SYNTHESIS, CHARACTERIZATION AND VOLTAMMETRIC STUDIES OF POLYANILINE-ILLITE CLAY NANOCOMPOSITE

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Abstract-Clay obtained from the banks of the river Thamiraparani was used for the synthesis of polymer-clay nanocomposite. EDAX analysis of the clay sample predicted its mineralogy to be Illite clay. Nanocomposite was synthesized by polymerizing aniline by chemical oxidation method using potassium perdisulphate and by taking minimum quantity of illite clay. The as prepared polymer–clay nanocomposite showed good solubility in DMF and it was characterized by FTIR, UV–visible, XRD and SEM. The spectral studies demonstrated that aniline has been polymerized to its conducting emeraldine form. The interaction between clay and the polymer in the nanocomposite has been confirmed by the shift in amine vibrational peak to 3531cm^{-1}. The XRD studies show an increase in d-spacing of pristine clay from 0.247nm to 0.313nm in the nanocomposite indicating intercalation of Pani into the clay galleries. It also revealed the formation of composite in the nanoscale as indicated by the broadening of the peaks and the average particle size was found to be 38.6nm. SEM and EDAX analysis showed the presence of both the spherical Pani and layered illite in the nanocomposite. CV studies exhibited good adherent behaviour on electrode surface at pH 1.0 with two oxidation peaks at 0.3 and 0.8V and two reduction peaks at 0.67 and 0.05V showing that the redox process is reversible and the nanocomposite is electrochemically stable.
Keywords: Illite, Nanocomposite, UV, FTIR, XRD, TGA , SEM and CV.

1. INTRODUCTION

Development of Polymer – nano sized filler composites is an important milestone in the field of nanotechnology as these hybrid materials have a wide spectrum of applications ranging from providing photo-catalyst activation [1] and conductivity [2, 3] to improving melt processability [4-7] and moisture barrier properties [8]. Among the numerous inorganic fillers, smectite clays [9] are the abundantly used ones as they have unique layered structure, high mechanical strength, good expandability, chemical resistance as well as cation exchangeability besides being natural, abundant and inexpensive minerals. The combination of conducting polymers with nanoclays having different characteristics opens a way to new hybrid materials showing novel properties. It has already been reported in literature that these conducting polymer/nanocomposites based on nanoclays have gained attention due to their ability to improve mechanical, [10,11] thermal, [12,13] barrier, [14,15] fire retardant [16-20] and biodegradability [21] properties of polymers. The special properties of these materials are due to their size and high relative surface to volume ratio. A small weight percentage of layered silicates that are properly dispersed throughout the polymer matrix thus creates a much larger surface area for polymer-filler interfacial interactions than do conventional composites [22]. These properties have led to considerable interest in theory and simulations addressing the preparation and properties of these materials [23-30], and they are also considered to be unique model systems to study the structure and dynamics of polymers in confined environments [31-37]. Our present work focuses on making use of well established and extensively studied conducting polymer viz., polyaniline to synthesise these hybrid nanocomposites with locally available clay as fillers and to establish their morphology, interaction and electrochemical behavior through spectral, thermal, microscopic and electrochemical techniques. The choice of the polymer is not only for the extensive literature available but also for their simple synthesis, high conductivity and excellent environment stability. Our attempt to make use of locally available clay is a step towards exploring the indigenous resources.

2.EXPERIMENTAL

The clay was collected at a depth of two feet on the bank of river Thamiraparani and a distance of five feet from the running water and was purified as per the standard procedure [38]. Potassium perdisulphate (EMerck) and hydrochloric acid were used without further purification. Aniline was distilled under vacuum prior to use.

2.1 Synthesis

The polymer clay nanocomposite was synthesized by taking minimum quanitity of purified clay (0.25g). Bulk polymerization was carried out by adding clay into a mixture of 9 ml of 0.5M aniline and 6ml of 1M hydrochloric acid and made upto 200ml using conductivity water. To this the oxidant viz., potassium peroxodisulphate was added with constant stirring. The change in color from grey to green was indicative of the polymerization of the monomer. The reaction was further continued for 3 h by stirring. The polymer clay nanocomposites obtained were then maintained at a temperature of ±5ºC for 24 hours and washed

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several times with distilled water, until a colourless wash solution without oligomers was obtained. All the materials were dried at room temperature.

