

# Synthesis of Polyaniline: Clay-Chain Nanocomposites by Mechanochemical intercalation Method and study its optical properties

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## Abstract

Polyaniline/clay nano composite can be prepared by mechanochemical method. The characteristics of various polyaniline-clay nano composite were investigated using UV- visible, FT-IR, and X-ray diffraction. We have also determined grain size ( $D=0.587$  nm). Transmittance measurements in the wavelength range (190-900)nm are used to calculate the refractive index( $n$ ), extinction coefficient ( $k$ ) and the optical band gap  $E_g^{opt}$ .

**Keywords:** polyaniline, clay chain nan composite, mechanochemical method ,grain size.

## 1-Introduction

Inorganic- organic nano structured materials have become a field of intensive interest and industrialists due to their multifaceted properties (Gomez 2001).

Polyaniline is one of the most studied conducting polymers because of their high stability, enhanced conductivity and process ability. They are widely used in different areas of research including electronics, solar cells, batteries, electromagnetic shielding devices, anticorrosive coating and sensors (Malinauskas 2001, Huang J& Shabnam 2004). It has been proved that the bulk electronic properties of PANI can be modified by templates assisted synthesis of polyaniline/clay nano composites (Yeh J M & Liou S J 2001, Yeh J M, Liou S J 2001).

A multi- layer assembly of clay plates in presence of conjugate polymer system can be used to regulate the tunneling of charge carriers and the electron transfer properties (Jing C, Chan L, Shi Y and Jin X, Eur Polm J 2005 & Eckle M and Decher G, Nano Lett 2001). Clays are natural substances having interesting properties due to their geometries, surface area and electrostatic charge.

Incorporation of guest electro active polymers such as polyaniline(PANI), polypyrrole(PPY), ...etc, into host clay particles has attracted great attention because of their better processibility with colloid stability, mechanical strength and novel electrical, catalytic properties (Alexandre M and Dubois P 2000).

Polyaniline/clay nano composite can be synthesized by intercalation of monomer at elevated temperature followed by oxidative polymerization of aniline in presence of oxidant like  $(NH_4)_2S_2O_8$  (Lee T W, Park O O 2001 & do Nascimento G M, Constantion V R L and Temperini M L A)

In the present investigation, we have synthesized polyaniline clay nano composites by mechano chemical method.

## 2-Experimental Procedure

Three-necked flask equipped with thermometer and stirrer, charged with (0.27 mol) (Aniline) monomer, which dissolved with 1M HCl and cooled to (0 °C). Clay- Chain China clay was milled by electric machine until became soft clay granules and very soft fractions. China clay was mixed with distilled water and added to the

solution Aniline and put on three-necked flask with the stirred .(0.343mol) of Ammonium persulphat ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (oxidizing agent) dissolved in 1M HCl, added slowly and very carefully to the flask. After that, the reactor mixture was kept under constant stirring for 24hr's.

The product of the greenish-black precipitate of the polymer was isolated by filtration and washed with 1M HCl for three times.. The resultant Polyaniline - Clay was filtered, washed successively with water, methanol and acetone to remove the un-reacted starting materials and oligomers, then was dried in vacuum oven at 60 °C for (12 hr's).

After the synthesized polyaniline- clay (PANI- clay) by chemical polymerization method. The (PANI- clay) powder was added to DMF solvent and mixed under constant stirring at room temperature. After completing the mixing process, the polymer was filtered under vacuum, then the mixture was deposited on glass substrates as a thin films by using spin coating.

### 3-Results and discussion

#### 2-1 XRD characteristics & study

X-ray diffraction measurement was used to confirm by the polycrystalline nature of clay chain and polyaniline/clay films. These measurement were carried out using Pert Pro MPD-Philips of Nether land operated at 40KV AND 20mA, using a  $\text{CuK}\alpha$  as a source of radiation with ( $\lambda=1.5406\text{\AA}$ ) and Ni(filter), with a scan rate of 2° min, and scan range of ( $0<2\theta<60$ ). Measurement was carried out at RT. The diffracted intensity as a function of the reflective angle was measured automatically by the X-ray diffraction. The figure(1) shows XRD chart of (PANI) with clay.

