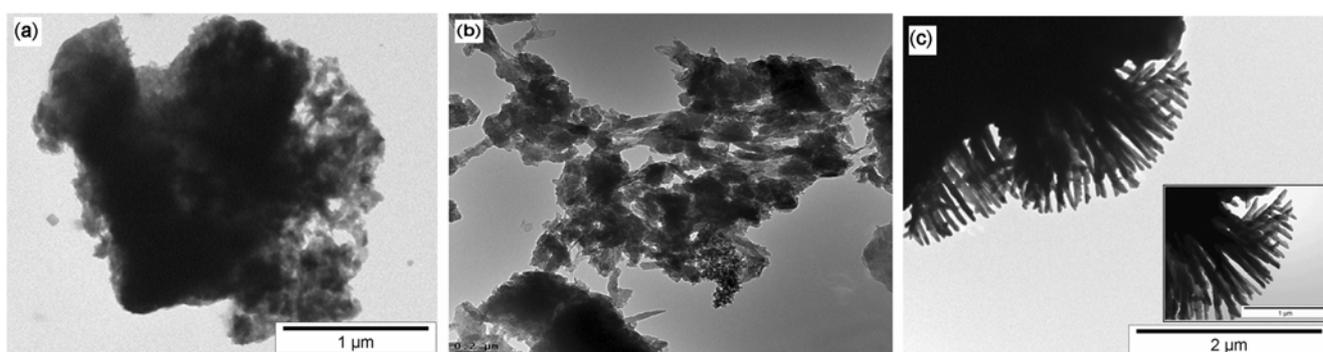

Figure 1. Energy dispersive X-ray spectra of illite.

Figure 2. XRD spectra of (a) pure polyaniline; (b) polyaniline-illite (10 wt% PANI) composite; (c) pure illite. (Inset: low angle XRD spectra of (a) pure illite; (b) polyaniline-illite (6 wt% PANI) composite; (c) exfoliated composite 50 wt% PANI.

Figure 3. TEM Image of (**a**) intercalated composite (10 wt% PANI); (**b**) partially exfoliated composite (40 wt% PANI); (**c**) exfoliated composite (50 wt% PANI).

interlayer spacing up to 1·14 nm in 6 wt% loading level. Whereas at higher loading level (spectra 'c') the gallery structure of the clay breaks due to pressure exerted by the intercalated polymer, leaving behind exfoliated composite. This leads in to disappearance of the peaks in the low angle XRD spectra.

3.3 *TEM*

TEM images are recorded for direct inspection of these composites. The TEM image of intercalated composite is given in figure 3a, which does not show any noteworthy structure of polyaniline. As the amount of monomer (and hence polymer) increased, the composite becomes exfoli-

ated (Chen 2004; Choi *et al* 2001). The TEM image at 40 wt% PANI (figure 3b) shows partially exfoliated nanocomposite. Delamination of clay galleries and beeping out of polyaniline from galleries is clearly seen at this stage. At 50 wt% PANI the rupture of clay galleries exposes the trapped polyaniline dendrites (figure 3c). The TEM images of these exfoliated composite show well defined dendritic structure of diameter ≈ 50 nm and length ≈ 700 nm (figure 4b).

3.4 *Electrical characterization*

The mechanism of composite construction is further verified by in-phase equivalent series resistance (ESR) meas-
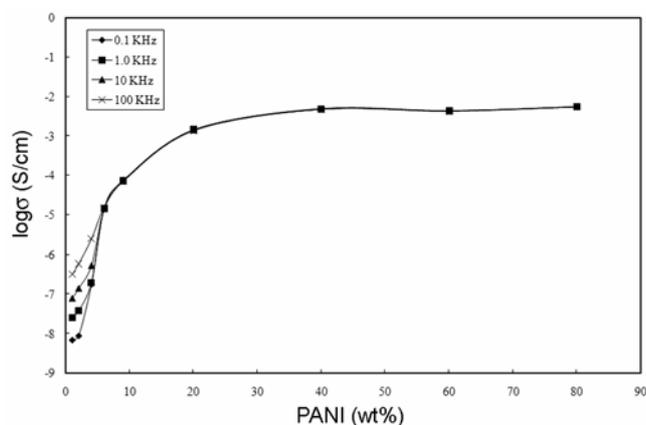
Figure 4. Variation of conductance of the composite as a function of amount of PANI loading at various frequencies (Hz) showing percolation behaviour.

urement. Figure 4 shows a plot between log of reciprocal of ESR vs. the loading level. This plot demonstrates typical percolation behaviour, with a percolation threshold around 9 wt%. The conductance of illite as measured by us at 100 Hz frequency is 3.94×10^{-9} S/cm, whereas the literature value is in the range of 10^{-7}–10^{-8} S/cm (Chen 2004). The electrical property of clay is mainly related to their ionic conductivity. The presence of hydrated cations in the interlayer space ensures conductivity in the interlayer region. Further, the conductance of the composite starts increasing rapidly as the polyaniline grows in the interlayer region. The conductance near the percolation threshold is around 10^{-3} S/cm. The percolation behaviour is observed due to formation of interpenetrating reticulate structure of the conducting polymer. At the percolation threshold the conductance of the material gets enhanced by many orders due to interconnection of conducting phase in the insulating matrix. High aspect ratio conductive fillers, like polyaniline dendrimers in current investigation, exhibit relatively low percolation threshold due to preferential alignment within the polymer matrix, which leads to anisotropic electrical properties favouring electron transport predominantly in the in-plane direction. A plateau in the conductance vs. composition plot has been observed after the percolation threshold. This behaviour is due to formation of enough channels and the number of charge carriers becoming limiting factor.

Further evidence of the netting of the polyaniline is its frequency dependence of the conductance. The conductance measured at 100, 1 K, 10 K and 100 K Hz is plotted in figure 4. A little frequency dependence at lower loading level, i.e. 2–6 wt%, may be due to interlayer capacitance and presence of hydrated cations. Formation of interconnecting polyaniline dendrites makes ohmic contacts, with disappearance of capacitive components and hence the frequency independence of conductance, at higher loading levels. Hence after percolation threshold we see superimposition of all the four plots in figure 4.

4. Conclusions

The results of current investigation demonstrated formation of intercalated composite of polyaniline in clay interlayer. The intercalation and exfoliation phenomenon of clay has been studied by various characterization techniques. The layered structure of the clay completely breaks after 50 wt% loading of PANI, showing unique dendritic growth of polyaniline.

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