2.2 Characterization

UV-Vis spectra of the samples, which were dispersed in DMSO were recorded on a JASCOV530 UV-Vis spectrophotometer. FTIR spectroscopy (Model: SHIMADZU) of the nanocomposite was studied in the frequency range of 400–4000 cm^{-1}. X-ray diffraction (WXRD) was carried out using the Bruker AXS D8 Advance using CuK$_\alpha$ radiation source energized at 40 KV (λ=0.154 nm). Samples were scanned at a rate 29.5° sec^{-1} from 1° to 80° in 2θ. Morphological study was carried out using scanning electron microscope (SEM Model: JEOL JSM 6360) operating at 25 kV. TGA of the samples were taken using Perkin Elmer, Diamond TG/DTA with programmable rate of 0.01-100°C/min. Cyclic voltammetry studies were carried out by CH Instrument Electrochemical workstation. TEM studies were made using TEM instrument (Model:PHILIPS – CM200) operating at 20-200 kv with a resolution of 2.4A°.

3. RESULTS AND DISCUSSION:

3.1 Minerology of clay

Minerology of the clay was found out by using FTIR, XRD, SEM and EDAX measurements. FTIR peak assignments as per table.1 indicates that the purified clay is of Illite mineral type whose Si-O stretching frequency is as per literature value [39]. XRD pattern of the clay mineral again coincides with the standard value for illite (2θ = 9.28°(001), 26.72°(003)) [40]. From the mass and atom percentage of the various elements present obtained from EDAX the empirical formula as well as composition of the clay mineral were arrived at. EDAX of the clay sample is shown in fig.1a. It can be observed that the sample contains SiO_2, Al_2O_3, Fe_2O_3, MgO, K_2O as well as H_2O. The empirical formula calculated on the basis of EDAX data is $K_{3.1} [Al_{8.6}(Mg.Fe_{3.9})] (Si_{18.3} O_{22.7})(OH)_4$. Comparison of our data with standard values demonstrates that the clay mineral we used was illite . Thus the clay obtained and purified was confirmed to be Illite from all the characterisation techniques. SEM micrograph of the clay sample shown in fig.1b indicates rock like spherical morphology with evenly distributed pores.

Table1

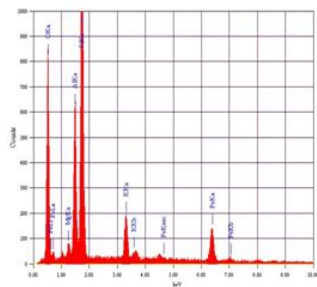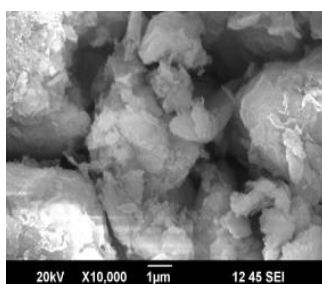| Assignments	Peak position(cm^{-1})
interlayer and intralayer H-bonded O-H	3550 & 3428
H-O-H bending	1641
Si-O stretching	1033
Al-O stretching	914
Si-O-Al stretching	536

Fig.1a.   Fig.1b.

3.2 UV-Vis and FTIR spectral studies of the nanocomposite:

From the UV-Vis spectra of the polymer and the nanocompsite shown in fig.2, it can be seen that the n-π* band observed at 270nm in the polymer has been shifted to longer wavelength in the nanocomposite while the polaron band indicating the formation of conducting form of the polymer has been blue shifted. This blue shift can be attributed to the linear arrangement of Pani within clay galleries.

FTIR spectra (figure not given) of the nanocomposite shows the characteristic peaks of both clay and the polymer indicating the presence of both the constituents in the nanocomposite. The Si-O-Si stretching vibration of clay matrix at 1033cm^{-1}[39] is merged with peak at 1132cm^{-1}in the composite and this peak appears as a broad one. This is an indication of the strong interaction between clay and polymer in the nanocomposite. The interaction between the clay and the polymer has also been confirmed by a slight shift in the amine vibration from 3500 [41] to 3531cm^{-1} in the nanocomposite.
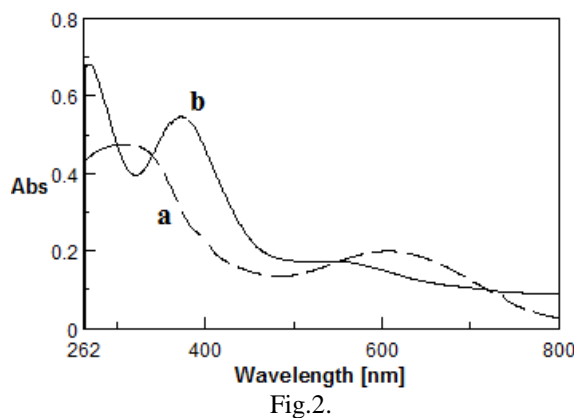
Fig.2.

