RESEARCH PAPER

Effect of Iodine Doping on the Polyaniline /Clay Nano Composite Thin Films Prepared by Mechanochemical Intercalation Method

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ABSTRACT

A mechanochemical approach is used to make a polyaniline:AIcaulan clay nano composite in this study. The presence of a green color indicates the formation of polyaniline/clay. Thin sheets of iodine-doped polyaniline/clay that have been pre-prepared are used. The weight percent of iodine in the nanocomposite films was 16%, 33%, and 50% wt percent of the total weight of PANI/ clay. These as-deposited films were analyzed for physicochemical and optoelectronic features using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray absorption spectra, and optical absorption spectra. FT-IR The chemical activity of both pure and iodine-doped thin polyaniline/clay sheets is then investigated using spectroscopic measurements.SEM images reveal an uneven distribution of grains throughout the subsurface, according to morphological analysis. The optical band gaps of the films are then investigated using absorption spectrum measurements. Indirect transitions' energy transition gaps are characterized and determined. The energy band gap will be shown to vary depending on the content of polyaniline and clay iodine. As iodine concentration rises, the optical band gap decreases from 3.47to 2.18eV.

INTRODUCTION

The effect of incorporating electrically active polymers such as (PANI), polypyrrole (PPy), and others with added clay particles improves the mechanical strength of the polymer, its colloidal stability and electrical properties due to the unique properties of clay represented by its surface area and electrostatic charge[1]. Various researches have been conducted by scientists on the insertion of electronically conductive polymer with clay[2]. The electrochemical structure of chemical materials was described and found that the materials have a higher anisotropic nano conductivity than the PANI-clay composite made from anilinium – montmorillonite[3].

A solvent-free polyaniline-clay nanocomposite, and the electrorheological properties of polyaniline-clay with montmorillonite clay was reported [4] . The interaction of the polymer and the clay results in an exfoliated structure, because the polymer utilizes the entire surface of the clay layers, who claimed that exfoliated nanocomposites are more exquisite[5]. The polymerization of aniline in the interlayers of clay made Pani/montmorillonite has a higher conductivity than pure polyaniline, which reduces defects and polymer bridges, as a result

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of the formation of a long chain[6]. The discovery of halogen doping of polyacetylene, which increased electrical conductivity significantly, had a significant impact on the development of practical applications of conductive polymers such as electrical devices and transistors in the field of (FTE) and others [7-11], which is a new approach in plastic electronics. Iodine doping has a wide range of applications, whether in vapor or solution, until the effect of halogen doping on polymer conductivity is discovered.In their natural state,(π-conjugated polymers) are insulators. Low donor electron concentrations in the doping process result in an increase in conductivity and charge carriers.

The charge transfer process is useful in the process of iodine uptake by (π -conjugated polymers)because iodine has multiple properties such as chemical stability and good conductivity. (PANI) is one of the conductive polymers in comparison to the rest of the polymers in terms of low production costs and polymerization in an aqueous medium that is non-toxic to the environment[12].

Iodine has a high vapor pressure at room temperature and a low sublimation temperature, making it difficult to treat iodine accumulation in air and water, and this vapor state complicates iodine accumulation even more. Iodine doping with (PANI) in the past [13-16]. Many practical applications of conductive polymers include capacitors and transistors [17],as well as optoelectronic devices [18]. PANI is a p-type conductive polymer that is easy to polymerize, chemically and environmentally stable[19,20]. The variable conductivity of PANI, which can be tuned using the doping/de b vdoping procedure, has sparked a lot of interest [21,22] .

(PANI) has been doped with various metals to improve its electrical properties [23,26], and a few researchers have also published a study on the interaction of (PANI) with iodine in addition to its conductive and electrical properties. The conductivity increased by eight times by volume when doping (PANI) with iodine in ethanol solution[27], and the conductivity increased by five times due to proton (PANI) with hydrogen iodide (HI) [28], where iodine I_2 had a significant effect on the regularity of the polymer chain.

Solvent casting, physical vapor deposition (PVD), and other techniques were used to make (PANI) films that were characterized as mechanically solid and thermally stable [29,30], and it is believed that once the plasma produces thin films of (PANI) that are good and uniform. Because of their chemical stability, moderate charge transfer capabilities, and environmental friendliness, n-type inorganic nanomaterials (TiO2,ZnO) and P-type organic materials (PANI) are considered conductive polymers [31]. The combination of PANI (P-Type) and TiO2 n-type has been used in a wide range of electrical devices, including solar energy systems [32] and Schottky diodes. It has been demonstrated that PANI/ZnO heterogeneous junctions have poor electrical properties when compared to PANI/TiO heterogeneous junctions, which generate a large volume of charge carriers and thus improve electrical properties [33,34].

