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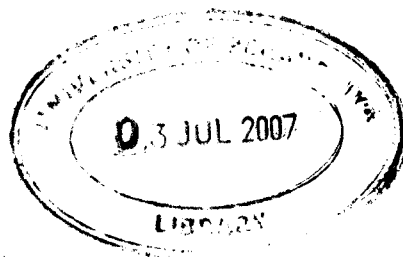
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# PREPARATION, CHARACTERIZATION, ELECTRICAL PROPERTIES AND APPLICATIONS OF 2:1 LAYERED SILICATE/CONDUCTING POLYMER NANOCOMPOSITES

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Looking ahead from the inception of the 21<sup>st</sup> Century, nanoscience can be visualized as a field of study that will contribute at the highest level to the scientific and technologies developments. Hybrid Organic-inorganic nanocomposites will play a major role in the development of advanced functional nanomaterials. Such materials can be synthesized by combination of the corresponding properties of the host material and the guest polymers. This thesis is concerned with the preparation, characterization, electrical properties and application of 2:1 layered silicate (montmorillonite (MMT)) and electrically conducting polymers (polyaniline (PANI) /polypyrrole (PPY)) nanocomposite. One series of PANI-MMT nanocomposite samples were prepared where PANI is present only within the intergallery space of MMT [EMS-MMT series]. For that, anilinium ions exchanged MMT was thoroughly washed several times with deionized water (Including washing procedure). A procedure for the successive introduction of PANI chains within the interlayer space of MMT was developed. The d-spacing, measured after heat treatment at various temperatures serves as a measure of the amount of polymer inserted in the clay intergalleries. FTIR spectroscopy reveals the presence of host-guest interactions of a hydrogen-bonded nature. In addition, particular attention has been given to the orientation of organic molecules when they are intercalated in the silicate structures. The DC conductivities of MMT containing successive introduced polyaniline samples i. e once, twice and thrice polyaniline loaded MMT (EMS1-MMT, EMS2-MMT and EMS3-MMT) are  $4.5 \times 10^{-5} \text{ S cm}^{-1}$ ,  $3.0 \times 10^{-4} \text{ S cm}^{-1}$  and  $1.0 \times 10^{-3} \text{ S cm}^{-1}$  respectively. They were found to increase with the amount of PANI intercalated. In addition, Parallel batch of experiments were carried out with 1:1 non-expandable clay (kaolinite). Anilinium ions supported on kaolinite tended to dislodge from the surface upon repeated washing with deionized water as shown by the absence of polymer formation on such samples upon treatment with the oxidant.

Another series of nanocomposites of PANI-MMT were prepared in which PANI is present within the interlayers as well as is present adsorbed on to the external surfaces of the clay particles (excluding washing procedure) [ES-MMT (2) series]. Conductivities of the corresponding samples prepared by excluding the washing procedure had the values  $4.0 \times 10^{-4} \text{ S cm}^{-1}$ ,  $1.0 \times 10^{-2} \text{ S cm}^{-1}$  and  $1.0 \times 10^{-1} \text{ S cm}^{-1}$  respectively. The ES-MMT (2) members show higher electronic conductivities than EMS-MMT members. The FTIR band appears around  $1140 \text{ cm}^{-1}$ , which is assigned to B - NH<sup>+</sup> = Q, gives supportive evidence whether the synthesized material is a good conductor or not. AC impedance analysis shows that ES-MMT (2) system posses electronic conduction and it increases with successive loading with polyaniline. Under the identical conditions of sample preparation, the d-spacing enhancement upon the polymer intercalation is the same regardless of whether the polymer is present only within intergalleries or both internal and external surfaces of MMT [ES-MMT]. The decrement of Si-O-Si band area in the progressively intercalated samples

shows the continued incorporation of PANI to the interlayer space of MMT. This trend is not such in the kaolinite/polyaniline [ES-Kn] system. The influence of  $\text{AN}^+(\text{mol}): \text{MMT}(\text{g})$  ratio on the formation of ES-MMT series of nanocomposite is also studied. Ratio of the number of moles of anilinium ions to the mass of the MMT clay influences greatly on the formation of conducting form of polyaniline of these classes of materials. When the ratio of  $\text{AN}^+(\text{mol}): \text{MMT}(\text{g})$  is decreased, the band at  $1140\text{ cm}^{-1}$ , which is attributed to the  $\text{B-NH}^+=\text{Q}$ , disappears, confirming the reduction of the conductivity. In addition, a batch of experiments was carried out with non-aqueous medium. In order to render the clay more organophilic and intercalate more anilinium ions, instead of water Dimethylformamide (DMF), highly dipolar organic solvent is used. It is found that samples prepared under such conditions neither exhibit well crystalline peak in XRD analysis nor possess high conductivity. Cyclic voltammetric studies reveal that the electroactivity of the composite material is limited by the accessibility of solution species into the intergalleries in a diffusion-controlled manner. The EIS studies reveal that the ES-MMT (2) members have both electronic and ionic conductivities with similar transport numbers even when the polymer is in its fully electronically conducting state. Four different and mutually independent techniques used to characterize the composites give strong evidence to confirm that there is a limit to the repetitive polymer loading within the intergalleries of clay particles. The limited interspacing with all repeated polymer-loading may be due to the saturation of all ion-exchangeable sites of montmorillonite by the positive charges of the polymer. For better comparison, Fuller's earth clay and polyaniline system is also studied.

In addition, polypyrrole/montmorillonite (PPY-MMT) nanocomposite is further studied to understand variation of chemical and physical properties. Pyrrole molecules were exchanged for lithium ions in MMT. As in the case of anilinium exchanged montmorillonite, similar procedure was followed to polymerize the pyrrole. FTIR spectra of the corresponding samples prepared by including washing procedure do not show the characteristic bands of polypyrrole while that of PPY-MMT series followed by excluding the washing procedure shows giving indication of the formation of polypyrrole in *in-situ* and *ex-situ* of MMT. The ionic conductivity of PPY-MMT (excluding washing procedure) is higher than that of lithium ion exchanged MMT. Further, this PPY-MMT nanocomposites possess high electronic conductivity.

The clay-polymer nanocomposite can also be prepared by spontaneous polymerisation of the monomer within the interlayer spaces. Cupric ion-exchanged montmorillonite [Cu(II)- MMT] is first prepared. The Cu(II)-MMT sample is then treated with 0.1 M pyrrole in 0.1 M HCl(aq) solution. This has resulted in the intercalation of pyrrole within the interlayer regions of Cu(II)- MMT host followed by one-step spontaneous polymerization to result in Cu(I)-PPY-MMT nanocomposite material. Interestingly, pyrrole ions are polymerised spontaneously within the confined environment of Cu(II)-MMT but the same does not take place in the aqueous solution containing Cu(II) ions. This Cu(I)-PPY-MMT material possesses both ionic and electronic conductivity and ionic conductivity is predominately due to  $\text{Cu}^+$  ions. This has been shown by the assembly of an electrochemical cell with Cu(I)-PPY-MMT material. The  $\text{Cu}^+$  ions migrate through material forms  $\text{Cu}_2\text{SO}_4$  at the cathodic plate giving evidence that the motion ions are  $\text{Cu}^+$ . The conjugation length and the electronic conductivity decrease as the temperature is increased as confirmed by the FTIR spectroscopy. However, the ionic component of the conductivity increases with temperature. These materials behave as fast ion conductors. The effect of the cation, clay composition and the solvent for the synthesis of these types of materials is also studied.