

# Synthesis, Characterization And Electrical Conductivity Of Poly (2- Chloroaniline)/MMT And Poly (2-Chloroaniline)/Na-Bentonite Nano Composites In The Presence Of Surfactants

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**Abstract:** The poly (2-chloroaniline)/ Montmorillonite (P2ClAn/MMT) and poly (2-chloroaniline)/Na-Bentonite (P2ClAn/Na-Bentonite) nano composites were prepared by insitu chemical oxidative polymerization method using ammonium per sulphate (oxidant), HCl (dopant), sodium lauryl sulphate (surfactant) in the presence and absence of dodecyl benzene sulphonic acid (DBSA). The crystallite size of the polymer composites as calculated by Debye-Scherrer equation from XRD data shows the particle size in the range 20-35 nm. The composites were stable upto 550° C. The impedance and the conductance as measured in the frequency range from 20 Hz to 1 MHz at room temperature showed an increase in conductivity in the composite when compared to pure polymer. Among the P2ClAn/clay nano composites synthesized, the poly (2-chloroaniline)/Montmorillonite in the presence of dodecyl benzene sulphonic acid (P2ClAn-DBSA/MMT) has the maximum conductivity of  $3.6 \times 10^{-3}$  S/cm at room temperature. The crystallinity and orientation is retained in the P2ClAn-DBSA/MMT and hence it has high conductivity than the other composites. The composites synthesized behave as organic metals due to their semiconducting nature.

**Index Terms:** composites, dodecyl benzene sulphonic acid, electrical conductivity, montmorillonite, Na-Bentonite, poly (2-chloroaniline), Surfactants.

## 1. INTRODUCTION

Electrically conducting polymers are a class of synthetic metals that combine the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors [1]. Typical conducting polymers include polyacetylene, polyaniline, polypyrrole, polythiophene, poly (para phenylene), poly (phenylene vinylene), polyfuran etc. [2]. Ease of synthesis, environmental stability, easy transformation in cathodic protection, special electronic, optical and magnetic properties attract researchers to extensively study polyaniline in the recent past [3]. In spite of various advantages, polyaniline has certain limitations when it comes to its applications as it is neither soluble nor fusible in organic solvents as well as water [4]. In order to overcome such disadvantages, attempts have been made by the use of molecular design, modification of monomer structure, use of functionalized acid dopant, formation of blends/composites and copolymerization.[5] It has been reported that the torsion angle influences the electronic properties of various conducting polymers with aromatic backbones. Theoretical studies on polyaniline indicate that the ionization potential and band gap are affected by the torsion angle between adjacent rings on the polymer chain and substituents in polyaniline should affect this torsion angle. Moreover, the incorporation of substituents in the polymer backbone is a common technique to prepare soluble polymers [6]. Substituted polyanilines have various applications such as removal of heavy metals [7] and corrosion inhibition [8]. Conducting polymer/layered inorganic solid nanocomposites have been the subject of considerable interest because, being derived from a unique combination of organic and inorganic components at the molecular level, they show novel electrical, structural and mechanical properties [9]. Conducting polymer/inorganic nanoparticle composites have attracted attention due to their great potential for applications such as nanoelectronics, gas sensors, biosensors, capacitors and catalysts [10]. Among organic-inorganic nano composites,

polymer-clay nano composites are most prevalent and interesting due to their unique properties as well as wide applications, abundance, low cost and attractive features such as large surface area and ion-exchange properties [11]. Substituted polyaniline blends and composites such as PNEAn/chitosan, PNMAN/chitosan[12], P2ClAn/poly vinylidene fluoride[7], P2ClAn/Red Mud[13], substituted polyaniline/ MoS<sub>2</sub>[14,15], poly N-ethyl aniline/poly imide [16], poly N-methylaniline/ carbon nanotubes[17], and others have been reported. However to the best of our knowledge there are no reports on the study of P2ClAn/MMT and P2ClAn/ Na-Bentonite nano composites. In the present investigation P2ClAn/ MMT and P2ClAn/ Na-Bentonite nano composites were prepared for the first time by insitu chemical oxidative polymerization method using dodecyl benzene sulphonic acid and hydrochloric acid as dopants, ammonium per sulphate as an oxidant and sodium lauryl sulphate as a surfactant at 0-5° C. This pathway was selected because one expects that the P2ClAn-DBSA salt moieties of the polymer enhances the solubility and hence the processibility, while P2ClAn-HCl salt moieties provide a good conductive structure. The resulting polymer composites were characterized by FT-IR, UV, SEM and XRD. The thermal properties were studied by TGA and DTA analysis and the electrical conductivity measured by four point probe method.