Nanopolymers are a new type of compound made up of particles with a molecular dimension of 1 to 100 nanometers dispersed throughout [35]. Carbon nanotubes and clay are two of the most commonly used particles in strengthening polymer nanocomposites [36]. The composite (polymer / nanoclay) is a novel material family in which the nanoclay is influenced by the polymer matrix [35]. clay with a low levels.Through a previous study for nanocomposites based on saturated polyester UP/clay with a clay content of up to 5% by weight, and found an increase in tensile strength and tensile modulus[37],also in another study, the compound has better mechanical and thermal properties[38], and increasing the clay loading leads to an increase in the tensile modulus and fracture toughness[39], in addition to the fact that the brittleness in nanocomposites is a defect that limits their applications.

MATERIALS AND METHODS

Alcaulan was broken down using an electric machine until it was reduced to soft clay particles. Alcaulan clay is mixed with aniline monomer (7.27 mol), which is then dissolved in 1M H_2SO_4 and placed in a three-necked flask. The aniline: H_2SO_4 is then added, and the mixture is stirred continuously in an ice bath for 3-4 hours. The oxidizing agent, ammonium per sulphate $(NH_4)_2S_2O_8$, is dissolved in 1M H_2SO_4 and slowly and carefully added to the solution in the flask to begin the polymerization. The reactor mixture is then continuously stirred for 24 hours. When the polymerization is complete, the color of the solution changes from greenish black to greenish black. After that, the product is cleaned with acid before being packaged. Before

being characterized, the filtered powder is dried in a 50°C oven. To evaluate all samples in the wavelength range 400-4000 cm-1 under equal conditions, Fourier Shemadzu Co model 8400 Series uses transform infrared (FT IR) spectra with solid KBr discs.

RESULTS AND DISCUSSION
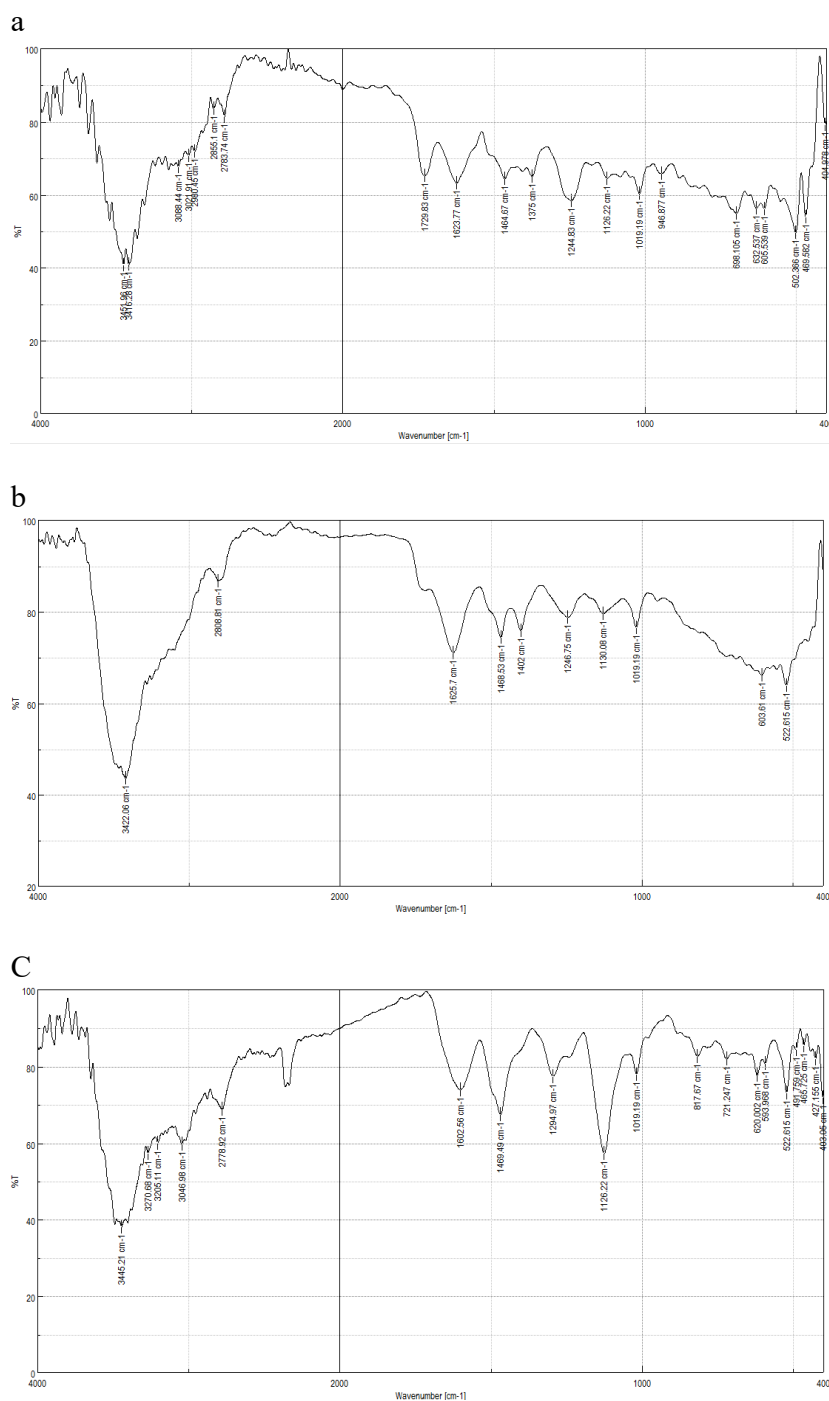### FT-IR analysis
The FT-IR spectrum of iodine doped Pani/ clay