4. SEM AND EDAX ANALYSIS

SEM micrograph of the nanocomposite is shown in fig.3a. It shows the granular spherical morphology of the clay with the rod like polymer intercalated into it. Thus the there is a slight change in the morphology of the clay and polymer in the composite. EDAX (fig.3b)shows the presence of both clay and the polymer in the nanocomposite.
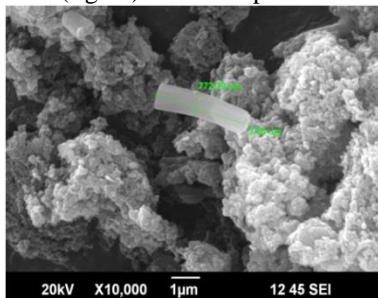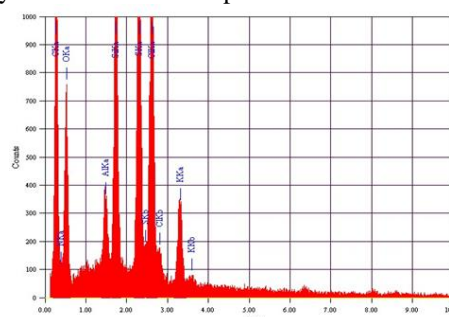

Fig.3a   Fig 3b.

5. XRD ANALYSIS

From the position of the low angle diffraction peaks and using Bragg's equation average d-spacing of the clay and the nanocomposite were calculated (table2). It can be seen that there is a slight increase in the d-spacing of the clay in the nanocomposite indicating that the clay galleries have expanded for the intercalation of the polymer. The average crystallite size calculated using Debye-Scherrer's equation is found to be 38.6nm (table 2) showing the formation of composite in the nanoscale. This has also been confirmed by broadening of the XRD peaks.

Table 2:

Sample	Average d- spacing(nm)	Crystallite size(nm)
Illite clay	0.247	10.22
Pani-Illite nanocomposite	0.313	38.6

6. ELECTROCHEMICAL CHARACERISATION

Cyclic voltammograms were recorded at room temperature by employing a three-electrode cell with platinum wire as an auxiliary electrode, an Ag/AgCl electrode as the reference electrode and nanocomposite coated glassy carbon (GC) as the working electrode. The CV were obtained in 1.0 M H_2SO_4 by casting the nanocomposite on GC working electrode and scanned between -1.2 to 1.2 V at scan rates between 50 and 500 mV/s. The voltammetric response were examined for charge-transfer cofactors observed for the modified GCE as a function of experimental parameters like pH and scan rate variation.

The well defined nature of the CV(fig 4) shows that the non conducting nature of the clay has been overridden by the conducting Pani within the inter layer spaces making the nanocomposite an interesting electrode material. CV depicts two well-defined oxidation-reduction (redox) peaks at 50mV/s. Two oxidation peaks at 0.3 and 0.8V and two reduction peaks at 0.67 and 0.05V. Peak potential separation has been used to determine the reversibility of an electrochemical redox reaction. Generally speaking, smaller peak potential separation usually relates to a reversible reaction,while larger peak potential separation is often observed in irreversible reactions [42]. Since only a small peak potential difference of 0.37V is observed the redox process taking place at the electrode can be said to be a reversible one.
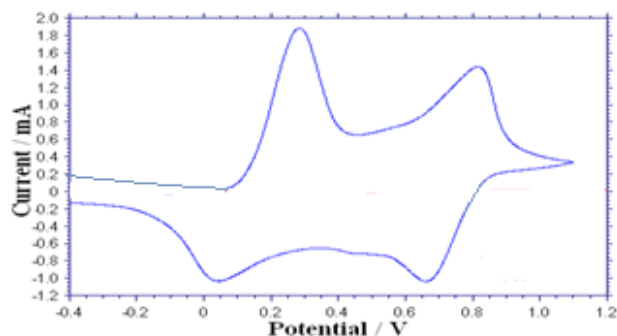
Fig 4.