## 2. EXPERIMENTAL

### 2.1. Synthesis of polymer/clay composites

2-chloroaniline, ammonium per sulphate and dodecyl benzene sulphonic acid were purchased from LOBA Chemic, Qualigens and Avra Synthesis Pvt. Ltd respectively. The MMT and Na-Bentonite clay minerals were purchased from Sigma Aldrich and all the chemicals were used as received. The P2ClAn-DBSA/clay (MMT/Na-Bentonite) nano composites were synthesized by insitu chemical oxidative polymerization method. MMT/Na-Bentonite nano clay (2.7 g) suspended in 100 ml 1M HCl

was kept in the freezing mixture. 2-chloroaniline (2.7 g) in 25 ml water was added slowly and dropwise to nano clay with constant stirring for a period of two hours. Ammonium per sulphate (7.15 g in 25 ml of water), dodecyl benzene sulphonic acid (2 ml in 25 ml of water) and sodium lauryl sulphate (0.8 g in 50 ml of water) were taken in separate beakers. The oxidant, dopant and surfactant were added slowly to the mixture containing 2-chloroaniline and clay (MMT/Na-Bentonite) and the stirring was continued for four hours. The product was placed in the refrigerator overnight. The green colored precipitate was filtered, washed and dried. About 5 g of the P2ClAn-DBSA/clay (MMT/Na-Bentonite) nano composites were obtained. Adopting the same procedure the P2ClAn/clay (MMT/Na-Bentonite) nano composites were prepared in the absence of DBSA. The prepared polymer composites in the presence of DBSA show greater solubility in most of the organic solvents (DMSO, acetone, etc.) than in the absence of DBSA. The presence of DBSA increases the solubility of the polymer composites.

## 2.2. Characterization

The FT-IR spectra of polymer/clay composites in KBr were recorded by Thermo Nicolet, Avatar 370 spectrophotometer from 500  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ . The UV-Visible spectra were recorded from 200-800 nm using Systronics double beam spectrophotometer 2201. XRD analysis of polymer/clay composites were performed on a Bruker AXS D8 advance X-ray diffractometer using Cu, wavelength 1.5406 Å. The surface morphology of the polymer/clay composites were studied using a JEOL model JSM-6390LV Scanning Electron Microscope at an accelerating voltage of 15 KV. Thermogravimetric analyses were carried out with a Perkin Elmer STA 6000 at the heating rate of 10° C / min from 40° C to 750° C under inert gas atmosphere. The electrical conductivity of the polymer composites were measured in the room temperature over a frequency range of 20Hz-1MHz using computer controlled HIOKI3532 LCR meter.

## 3. RESULTS AND DISCUSSION

### 3.1 FT-IR spectroscopy

The FT-IR spectra of MMT, P2ClAn-DBSA, P2ClAn/MMT and P2ClAn-DBSA/MMT and Na-Bentonite, P2ClAn-DBSA, P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite are shown in Fig. 1a and 1b respectively.

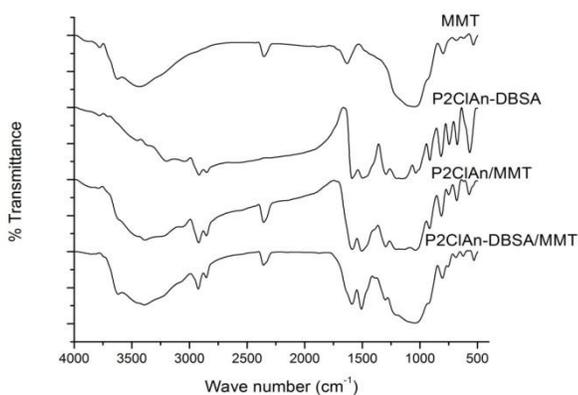


Fig. 1a. IR spectra of MMT, P2ClAn-DBSA, P2ClAn/MMT

and P2ClAn-DBSA/MMT.

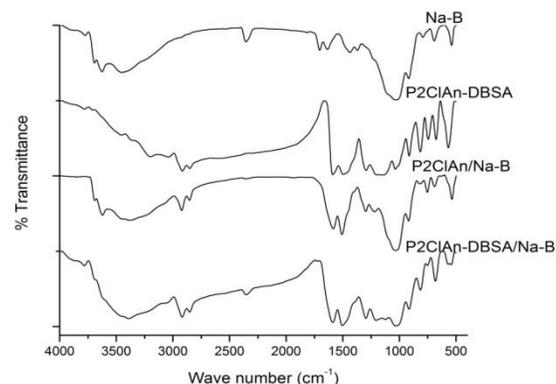
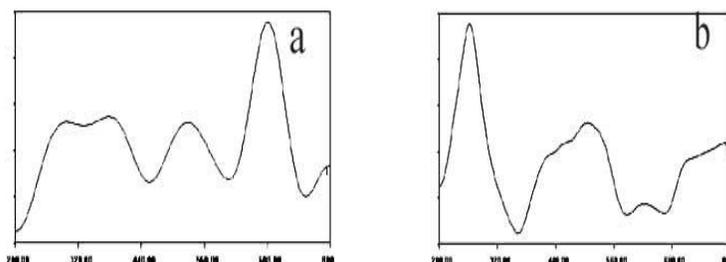


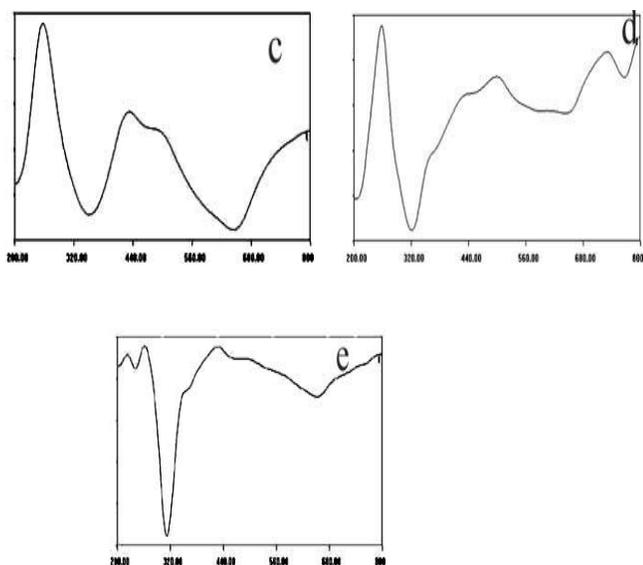
Fig. 1b. IR spectra of Na-Bentonite, P2ClAn-DBSA, P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite.

The N-H stretching frequency which occurs at 3452  $\text{cm}^{-1}$  in pure P2ClAn-DBSA is shifted to around 3386  $\text{cm}^{-1}$  in P2ClAn/clay composite which confirms that there is interaction between poly (2-chloroaniline) and the clay chains. The asymmetric and symmetric stretching frequency of  $-\text{CH}$  present in DBSA/SDS are observed at 2919  $\text{cm}^{-1}$  and 2852  $\text{cm}^{-1}$ . The characteristic peaks due to quinonoid and benzenoid rings of poly (2-chloroaniline) occur at 1587  $\text{cm}^{-1}$  and 1504  $\text{cm}^{-1}$ . The peak at 1296  $\text{cm}^{-1}$  is due to aromatic C-N stretching vibration. The bands at 913  $\text{cm}^{-1}$  and 815  $\text{cm}^{-1}$  are due to  $-\text{CH}$  out of plane bending vibration of 1, 2, 4 tri substituted aromatic rings. The characteristic bands corresponding to MMT and Na-Bentonite are shown at 1048  $\text{cm}^{-1}$  for Si-O-Si linkage and  $\sim 800 \text{ cm}^{-1}$  for  $\text{Al}^{4+}$  as in Fig. 1a and Fig. 1b. The peaks are also observed in the composite at 1040  $\text{cm}^{-1}$  and  $\sim 800 \text{ cm}^{-1}$ . A band  $\sim 800 \text{ cm}^{-1}$  in the clays and composites are due to stretching vibration of  $\text{Al}^{4+}$  tetrahedral [18]. It confirms the retention of basic clay structure. The band observed at 2355  $\text{cm}^{-1}$  in pure clay is also found in the composite which is due to carbonate present in clay [19]. The IR spectrum of the P2ClAn/clay composites shows both the characteristic bands of poly (2-chloro aniline) and clay which ensures the incorporation of clay in poly (2-chloro aniline). The same intensities of benzenoid and quinonoid peaks and dark green colour suggested that the polymer composites are in emeraldine salt form.

### 3.2 UV-Visible spectroscopy

Fig. 2 (a-e) shows the absorption spectra of poly (2-chloroaniline), P2ClAn/MMT, P2ClAn-DBSA/MMT, P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite respectively.