Fig. 1. FT-IR for Pani/clay for the a) ratio 16% I_2 b) ratio 33% I_2 c) ratio 50% I_2.

Table 1. Assignments of FT-IR the absorption bands for pure   polyaniline/clay, and iodine-doped polyaniline/clay.

Assignment	Pani/clay	Pani/clay/I₂/16%	Pani/clay/I₂/33%	Pani/clay/I₂/50%
	Wavenumber	Wavenumber	Wavenumber	Wavenumber
	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$
N-H	3211	3451	3422	3445
C-H stretch	-	3088	2808	2778
C-H stretch	-	3021	-	3046
C-C stretch (in ring)	1581	1623	1625	1602
Ring stretch	1496	1469	1468	1469
C-N stretch	1303	1244	1246	1294
C-N bending	-	1019	1019	1019

shows in Fig. 1a, b, and c.

The aromatic ring is retained in the polymer, as indicated by the peak at $1581 cm^{-1}$ [40]. At $3211 cm^{-1}$, the N-H vibration is detected. Peaks of substituted benzene can also be found at 798 and $609 cm^{-1}$ Table 1 shows the band assignments for the FT-IR absorption bands for pure, polymerized, and iodine-doped polyaniline/clay thin films.

In the iodine-doped polyaniline/clay, there is a shift in N-H stretching and C-N stretching bands, as shown in the Table 1. The N-H stretch absorbed in the N-H and C-N stretching bands indicated that iodine atoms may be attaching to polyaniline's amine nitrogen sites [41]. The key bands in the iodine-doped polyaniline that correspond to the aromatic rings are found to be shifted towards high wave number. This suggests that iodine doping alters the structure of aniline samples.

Morphological Analysis SEM

Polyaniline's as-deposited surface morphology Scanning electron microscopy is used to examine
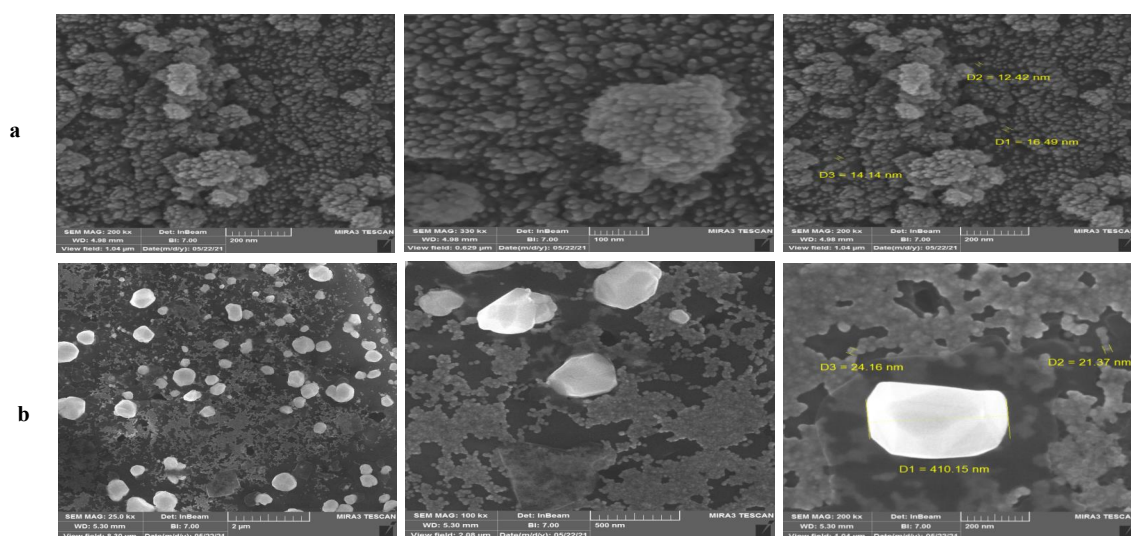

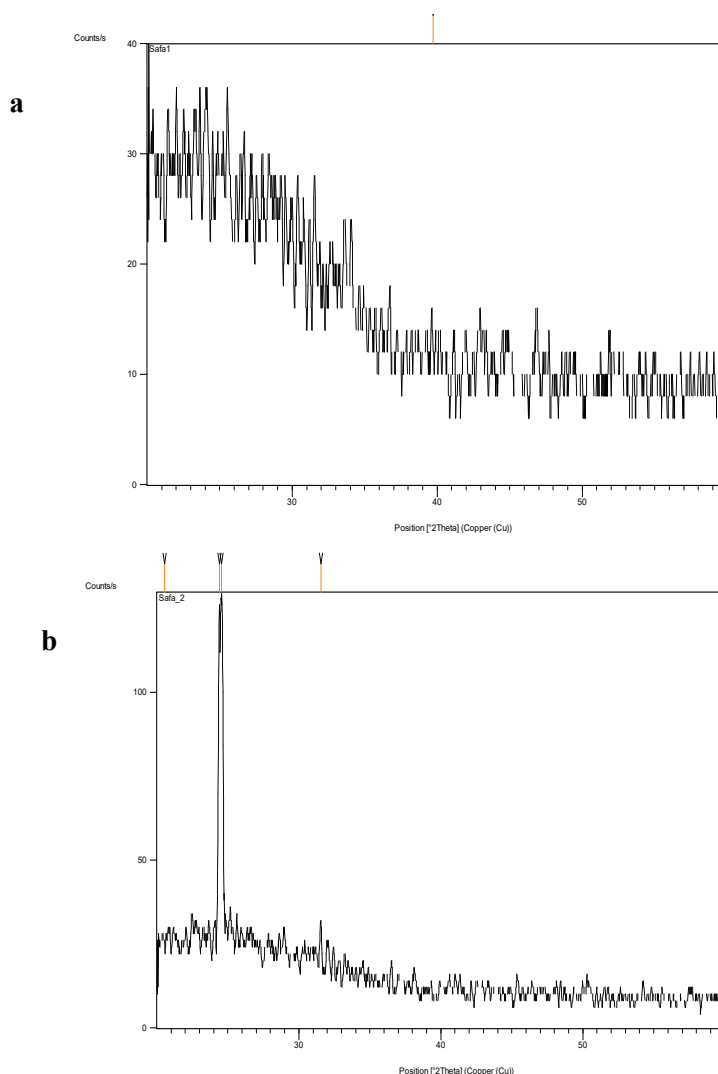Fig. 2. The image of SEM a) for PANI/clay b) for PANI/clay/iodine.

Fig. 3. a) XRD pattern of PANI/clay and b) XRD pattern of PANI/clay/iodine.

thin films. The technique of scanning electron microscopy (SEM). Fig. 2 depicts a SEM image of the sample.

In Fig. 2a PANI/ clay showed several micrometer areas dark and bright contrast are present , the dark portion indicates to clay particles with diameter 21.37 nm, the bright portion is due to PANI chains, the diameter of 410 nm. In Fig. 2b PANI/ clay/iodine showed small ball with diameter 14.14 nm attracted to clay and PANI.

Structural properties of the PANI/clay and PANI/ clay/iodin

Fig. 3a shows the PANI/clay X-ray diffraction pattern. The amorphous nature of PANI/clay is

suggested by its X-ray diffraction pattern. The X-ray diffraction pattern of PANI/clay/iodine is shown in Fig. 3b. The crystalline nature of the composite is indicated by the iodine peak, as shown in the figure. The additional peaks in Fig. 3b correspond to the iodine dispersion in PANI/clay when comparing the XRD patterns of PANI/clay/iodine.