#### 2-2 Determine of grain size of PANI with clay

XRD spectra were recorded to determine the degree of swelling in clays and to monitor ,the formation and structure of these nano composites.

The size of PANI:clay particles was determined from the broadening the X-ray diffraction peaks.

The grain size of the film from the XRD data was calculated using the Debye-Scherrer formula (Cullity B D, Stock S R 2001):

$$D = \frac{0.94}{\beta \cos \theta} \dots\dots\dots (1)$$

Where D is the grain size of the crystallite,  $\lambda(1.5406\text{\AA})$  is the wavelength of the X-rays used,  $\beta$  is the broadening of diffraction line measured at the half of its maximum intensity in radians and  $\theta$  is the angle of diffraction.

The value of grain size calculated from equation (1) is ( 0.587) nm.

#### 3-3 FT-IR spectrum

The FT-IR spectrum was obtained with a FT/IR model 8400s spectrophotometer by SHIMADZU, under ambient condition. Infrared spectroscopic studies were conducted to investigated the type of chemical bonding between clay chin and aniline .The FT-IR spectrum of polyaniline/clay are showe in Fig.( 2 ).The band at  $(800,1100)\text{cm}^{-1}$  is due to characteristic vibration of clay. The bands in the region  $(1245,1305)\text{cm}^{-1}$  have contribution mainly from C-N stretch and the band at  $1560\text{cm}^{-1}$  consist of quinoid form of polyaniline backbone and also this band implies that the charge neutralization with the counter ion present in the polyaniline chain. In the higher frequency side a peak at  $3250\text{cm}^{-1}$  is assigned for the N-H stretching vibrations.

The absorption spectra of the PANI: clay film on the glass substrate is shown in Fig.(3) .There are three peaks, the fundamental peak at 436.6nm, which is attributed to  $(\pi-\pi^*)$  transition, and localized state peak which appears at (436.6nm). The second peak due to by  $n-\pi^*$  transition, while the third peak at 470nm.. third peak due to by  $n-\pi^*$  .

The anilinium ion peak was disappeared after mechanochemical polymerization in presence of stoichiometric quantity of oxidizing agent,  $(\text{NH}_4)_2\text{S}_2\text{O}$ . Two new peaks were observed for the pani:clay

nanocomposite, one at(436)nm and another at (470) nm and were assigned as and localized polaron- transition. Due to the confined arrangement of polymer within the clay lattices, the polaron band is slightly blue shifted. Synthesis of ions PANI: clay nano composites.

Polyaniline is not completely soluble in common organic solvents because of the stiffness of its backbone. The incorporation of polar functional group or alkyl chain in the polymer backbone is become soluble in water or organic solvents. Since one ortho position is blocked in 2-substituted aniline, a lower content of ortho couplings can be expected to lead to a more regular head to tail polymer structure and thereby to higher polymerization yields. However, the conductivity of the alkyl ring substituted polymers is lower than those of the parent by two orders of magnitude. It has been reported that o- toluidine and o-anisidine are more easily oxidized than the unsubstituted aniline. The anodic peak potential for the oxidation of aniline is found to be 0.8 V vs. SCE where as the oxidation peak potential of 2- ethylaniline is found at 0.41 V vs. SCE 8. Based on the above fact we have compared the chemical oxidative polymerization of aniline and substituted anilines within clay galleries.

#### 2-4 Optical constant

The optical properties of PANI:clay were measured the transmission (T) and absorption (A) which recorded by using (CE-7200) spectrophotometer at the range of (300-900)nm.The optical absorption coefficient ( $\alpha$ ) can be calculated using this relation ( Sabari Girisun T C, Dhanuskodi S 2009):

where d is the thickness of polymeric samples.

The extinction coefficient k can be obtained from the relation ( Sabari Girisun T C, Dhanuskodi S 2009):

$$k = \frac{\alpha d}{4\pi} \quad \text{----- (2)}$$

The linear refractive index is given by (Deshmukh S H, Burghate D K 2008) :

$$n = \frac{1+\sqrt{k}}{1-\sqrt{k}} \quad \text{----- (3)}$$

The spectral distribution of the mean values of n and k versus wavelength ( $\lambda$ ) for the PANI:clay can be shown in Fig.( 4) & (5 ).

.The optical absorption edge is analyzed by using the following relation (Kenny N, Kannewurf C R, Whitmore D H 1999 & Mott N F, Davis E A 1979 ):

$$\alpha h\lambda = A(h\nu - E_g^{opt})^r \quad \text{----- (4)}$$

where h: Plank's constant, A: the edge width parameter representing the film quality which is calculated from the linear part of this relation,  $E_g^{opt}$  : the optical energy gap of the material and r: determines the type of transition.

#### Conclusion

A detailed investigation has been carried out on the synthesis of various substituted polyaniline:clay nano composited by mechanochemical method. From the UV- visible spectra studies, it is concluded that the maximum exchange of aniline ion was achieved by this method. The crystal structure of PANI:clay thin film was investigated by XRD pattern.

Optical constant such as the refractive index n and extinction coefficient k were determined from the transmittance spectra in the UV-visible regions.

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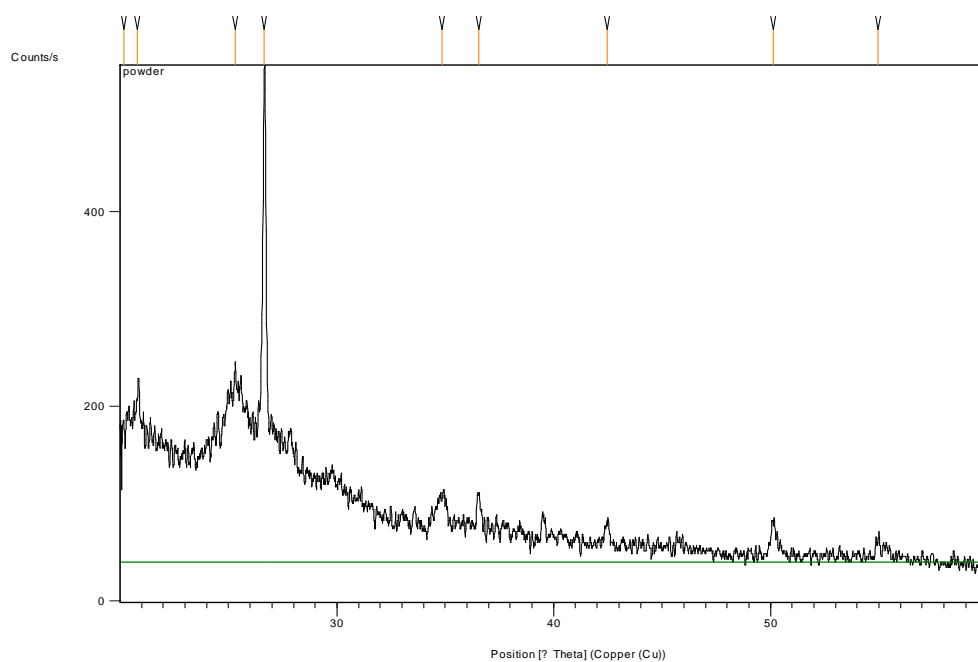


Fig.(1): XRD of PANI:clay thin film at R.T

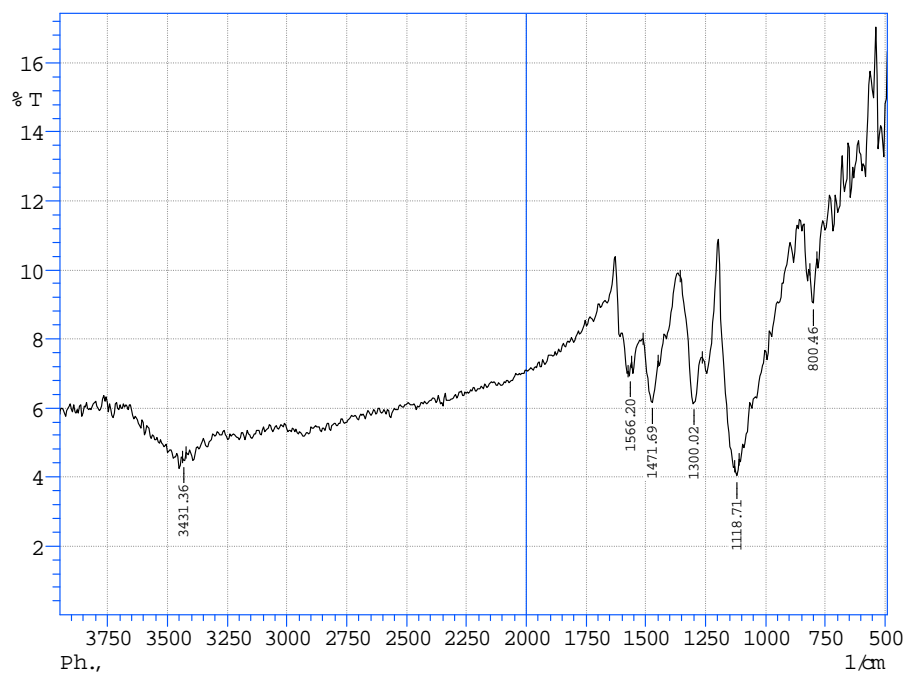


Fig.(2): spectra of (PANI) with clay

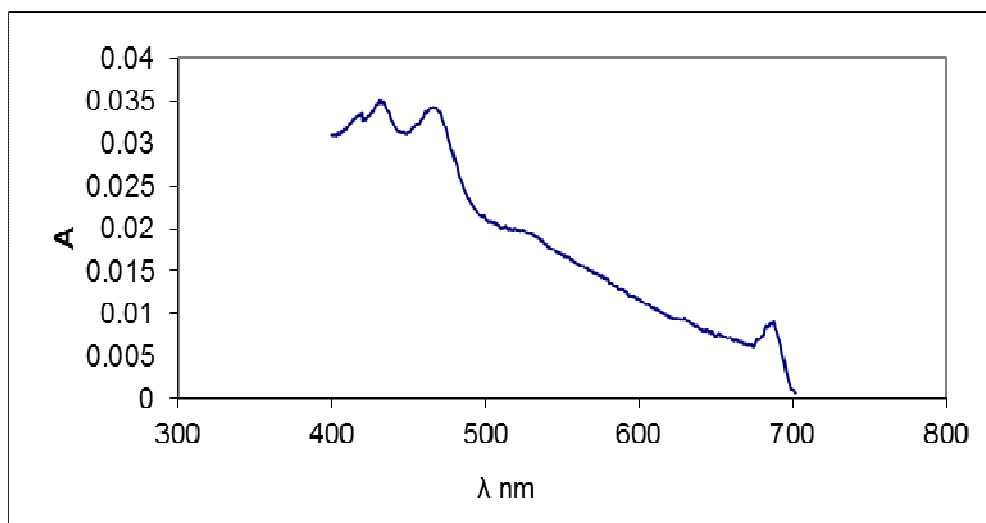


Fig.(3): UV- visible spectra of PANI:clay

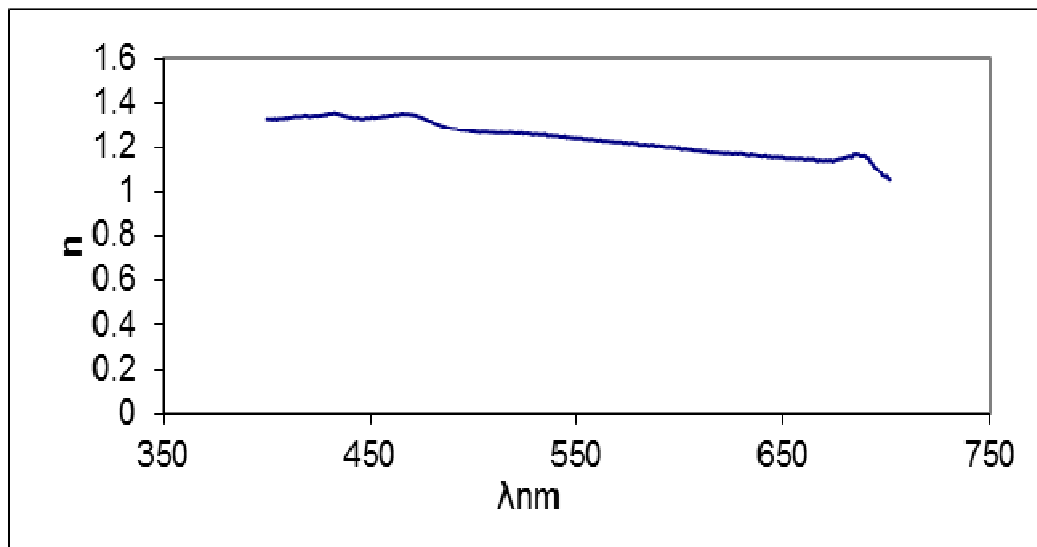
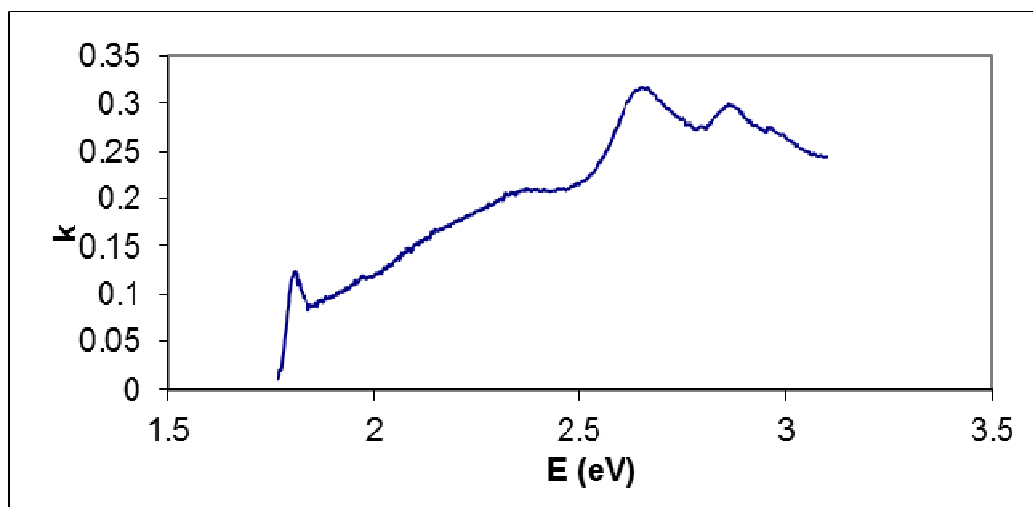