7. EFFECT OF PH

The effect of pH on the voltammetric response was studied to determine the catalytic condition of the redox process at the nanocomposite modified GCE in the range of pH 1.0 to 13.0, using pH buffer solutions adjusted to desired condition. Fig 5 shows the effect of pH. Background current or capacitative current is generally pH dependent. It usually increases with increase in acidity at the Pani-Illite nanocomposite/GCE. As a result, the redox peaks become smaller as pH is increased from 1.0 to 13.0. The optimum pH range for good sensitivity response appears to be pH 1.0 consequently pH1.0 is chosen for subsequent studies.
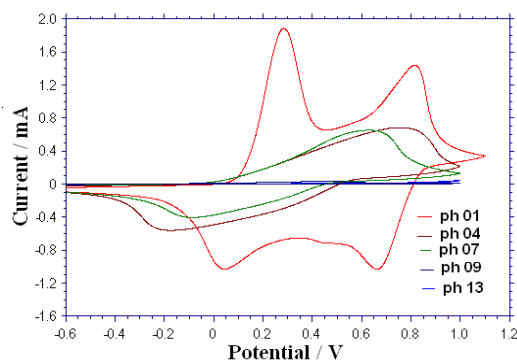

Fig 5.

8. EFFECT OF SCAN RATE

The effect of varying scan rate (fig.6) ranges between 50 mV/s and 500 mV/s was studied at the nanocomposite modified GCE in 1 M H_2SO_4. With an increasing scan rate the peak current also increased thus indicating good adherence of the nanocomosite onto the GC electrode surface, the peak current separation increased, and also the peak potential shifted slightly with the anodic peak to positive and the cathodic peak to negative potential directions. This is because the charging and discharging of the electro-active conducting polymer is rate determining. From the plot of logarithm peak current against logarithm of scan rate as shown the current increases approximately in linear approach as described by Y= 0.501X -0.952; R^2=0.994 for the anodic peak currents. The experimental slope is 0.501 suggests that the redox reaction of Pani in the nanocomposite is adsorption controlled [43].
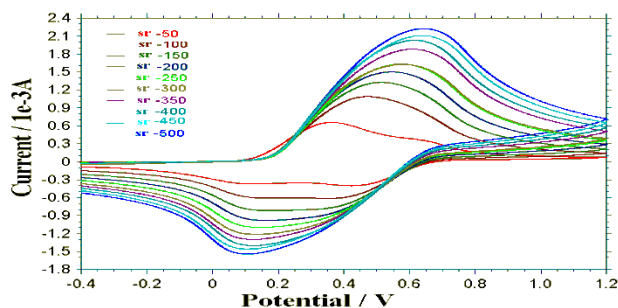

Fig 6.

9. CONCLUSION

Clay obtained from the banks of the river Tamiraparani, Tamilnadu, India was purified and characterized and the mineralogy was found to be Illite. Minimum quantity of this clay was used to synthesise Pani-Illite nanocomposite by bulk polymerization using potassium peroxodisulphate as external oxidizing agent. The intercalation of the polymer onto the clay layers has been confirmed by increase in the d-spacing as evidenced from XRD data and UV . Formation of the composite in nanoscale has also been confirmed by XRD, UV and SEM. The interaction between clay and polymer has been confirmed by UV-Vis and FTIR spectral studies. Electrochemical result shows that the nanocomposite modified GCE is highly sensitive and stable in electrochemical measurement. Voltammograms show that redox reaction of Pani in the nanocomposite is reversible and adsorption controlled. Electrochemical response was dependent significantly on the scan rate and pH.