**Fig. 2.** Absorption spectra of a. P2ClAn-DBSA, b. P2ClAn/MMT, c. P2ClAn-DBSA/MMT, d. P2ClAn/Na-Bentonite and e. P2ClAn-DBSA/Na-Bentonite.

The Table 1 gives the various transitions that take place in the polymer and polymer clay composites. When compared to poly (2-chloroaniline) the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions are shifted to lower wavelengths. In poly (2-

Polymer	$\pi$ - $\pi^*$ (nm)	$n$ - $\pi^*$ (nm)	Charge transfer (nm)
P2ClAn-DBSA	296	524	680
P2ClAn/MMT	260	504	620
P2ClAn-DBSA/MMT	255	430	788
P2ClAn/Na-Bentonite	259	495	725
P2ClAn-DBSA/Na-Bentonite	262	423	680

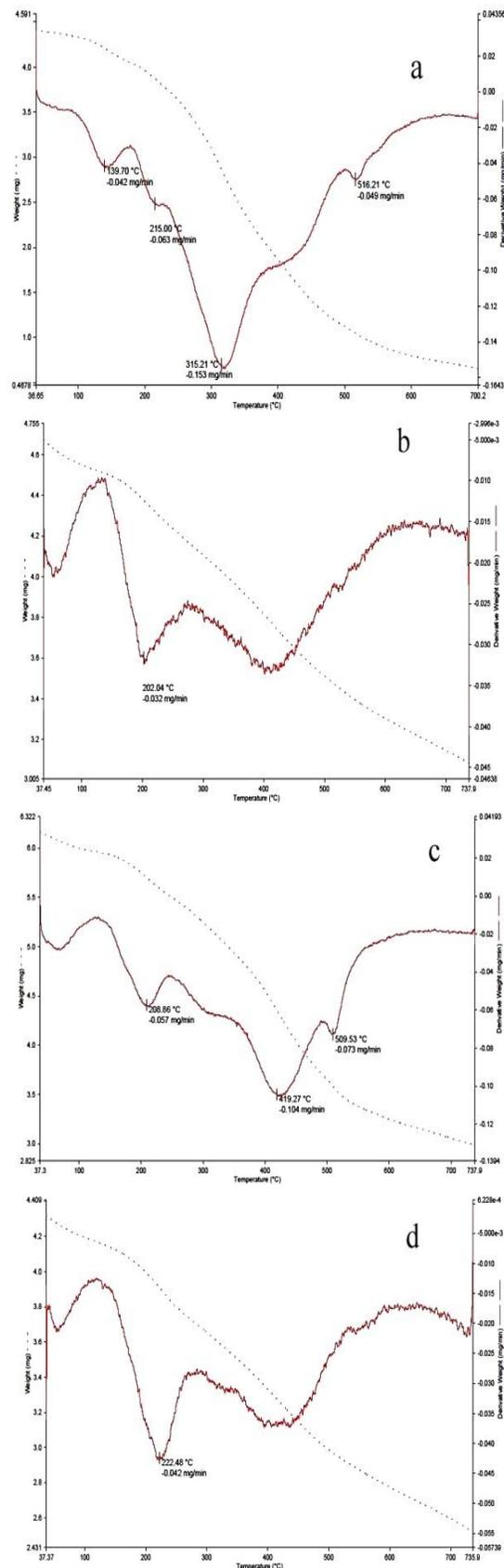
**TABLE 1**

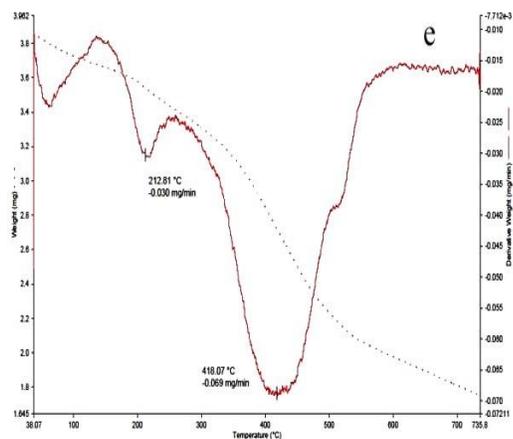
ABSORPTION BANDS OF POLYMER AND POLYMER CLAY COMPOSITES

chloroaniline) the  $\pi$ - $\pi^*$  transition occurs at 296 nm and  $n$ - $\pi^*$  transition occurs at 524 nm. In the composites the transitions are taking place at lower wavelength due to the reduced  $\pi$  electron delocalization. The third absorption bands are due to quinonoid ring transition-charge transfer from the highest occupied molecular orbital of the benzenoid ring to the lowest unoccupied molecular orbital of the quinonoid ring [20, 21, 22].

**3.3. TGA/DTA**

TGA/DTA of P2ClAn, P2ClAn/MMT, P2ClAn-DBSA/MMT, P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite are shown in Fig. 3(a-e) respectively.



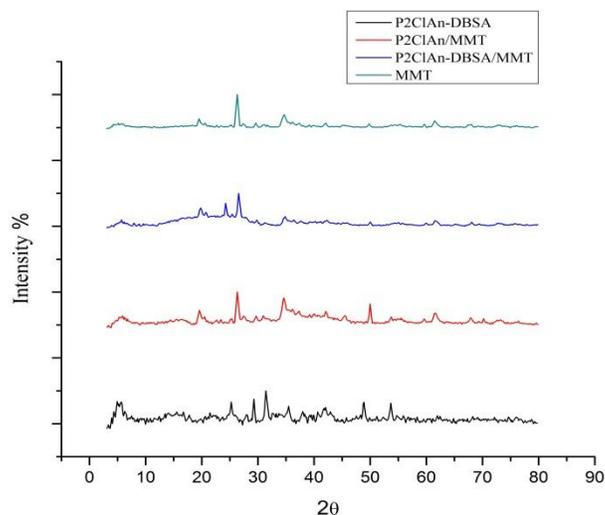


**Fig. 3.** TGA/DTA of a. P2ClAn/MMT, b. P2ClAn-DBSA/MMT, c. P2ClAn/Na-Bentonite and d. P2ClAn-DBSA/Na-Bentonite.

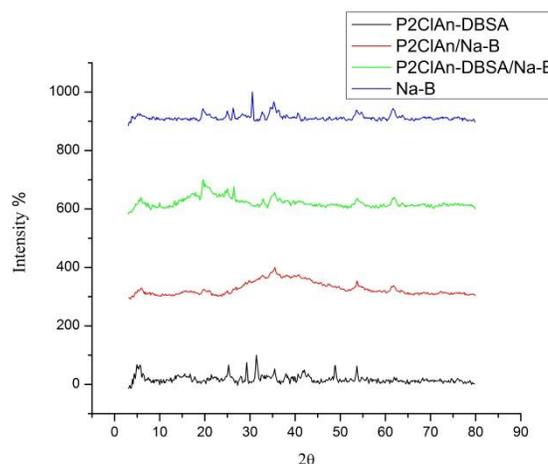
The P2ClAn-DBSA undergo four step weight losses, first is due to loss of moisture, second is due to loss of HCl, third is due to loss of SDS, fourth is due to loss of DBSA and the polymer is decomposed exothermically around 550°C. The P2ClAn/MMT and P2ClAn/Na-Bentonite composites undergo weight loss in three steps, the first at 100°C due to the loss of moisture, second at 200°C due to loss of HCl and the third weight loss around 400°C due to the loss of SDS anion which is incorporated into the polymer chain. The degradation of the polymer composites takes place exothermically around 550°C and is continuous up to 730°C. 45% residue is observed due to clay moieties. But P2ClAn-DBSA/MMT and P2ClAn-DBSA/Na-Bentonite composites undergoes weight loss in four steps, the first around 100°C and second at 200°C due to removal of moisture and HCl respectively, the third weight loss in P2ClAn-DBSA/MMT at 419°C due to removal of SDS and fourth weight loss at 509°C due to removal of DBSA dopant. In P2ClAn-DBSA/Na-Bentonite the weight loss around 418°C is due to the removal of both SDS as well the DBSA dopant as shown by the area of endothermic peak. The exothermic decomposition of P2ClAn-DBSA/MMT and P2ClAn-DBSA/Na-Bentonite composites takes place around 550°C. The area of the endothermic peak is an evidence to show the incorporation of more DBSA dopant in the polymer chain. When compare to the polymer the polymer composites have almost 50% of the residue at 730°C which indicates that the presence of clay prevent the complete decomposition of the polymer composites.

### 3.4. X-Ray Diffraction studies

The XRD patterns of P2ClAn-DBSA, MMT, P2ClAn/MMT, P2ClAn-DBSA/MMT, Na-Bentonite, P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite are shown in Fig. 4a and 4b.



**Fig. 4a.** XRD pattern of P2ClAn-DBSA, P2ClAn/MMT, P2ClAn-DBSA/MMT and MMT.



**Fig. 4b.** XRD pattern of P2ClAn-DBSA, Na-Bentonite, P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite.

The diffraction peaks of poly(2-chloroaniline) synthesized in the presence of DBSA shows around  $\sim 2\theta = 25^\circ, 29^\circ, 31^\circ, 48^\circ$  and  $53^\circ$  indicate the crystalline nature of emeraldine salt structure. The  $\sim 2\theta = 26^\circ$  represents the (1 1 0) reflection of emeraldine salt [23]. The MMT shows the sharp peak at  $2\theta = 26^\circ$ . In case of the P2ClAn/MMT and P2ClAn-DBSA/MMT the polymer peaks are diminished and the intensities of the MMT peaks are reduced because of the interaction between the clay and the polymer chain. But in the P2ClAn-DBSA/MMT the presence of DBSA protects the polymer peak at  $2\theta = 26^\circ$ . When compare to the peak at  $2\theta = 26^\circ$  in MMT there is no increase in the interlayer space (d space) in polymer clay composites which indicates that the interaction between the polymer and clay is not an intercalation. This ensures that the polymer chain has not been intercalated between the clay chains. The presence of a bulky chlorine atom at the ortho positions along the chain prevents the intercalation. Hence we concluded that the interaction between the polymer chain and the clay results in exfoliation which is also supported by SEM. We report for

the first time the exfoliation type of interaction between poly(2-chloroaniline) and clay. The Na-Bentonite shows a sharp peak at  $2\theta = 30^\circ$ . There is a broad halo in the XRD pattern of P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite which indicates the decrease in the crystallinity which is substantiated by the presence of Na-Bentonite which has excellent colloidal properties. From the XRD data the average crystallite size has been calculated by using Debye-Scherrer equation [9, 24].

$$D = 0.89\lambda / \beta \cos\theta$$

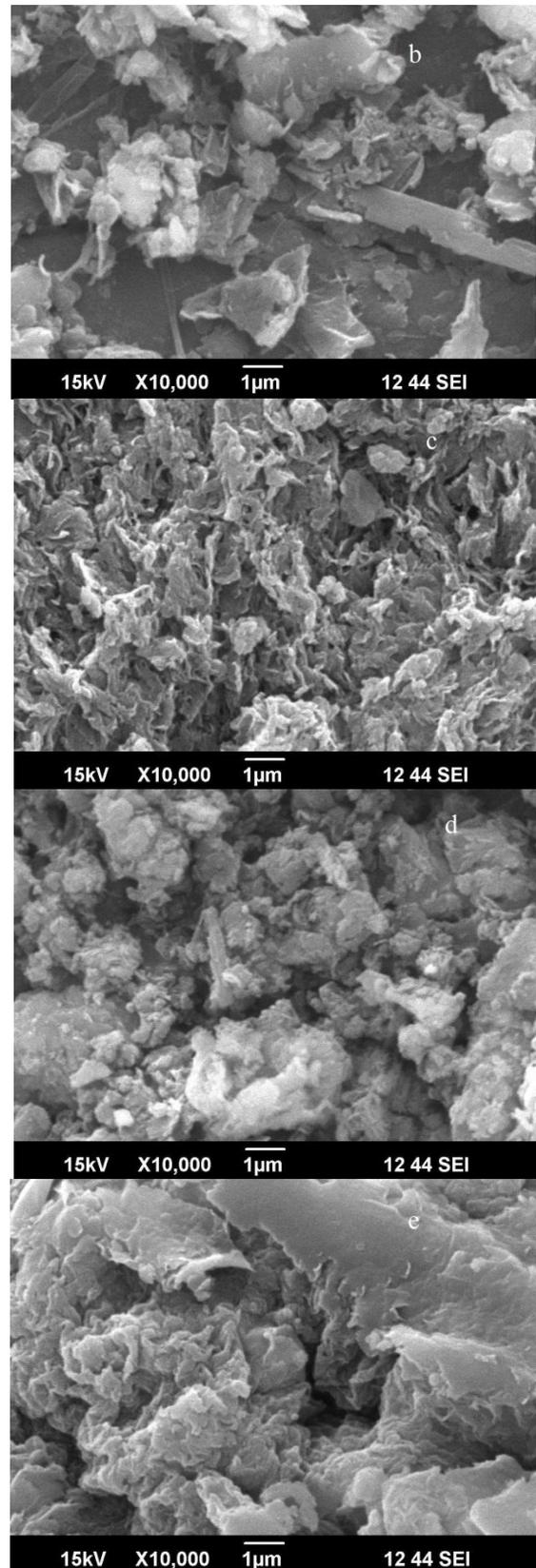
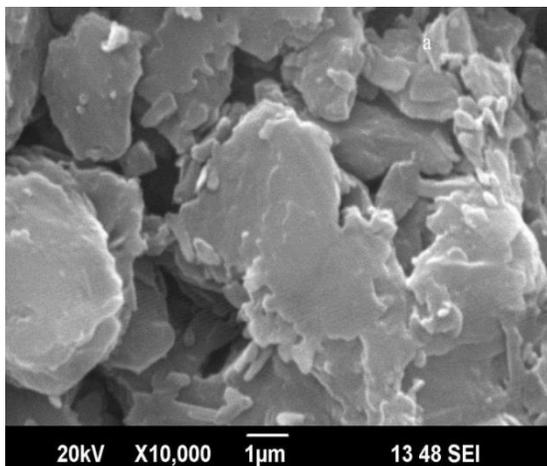
Where ' $\lambda$ ' is wave length of X-ray (0.154 nm), ' $\beta$ ' is FWHM (full width at half maximum), ' $\theta$ ' is Bragg angle and ' $D$ ' is average particle diameter size. The crystalline sizes of the P2ClAn/MMT, P2ClAn-DBSA/MMT and P2ClAn-DBSA/Na-Bentonite composites are tabulated in Table 2. The crystallite size indicates the formation of nanocomposites.