UV-VIS absorption studies

Fig. 4 shows the UV-visible spectra of intercalated PAni/clay/iodine. For the n-π*transition of PAni/clay/iodine dopent, sharp UV absorption peaks were observed between (350-390) nm [42].

Enough light energy must be absorbed to transfer electrons from the valence band to the
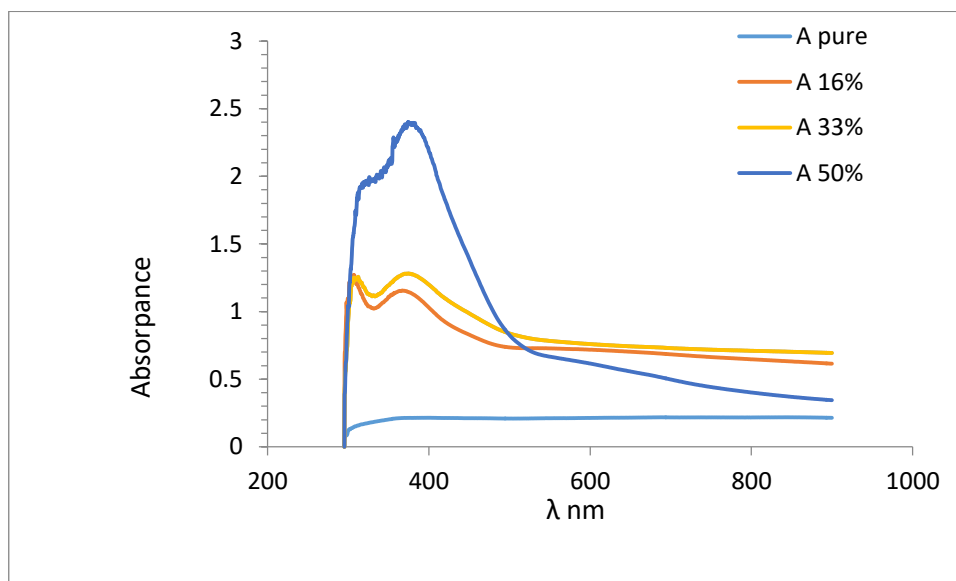
Fig. 4. Dependence of absorbance on the wavelength for PANI/clay pure and its iodine dopant.

conduction band; this energy is equal to the energy gap, and the relationship that shows the absorbed energy (h) is[43,44].

$$\alpha h\upsilon = A(h\upsilon - E_{opt})^n \tag{1}$$

where α is the absorption coefficient , $h\upsilon$ is the photon energy , A a constant. The symbol represents the power coefficient. It's calculated by examining the various types of electronic transitions that are possible, with 1/2 indicating direct permitted and 3/2 indicating direct prohibited [45,46].The plotting of $(\alpha h\upsilon)^{1/2}$ against $h\upsilon$ as shown in Fig. 5 of polyaniline / clay in iodine doped form .

Fig. 5 shows that when the weight ratios of iodine are added to PANI/clay, the energy gap narrows as the percentage of addition increases, clearly demonstrating the effect of iodine on the PANI/clay compound as shown in Table 2. Table 2 shows the effect of iodine on the PANI/clay compound. It is seen that the iodine doping decrease the optical band gaps from 2.6 eV for Pani/clay doped with 16% iodine to 1.8 eV for Pani doped with 50% iodine

The adjustment of the polymer structure is responsible for the change in the optical band gap. Due to the insertion of the charged species, doping causes structural ordering of the polymers.

Electrical conductivity (σ_{dc})

Because electrical conductivity is a property of polymeric materials and materials due to the presence of an ionic impurity, materials are categorized into three categories based on their continuous electrical conductivity (insulators, semiconductors, conductors, and superconductors) [47]. The electrical conductivity of materials can change by adding impurities, a process known as doping, hence the electrical conductivity of these materials is low. And when impurities are impurities, this ability alters, and depending on the type of impurities employed (maturations or donors), a type (n) or a type (p) can be obtained [48].

The following equation [49] can be used to compute electrical conductivity (σ_{dc}).

$$\sigma = \frac{1}{R} \times \frac{d}{A} \tag{2}$$

Where: R stands for electrical resistance, measured in Ω, d: thickness of the embrane.

A: Electrode area.

According to the equation [50], the value of electrical conductivity changes exponentially with absolute temperature.
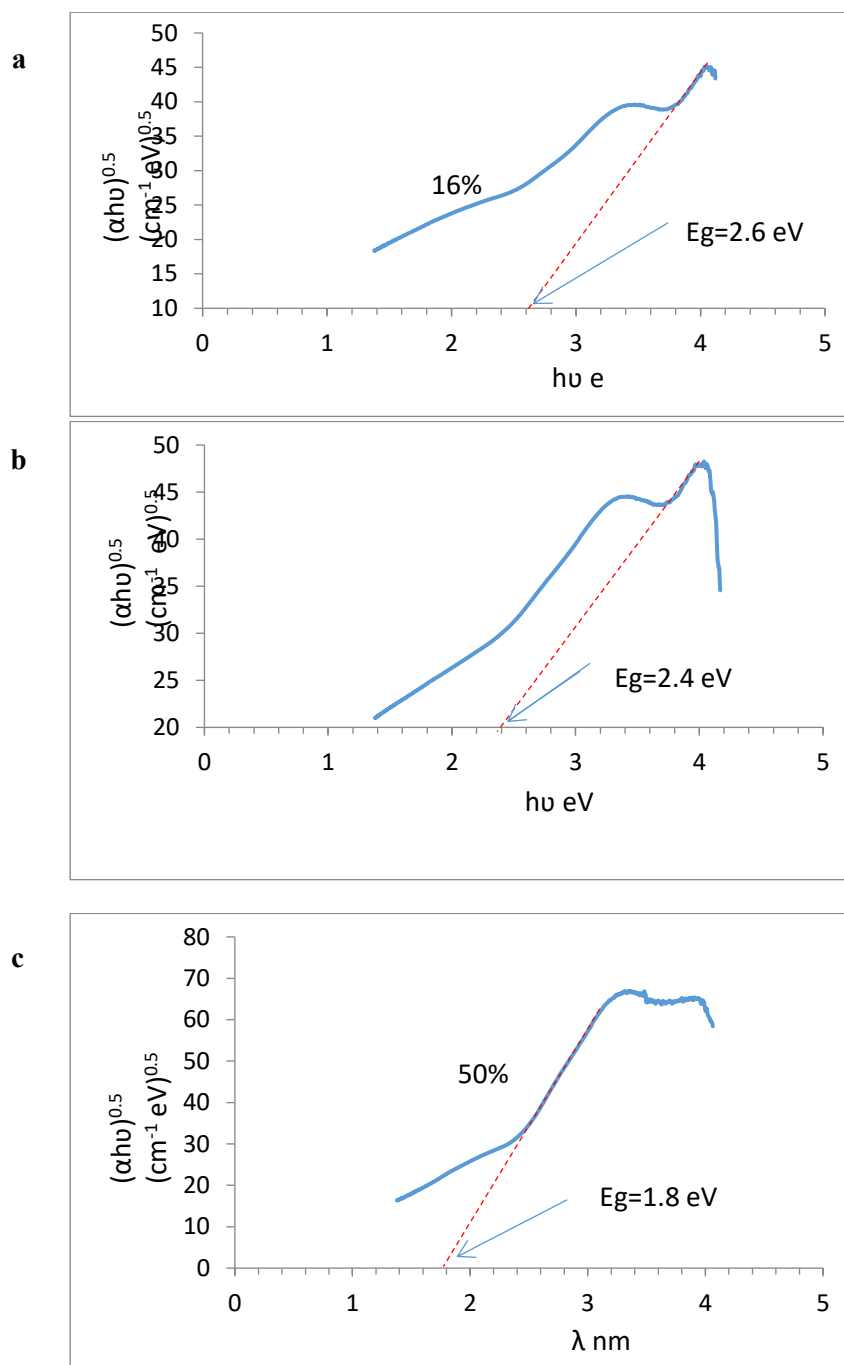
$$\sigma = \sigma o \exp[-E_a/K_B T] \tag{3}$$

Fig. 5. Dependence of $(\alpha h\upsilon)^{1/2}$ on the photon energy $h\upsilon$ for PANI/clay/ for the ratio of a) 16% I_2.b) 33% I_2 c) 50% I_2.

where σ_o: conductivity at a temperature (0^0C), Ea: the value of the activation energy, T: temperature in Kelvin, K_B: Boltzmann's constant.

The membrane's characteristic (current-voltage) at various temperatures within the range

Table 2. The values of energy gap of PANI/clay/iodine I_2 ratio.