10. ACKNOWLEDGEMENTS

11. REFERENCES:
[1]   Drew C., Bruno F.F., Wang X., Ku, B.C., Samuelson L.A., Kumar J., Polymeric Mater: Sci. Eng. 91 (2004) 945.
[2]   Drew C., Wang X., Senecal K., Schreuder Gibson H., He J., Tripathy S., Samuelson L., ANTEC 58th, 2 (2000)1477.
[3]   Ki H. S., Sung J. H., Choi H. J., Cin I. J., Jin H.J., Polymer Preprints, 46 (2005), 736.
[4]   Hwang W.G., Wei K.H., Wu C.M., Polym. Eng. Sci. 44 (11) (2004), 2117.
[5]   Hambir S., Bulakh N., Jog J.P., Polym. Eng. Sci., 42 (2002) 9, 1800.
[6]   Jayraman K., Maechant D., Antec (2001) 654.
[7]   Wang K. H., Choi M. H., Koo C. M., Xu M., Chung I. J., Jang M. C., Choi S.W., Song H.H., J. Polym Sci. Part B: Polym. Phys., 40 (2002) 1454.
[8]   Lu C., Mai Y. W., PRL, 95 (2005) 088303-1-4.
[9]   Vermogen A., Varlot K.M., Séguéla R., Macromolecules 38 (2005) 9661.
[10] Bureau M. N., Denaul, J., Antec 2001 Conference proceedings, II (2001) 2125.
[11] Svoboda P., Zeng C., Wang H., Lee L. J., Tomasko D. L., J Appl Polym Sci 85 (2002)1562.
[12] Zanetti M., Camino G., Reichrt P., Mülhaupt R., Macromol. Rapid Commun., 22 (2001) 176.
[13] Modesti M., Lorenzetti A., Bon D., Besco S., Polym. Degr. Stab 91 (2006) 672.
[14] Gorrasi G., Tortora M., Vittoria V., Kaempfer D., Mülhaupt R., Polymer 44 (2003) 3679.
[15] Osman M.A., Atallah A., Macromol Rapid Commun 25 (2004) 1540.
[16] Hull T.R., Price D., Liu Y., Wills C.L., Brady J., Polym Degr Stab 82 (2003) 365.
[17] Qin H., Zhang S., Zhao C., Hu G., Yang M., Polymer 46 (2005) 8386.
[18] Gilman J.W., Jackson C.L., Morgan A.B., Harris Jr. R., Manias E., Giannelis E.P., Wuthenow M., Hilton D., Phillips S.H., Chem Mater 12 (2000) 1866.
[19] Zanetti M., Kashiwagi T., Falqui L., Camino G., Mater 14 (2002) 881.
[20] Tang Y., Hu Y., Li B., Liu L., Wang Z., Chen Z., Fan W., J Polym Sci Part A: Polym Chem 42 (2004) 6163.
[21] Sinha Ray S., Yamada K., Okamoto M., Ueda K., Nano Lett 2 (2002)1093.
[22] Chen J.S., Poliks M.D., Ober C.K., Zhang Y., Wiesner U., Giannelis E.P., Polymer 43 (2002) 4895.
[23] Dabrowski F., Bourbigot S., Delbel R., Bras M.L., Eur Polym J 36 (2000) 273.
[24] Baljon A.R.C., Lee J.Y., Loring R.F., J Chem Phys 111 (2000) 9068.
[25] Ginsburg V.V., Singh C., Balazs A.C., Macromolecules 33 (2000) 1089.
[26] Kuznetsov D., Balazs A.C., J Chem Phys 112 (2000) 4365.
[27] Lee J.Y, Baljon A.C.R, Sogah D.Y., Loring R.F., J Chem Phys 112 (2000) 9112.
[28] Singh C., Balazs A.C., Polym Int 49 (2000) 469.
[29] Manias E., Chen E., Krishnamoorti R., Genzer J., Kramer E.J., Giannelis E.P., Macromolecules 33 (2000) 7955.
[30] Ginsburg V.V., Balazs A.C., Adv Mater 12 (2000) 1805.
[31] Mittal V., Materials 2 (2009) 992.
[32] Hackett E., Manias E., Giannelis E.P., Chem Mater 12 (2000) 2161.
[33] Anastasiadis S.H., Karatasos K., Vlachos G., Manias E., Giannelis E.P., Phys Rev Lett 84 (2000) 915.
[34] Zax D.B., Yang D.K., Santos R.A., Hegmann H., Giannelis E.P., Manias E., J Chem Phys 112 (2000) 2945.
[35] Manias E., Kuppa V., In: Vaia R.A., Krishnamoorti R., editors Polymer nanocomposites ACS symposium series 804 Oxford: Oxford University Press; (2002).
[36] Kuppa V., Manias E., Chem Mater 14 (2002) 2171.
[37] Manias E., Kuppa V., Colloids Surf A 187 (2001) 509.
[38] Bergaya, F., Theng, B.K.G., Lagalay, G., 2006. Handbook of Clay Science, first ed. Elsevier, Newyork 766-789 .
[39] Lenka Vaculíková, Eva Plevová, Acta Geodyn Geomater 2 (2005) 167.
[40] Lugwisha E.H.J,Tanz. J. Sci. 37 (2011) 167.
[41] Ricardo H. Goncalves, Wado Herving Schreiner , Edson R. Leite Langmuir Articl 26 (2010)11657.
[42] Gao Y, Chen S, Cao D, Wang G, Yin J. J Power Sources 195(2010) 1757e60.
[43] Fusalba F, Gouérec P, Villers D, Bélanger D. J ElectrochemSoc 148(1) (2001) A1e6.

List of figures and tables: