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Adsorption of dye on clay and its thermal studies

Tanushree Choudhury*, N.M.Misra

Dept. of Applied Chemistry, Indian School of Mines University, Dhanbad - 826 004, (INDIA)

E-mail: tanu_c79@yahoo.co.in

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ABSTRACT

Dyes are flat polyaromatic molecules that bind selectively to the clay surface over a wide a wide pH range. Dyes are generally hydrophobic in nature and generally adsorb in aggregates at the flat silica faces of clay mineral which is made hydrophobic by cation exchange process. The present work involves use of natural turmeric dye which is adsorbed on clay surface. The role of the resulting hybrid material as potential indicator is studied for the development of biosensor. The thermal stability is studied using DSC. Binding of clay and dye is studied using FTIR. Morphological structure of the hybrid material is studied using SEM.

KEYWORDS

Nanoclay;
Exfoliation;
Turmeric dye;
Hybrid;
Thermal stability.

INTRODUCTION

Polymer layered silicate nanocomposites are a new class of materials with dimension typically in range of 1-100 nm. Ultra fine phase dimensions of the nanocomposites leads to new and improved properties such as thermal, mechanical, flammability, barrier and solvent resistance are significantly higher than those achieved in traditional filled polymers[1-5].

Structure and properties of surfactants used in fabrication of organo montmorillonite could play a very important role in determining the properties of final polymer clay nanocomposites[6]. If the processing temperature is higher than the the thermal stability of organoclay, decomposition will occur, altering the interface between filler and matrix polymer. To obtain nanocomposites without thermal degradation during the process, use of thermally stable organoclay is proposed and much research has been directed towards the preparation of organoclays that are thermally stable at high temperature[7].

Dyes are generally hydrophilic in nature and generally adsorb in aggregates at the flat silica faces of clay mineral which is made hydrophobic by cation exchange process. Many works have been carried out in quantitative aspects and model the adsorption behaviour of dye molecules to the clay surface[8]. In the present work, natural turmeric dye (natural yellow) is adsorbed on to the surface of clay where clay platelets have been tried to exfoliate using a natural dispersant. The enhanced thermal stability of the green material developed is studied using DSC.

EXPERIMENTAL

Materials

Clay used in this experiment was mainly Bikaner Bentonite. Natural dispersant (soap stone powder) was

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used to disperse clay and was obtained from natural source. Turmeric dye which was used to adsorb on clay surface was obtained from natural source. NaOH and HCl were obtained from Glaxo Laboratory.

Method

A few drops of turmeric dye were added to clay suspension (dispersed by natural dispersant and untreated clay), stirred for 2-3 hours, so that the dye gets adsorbed. It was then centrifuged and dried at room temperature.

Turmeric dye as indicator was observed in presence of both acid and alkali. The reaction was reversible showing dark red in alkaline medium (few drops of 0.1N NaOH) and yellow in acid medium (few drops of 0.1N HCl) which is the colour of the dye. When turmeric dye was added to untreated clay, dark red colour was observed which was not so intense in clay dispersed by natural dispersant one.

Turmeric $\xrightarrow{OH^-}$ Dark red

(yellow) $\xleftarrow{H^+}$

Instrumentation

DSC of dye adsorbed clay hybrid material was performed on Differential Scanning Calorimeter Perkin Elmer DSC-7 under nitrogen atmosphere at a scan rate of 20^0C/min. SEM was taken using Hitachi S-3400N Japan using 3 KV. IR was done on Perkin Elmer FTIR spectrometer Spectrum 2000.

RESULTS AND DISCUSSION

IR analysis

Action of alkali and acid on turmeric can be inferred from IR spectra. IR spectra reveal the presence of aromatic esters in turmeric dye as in Figure 1. The group wave numbers corresponding to this are C=O stretch at 1730-1715 cm^{-1}, C-C-O stretch at 1310-1250 cm^{-1}, and O-C-C stretch at 1130-1000 cm^{-1}. Presence of $-CH_2$ asymmetric peak at 2928.49 cm^{-1} and $-CH_2$ symmetric peak at 2857.45 cm^{-1} are shown. Presence of Isopropyl alcohol is also indicated at 1384 cm^{-1}.