Fig.(4 ):shows the plot of refractive index  $n$  vs. wavelength



Fig(5) : shows the plot of absorption index  $k$  vs. wavelength.

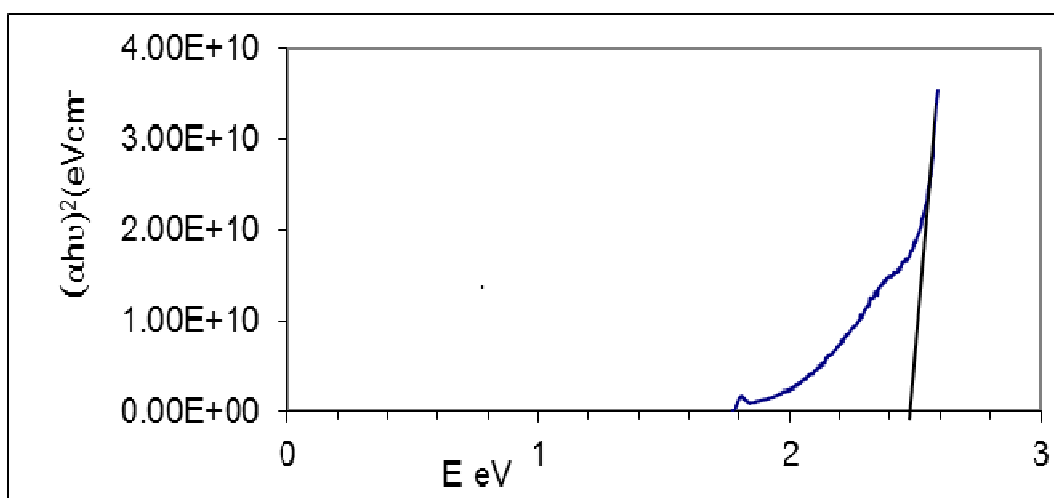


Fig.(6) shows the plot of  $(\alpha h\nu)^2$  vs.  $h\nu$  for PANI:clay .

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