**TABLE 2**  
PHYSICAL PARAMETERS OF POLYMER AND POLYMER/CLAY NANOCOMPOSITES FROM XRD STUDIES

Polymer	$2\theta$	FWHM (radians)	Crystallite size (nm)	d spacing (nm)
P2ClAn-DBSA	25.280	-	-	3.51
MMT	26.314	0.0066	25.01	3.38
P2ClAn/MMT	26.329	0.0066	21.34	3.38
P2ClAn-DBSA/MMT	26.548	0.0048	29.14	3.35
Na-Bentonite	30.526	0.0039	36.44	3.56

### 3.5 Surface Morphology

Fig 5(a-e) depicts the SEM micrograph of P2ClAn/MMT, P2ClAn-DBSA/MMT, P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite respectively.

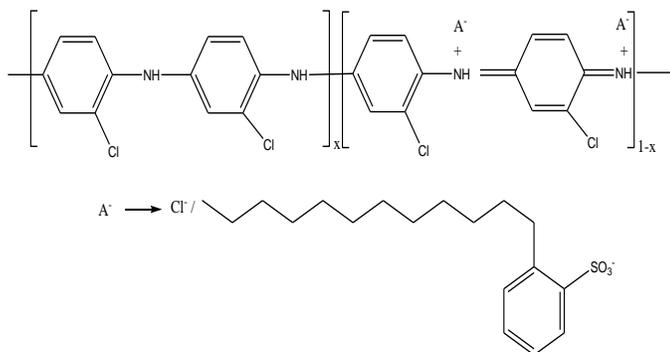


**Fig. 5.** Surface morphology of a. P2ClAn-DBSA, b. P2ClAn/MMT, c. P2ClAn-DBSA/MMT, d. P2ClAn/Na-Bentonite and e. P2ClAn-DBSA/Na-Bentonite.

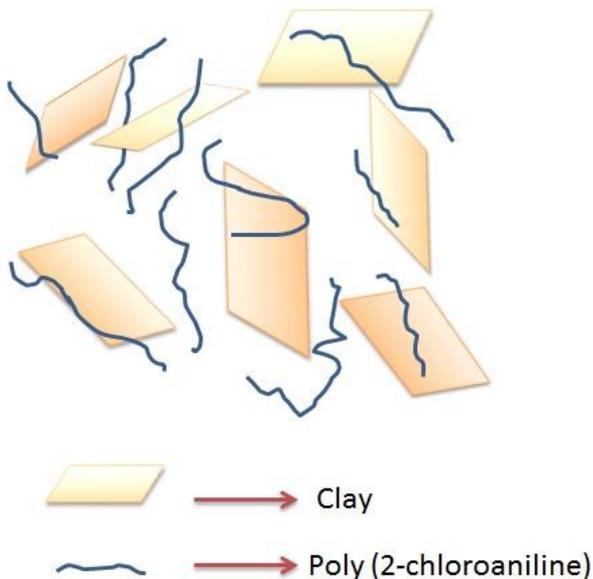
P2ClAn-DBSA is in the flake like structure. The ordered flake is disturbed by the interaction of the clay with the polymer. While comparing the P2ClAn/clay in the presence and absence of DBSA, high compactness has been predicted in the presence of DBSA. The DBSA increases the compactness of the polymer composite. The surface morphology does not show any ordered arrangements which confirms that the interaction between the polymer and the clay is exfoliation and not intercalation. The P2ClAn/MMT and P2ClAn-DBSA/MMT composite are fibrillar in nature and the P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite are granular in nature. The nature of the clay minerals affects the morphology of the polymer composites entirely leading to the difference in mechanical and electrical properties.

### 3.6. Proposed structure

The proposed structure of the P2ClAn in the presence of DBSA is shown in scheme 1. Both DBSA and HCl are act as the dopants. The interaction between the polymer and clay are exfoliation because the presence of a bulky chlorine atom at the ortho positions along the chain prevents the intercalation. The exfoliation type of interaction is shown in scheme 2. This type interaction is supported by XRD and SEM.



**Scheme 1.** Structure of P2ClAn-DBSA



**Scheme 2.** Exfoliation between the polymer and the clay

### 3.7. Electrical conductivity

The P2ClAn/clay composites were finely powdered and pressed into a pellet using IR sample Press using Model AVATAR-370 Thermo Nicolet with a maximum pressure of 15 tons/cm<sup>2</sup> to form circular pellets of 1.2 cm diameter. The thickness of the pellet was measured using screw gauge. The measurement was done by placing the pellet between two silver electrodes and the bulk resistance (R) was measured using computational analysis using HPVEE programme. The electrical conductivity of P2ClAn/clay composites were calculated using the formula

$$\sigma = t/RA$$

Where 'σ' is the electrical conductivity, 't' is the thickness of the pellet, 'R' is the bulk resistance and 'A' is the area of the pellet. The electrical conductivity of P2ClAn/MMT, P2ClAn-DBSA/MMT, P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite at room temperature is tabulated in Table 3.

**TABLE 3**  
THE BULK CONDUCTIVITY OF POLYMER CLAY COMPOSITES

Polymers	Area (cm <sup>2</sup> )	Thickness (cm)	Bulk Resistance (S)	Conductivity (S/cm)
P2ClAn/MMT	1	0.017	1.41 x 10 <sup>5</sup>	1.21 x 10 <sup>-7</sup>
P2ClAn-DBSA/MMT	1	0.017	4.693	3.60 x 10 <sup>-3</sup>
P2ClAn/Na-B	1	0.017	1.35 x 10 <sup>5</sup>	1.26 x 10 <sup>-7</sup>
P2ClAn-DBSA/Na-B	1	0.017	2.59 x 10 <sup>4</sup>	6.56 x 10 <sup>-7</sup>

The protons of DBSA interact with imine nitrogens resulting in the formation of holes on polymer/clay backbone leading to the increase in the electrical conductivity.

### 4. CONCLUSION

The P2ClAn-DBSA, P2ClAn/MMT, P2ClAn-DBSA/MMT, P2ClAn/Na-Bentonite and P2ClAn-DBSA/Na-Bentonite nanocomposites were synthesized by in situ chemical oxidative polymerization method using ammonium persulphate as oxidizing agent, sodium lauryl sulphate as surfactant and HCl and DBSA as dopants. The interaction between the polymer and the clay mineral was confirmed by IR. When compared to pure poly(2-chloroaniline) the absorptions were shifted to lower wavelength in polymer composites which indicates the reduced π electron delocalization due to the incorporation of clay minerals. TGA analysis illustrates that some of the SDS molecules also got incorporated into the polymer chain. The formations of nanoparticles were confirmed by the XRD data using Debye-Scherrer equation. We report for the first time

the exfoliation type of interaction between poly(2-chloroaniline) and clay. The broad halo in the XRD patterns of P2ClAn/Na-B and P2ClAn-DBSA/Na-B indicates the decrease in the crystallinity which is substantiated by the presence of Na-Bentonite which has excellent colloidal properties. SEM morphology clearly illustrates that the nature of the clay modified the landscape of the polymer composites and the compactness of the polymer composites were increased by DBSA. The P2ClAn-DBSA/MMT had the maximum conductivity of  $3.6 \times 10^{-3}$  S/cm at room temperature. Crystallinity and orientation of conducting polymers are of much interest because the more highly ordered systems could display a metallic-like conductive state. This crystallinity and orientation is retained in the P2ClAn-DBSA/MMT and hence it has high conductivity than the other composites and all the polymer composites were semiconducting in nature.

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