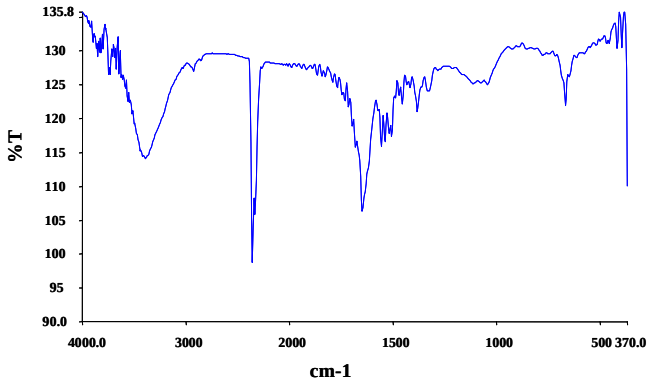

Figure 1 : IR spectrum of dye

In the presence of acid, IR spectrum of dye as in Figure 2 shows asymmetric CO_2 stretch at 1635.85 cm^{-1}. Inorganic carbonate at 1495.01 cm^{-1}.

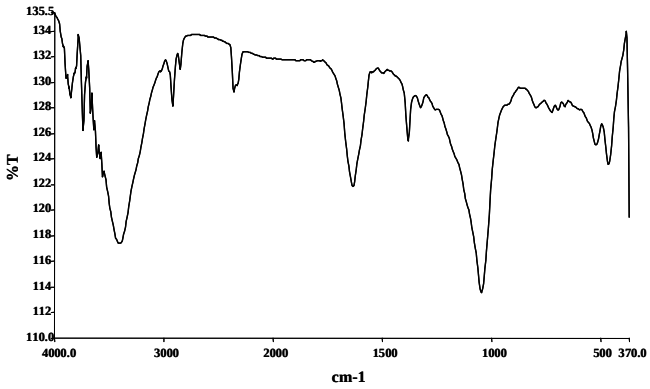

Figure 2 : IR spectrum of dye+acid

In the presence of alkali, apart from asymmetric CO_2 stretch and symmetric CO_2 stretch, presence of 1^0 alcohol at 1053.60 cm^{-1} (C-O stretch) is observed as in Figure 3. Thus it indicated the formation of enol. Thus the purpose of indicator is being achieved.

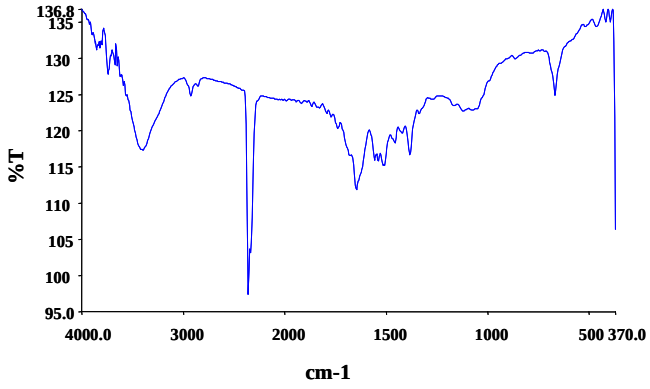

Figure 3 : IR spectrum of dye+ alkali

Dye adsorbed on clay dispersed by natural dispersant shows the following changes.

Pure clay shows $-CH_2$ asymmetric peak at 2927.72

cm^{-1}, $-CH_2$ symmetric peak at 2856.47 cm^{-1}, -OH group at 3500 cm^{-1}, silanol O-H stretch at 3700-3200 cm^{-1}, Si-O-Si asymmetric stretch at 1041 cm^{-1}, Si-O stretch at 940 cm^{-1}, Si-O-Si symmetric stretch at 801.11 cm^{-1}, Si-O-Si bend at 468.53 cm^{-1}. When clay is treated with natural dispersant, Si-O stretch peak at 940 cm^{-1} is lost. When dye is adsorbed on this dispersed clay, Si-O-Si symmetric stretch at 801.11 cm^{-1} is lost thus indicating reaction between clay surface and dye molecule. This has been shown in Figure 4.

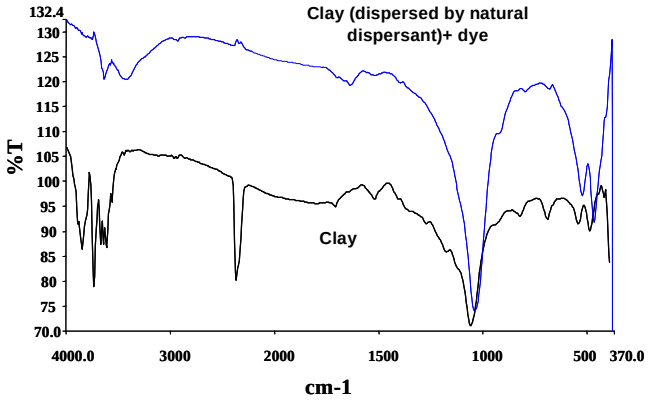

Figure 4 : IR spectrum of clay+dye compared with pure clay

DSC analysis

Untreated clay with dye showed two endotherms at 90^{0}C and another at 150^{0}C. For dye adsorbed on clay dispersed by natural dispersant, moisture loss peak is very nuch reduced around 90^{0}C and another endothermic peak at around 150^{0}C. Comparing these two with clay dispersed by natural dispersant shows only one endotherm at 120^{0}C. Thus it can be said that dye adsorbed on clay dispersed by natural dispersant is thermally more stable as shown in Figure 5.