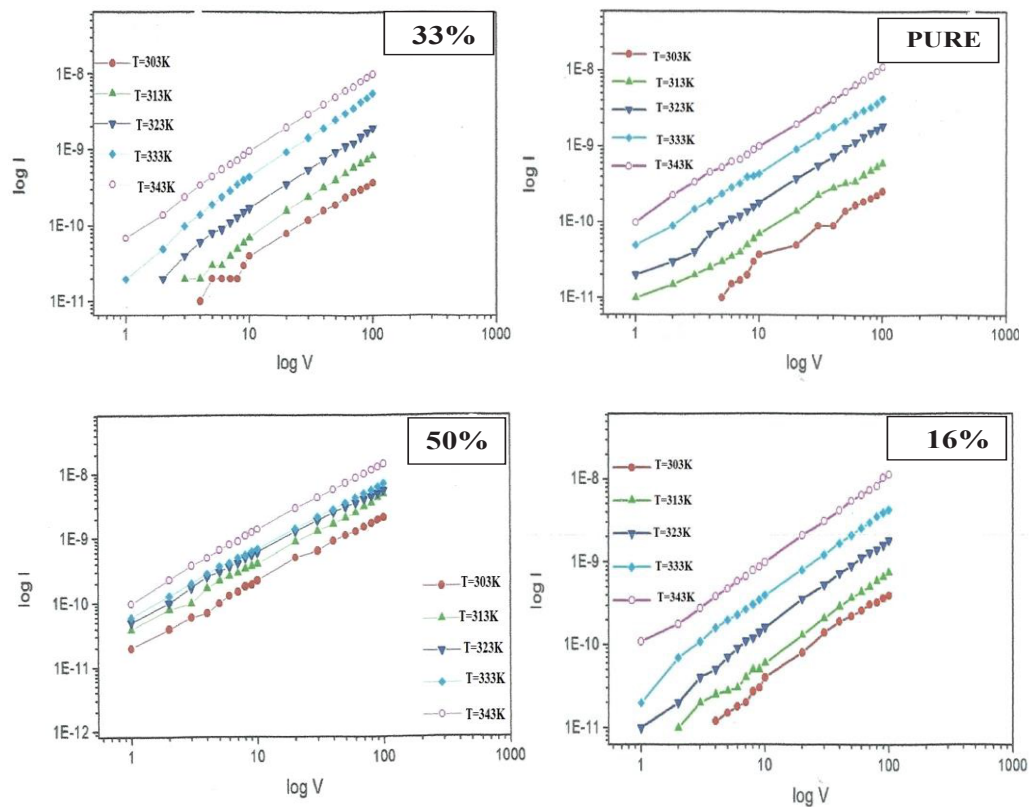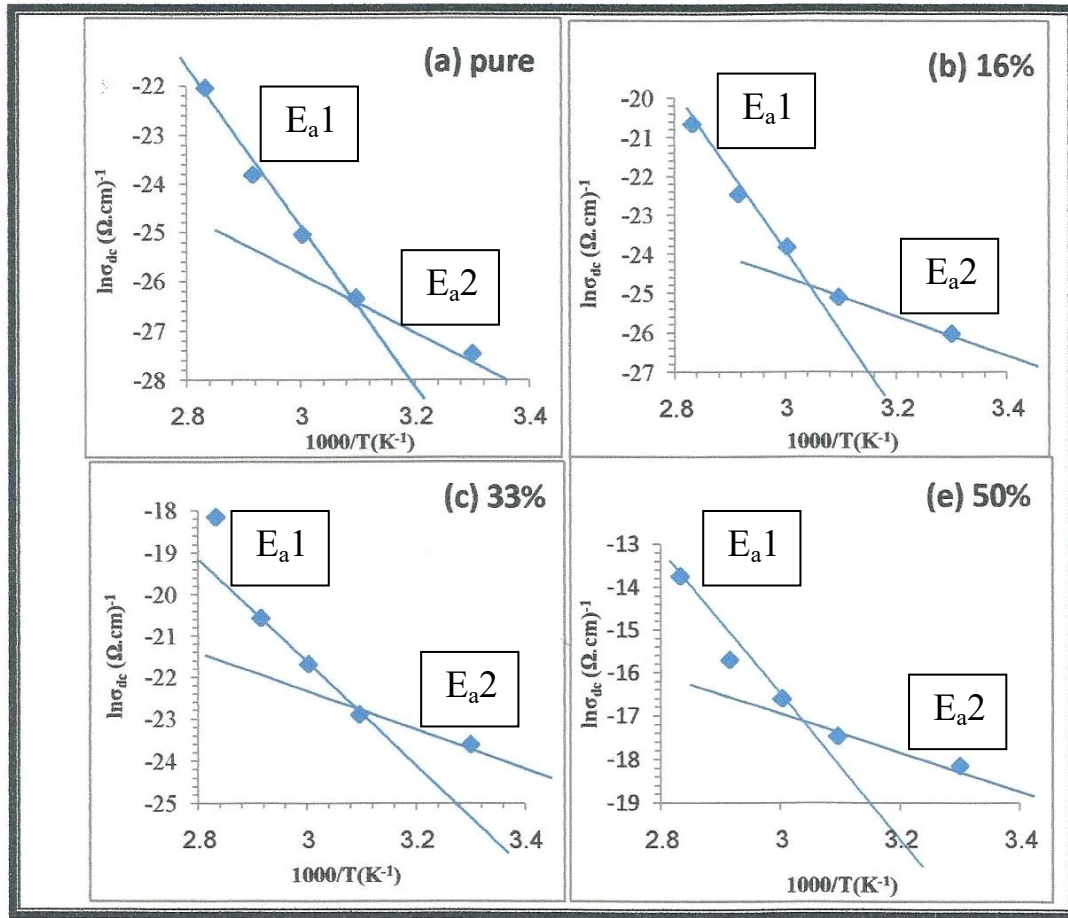| Iodine ratio	Energy gap[eV]
16%	2.6
33%	2.4
50%	1.8