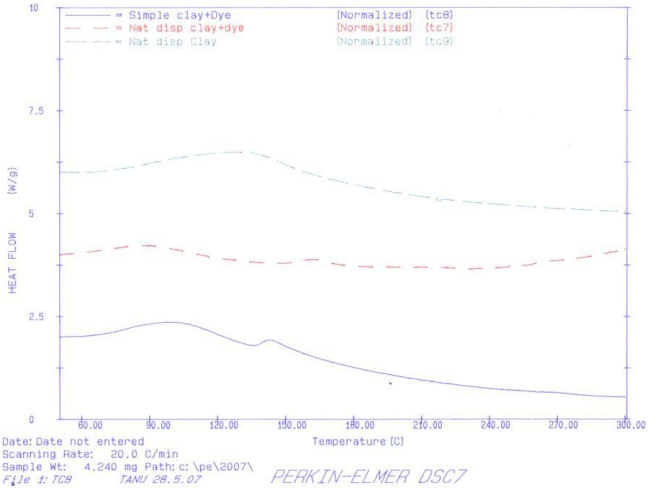

Figure 5 : DSC showing comparison between thermal stability of clay hybrid materials and pure clay

Clay dispersed by natural dispersant shows enhanced thermal stability compared with pure clay as is evident from Figure 6 thus giving a thermally stable organoclay.

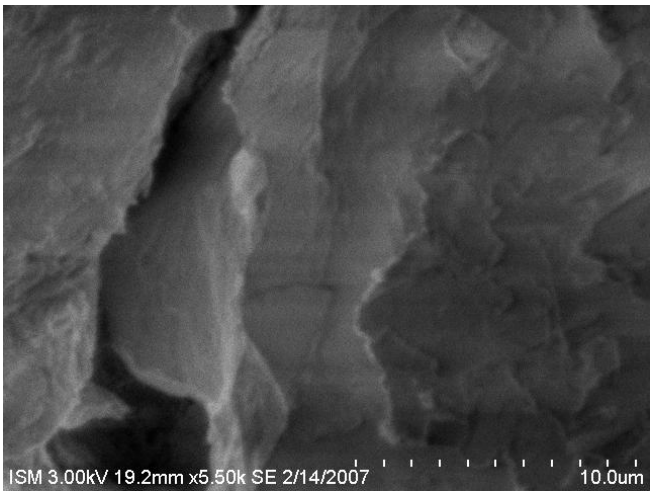

Figure 6 : DSC showing thermal stability of orgamoclay

SEM analysis

SEM micrograph of the dye adsorbed clay hybrid material as shown in Figure 7 shows considerable exfoliation of clay platelets.

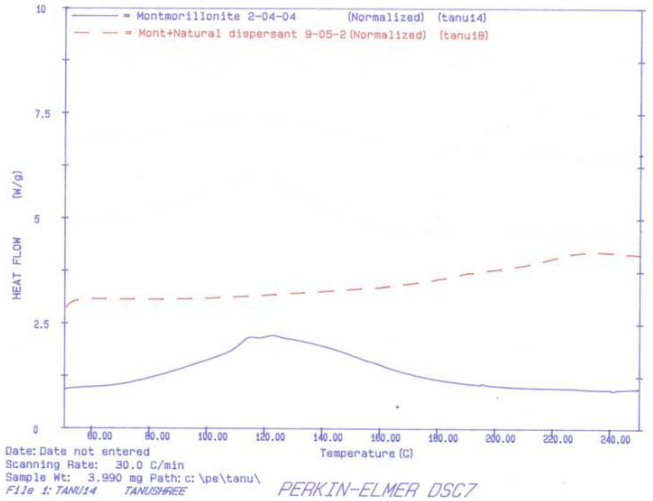

Figure 7 : SEM of dye adsorbed clay hybrid material

CONCLUSION

Natural dispersant has proved to be a good dispersant in exfoliating clay platelets and produces a thermally stable organoclay. Dye adsorbed clay hybrid

material shows enhanced thermal stability compared to pure clay. This functional hybrid material can be employed in making biosensors.

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