Fig. 6. The I-V for PANI/clay with different ratio of I_2.

Table 3. The values of activation energy Ea for PANI/clay with deferent ratio I_2.

$T(K)^0$	E_{a1}(eV)	E_{a2}(eV)	100%
298-343	3.16	3.35	Pure
298-343	3.05	3.3	16%
298-343	3.04	3.24	33%
298-343	3.03	3.2	50%

Fig. 7. Activation energy Ea for PANI/clay with different ratio I_2.

Table 4. The values of electric conductivity for PANI/clay pure and(PANI /clay+I_2) in variant temperature.

$T(K)^0$	σ (s.cm^{-1}) (PANI /clay)	σ (s.cm^{-1}) (PANI /clay+I_2) (16%)	σ (s.cm^{-1}) (PANI /clay+I_2) (33%)	σ (s.cm^{-1}) (PANI /clay+I_2) (50%)
303	0.5×10^{-7}	4×10^{-7}	5.3×10^{-7}	6×10^{-7}
313	0.55×10^{-7}	4.8×10^{-7}	8×10^{-7}	9.4×10^{-7}
323	0.61×10^{-7}	6.1×10^{-7}	12×10^{-7}	14.7×10^{-7}
333	0.77×10^{-7}	7.3×10^{-7}	13.4×10^{-7}	19.2×10^{-7}
343	0.83×10^{-7}	8×10^{-7}	14×10^{-7}	20.1×10^{-7}

(303-34300K).

The current-voltage feature is shown in Fig. 6 for temperatures ranging from 303 to 3430K. The conduction mechanism has improved compared to the undoped membrane, and this is due to the proportion of doping by the oxidizing agent iodine.

For PANI/clay films, a relationship was made between the reciprocal of temperature 1000/T and $\ln\sigma_{d.c}$, from which the activation energy Ea could be estimated from the slope of the straight line using the following relationship [49]:

$$Ea=2.303*8.6*10^{-5}*Slope \qquad (4)$$

Table 3 shows the values of activation energy Ea for PANI/clay with deferent ratio I_2.

Table -4 shows the values of electric conductivity for PANI/clay pure and (PANI /clay+I$_2$) in variant temperature.

CONCLUSION

Our findings show that a method of Mechanochemical in intercalation can be used to obtain Pani-H$_2$SO$_4$/Alculan clay.

Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray absorption spectra, and optical absorption spectra were used to examine the deposited films for physicochemical and optoelectronic features.

SEM revealed that PANI/clay/iodine has a small ball with a diameter of 14.14 nm that is attracted to clay and PANI, and the X-ray diffraction pattern revealed the amorphous nature of PANI/clay and the crystalline nature of PANI/clay/iodine. The energy gap narrows as the percentage of iodine added increases, clearly demonstrating the effect of iodine on the PANI/clay compound. Iodine doping decreases the optical band gaps from 2.6 eV for Pani/clay doped with 16% iodine to 1.8 eV for Pani/clay doped with 50% iodine.

The temperature change with PANI/clay and PANI/clay/I$_2$ electrical conductivity was investigated. The electrical conductivity of PANI/clay was 0.5^*10^{-7} s.cm^{-1} at room temperature, while it was 6×10^{-7} s.cm^{-1} at 50 percent of the same temperature, according to the findings. It was discovered that as the proportion of doping increases and the temperature rises, the electrical conductivity rises as well.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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