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Synthesis, Characterization and study properties of poly para chloro aniline and poly para chloroaniline\MnO_2 nanocomposite

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Abstract

In this work, by oxidative polymerization, we prepared poly para chloro aniline (P (p-ClAn)) and their composites with nano manganese dioxide (MnO_2) in different percentages (13, 26, and52 %). It was characterization by the electronic scanning device, FT-IR infrared spectroscopy, H.N.M.R spectroscopy and differential scanning calorimetry, and also measured the electrical conductivity. By FT-IR and HNMR spectroscopy were confirmed of polymer structure, Also the material crystallinity was confirmed by characterization a differential scanning calorimetry (DSC). The electrical conductivity of the prepared polymer and their composites was also measured in different ratios and it was found that the conductivity decreases with the increase of the percentage of MnO_2. The surface morphology analysis of P(p-ClAn) \MnO_2 nanocomposite shows that polymer capped with inorganic material which is MnO_2.

Introduction

Polymers are simply insulators or plastics obtained through a chemical reaction called polymerization [1]. Dielectric polymers can be converted into conductive polymers which can be defined as are a new group of synthetic metals that collect the mechanical and chemical properties of polymers with the electronic properties of semiconductors for metals. It possesses distinctive optical, electrical, and electrochemical properties. It can be used in many diverse applications such as diodes, solar cells hydrogen storage, and anti-static coating [2-3]. Polymer properties, geometrical shape, the filler type, and distribution they are basic factors on which the electrical conductivity of the polymers depend heavily [4]. Conductive polymer composite (CPC) produces from mixing conductive fillers such as carbon nanotubes, carbon fibers, ceramic particles, metal particles, or carbon nanoparticles with an insulating polymer matrix. As the nanomaterials used serve as additional tools to reinforce a different of characteristics simultaneously without sacrificing any of the properties of the polymer matrix [5]. CPC has a range of ideal properties such as high conductivity, fatigue resistance, high temperature, corrosion resistance, high specific modules, and high specific power. They can also be used as practical materials for carry loads [6]. It attracts researchers to study extensively the effects of environmental stability, ease of transformation in cathode safety, ease of synthesis, different electrical, magnetic, and optical properties, this is because the

polymer with nanoparticles is of great importance [7-8]. Poly pyrrole, poly acetylene, and poly aniline (PANI) are some of the important conductive polymers used widely for a range of applications [9]. PANI is found in four cases: emaraldine salt (ES) is in conductive case, emaraldine base (EB) oxidative half case, pernigraniline an oxidation state for aniline in which the substance is completely oxidized and leucoemeraldine a form of aniline and is completely reduced [10]. As shown in figure 1.

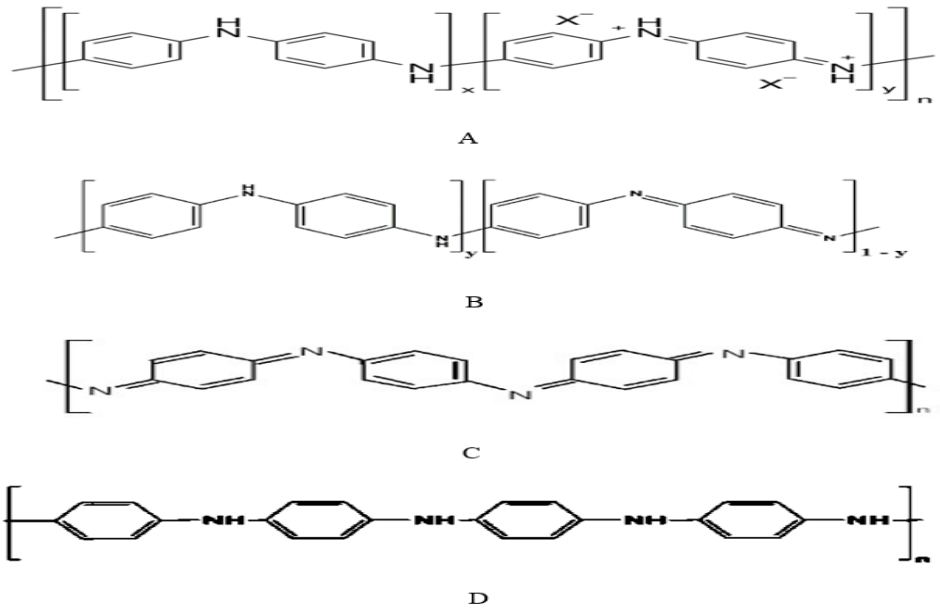


Fig. 1: (A) structure ES, (B) structure EB, (C) structure pernigraniline and (D) structure leucoemeraldine [11].

The nature of the substitutions on the aniline ring is what determines the electronic characteristics of aniline derivatives [12]. The presence of substituted collection on the aniline ring makes the aniline polymers slightly less conductive to electricity but more soluble in organic solvents compared to PANI. It's has been synthesis with distinctive properties such as higher dielectric constant, good charging, good field emission property, adsorbing material, and discharging ability [13]. The study of PANI halogen derivatives for example poly (iodo aniline), poly (chloro aniline), and poly (bromo aniline) is relatively less compared to the widely studied PANI [14]. In our study, P(p-ClAn) and P(p-ClAn) \MnO_2 nanocomposite with various amounts of MnO_2 (13, 26, and 52%) were prepared by chemical oxidative polymerization method utilized hydrochloric acid and potassium iodate (as an oxidative).

Material and Methods

Instrumental:

Electric Balance (MEttler- toleedoo) , Oven (Fanem/ Orion 520), Magnetic Stirrer (Qallenhamp England) , scanning electron microscope (SEM) Hitachi-S 4160, FT-IR using (Shimadzu– spectrometer) ,spectroscopy H.N.M.R (Bruker NMR,) and Differential scanning calorimetry (DSC) Mettler Toledo.

Chemical Materials:

Para chloroaniline, KIO_3, sodium hydroxide, Manganese sulfate from (Sigma Aldrich), hydrochloric acid (GCC), Ethanol, methanol (BDH), and ionized water was used for the synthesis of materials.

Synthesis of P(p-ClAn)

P(p-ClAn) was synthesized by dissolving 1.69g from para chloro aniline in 50 ml of HCl [1M], the solution kept at 5°C, prepared another solution via dissolve 3.7g from KIO_3 in 50 ml HCl [1M], stir the first solution (para chloro aniline with HCl) using magnetic stirrer, the second solution (KIO_3 with HCl) is added drop by drop to the first solution with stirring continuing for 2 hours, kept a mixture for the second day at 5 °C and then stirred again for 4 hours. Solution stirring was stopped and left for an hour after which it was filtered and washed with deionized water several time and the product was glossy brown colour. It was washed off with 3 ml of hydrochloric acid supplemented with ionized water to 100 ml this is for the purpose of increase doping it finally, dry in oven 40-50° C[15]. A figure 2 show suggested chemical structure of the P(p-ClAn).

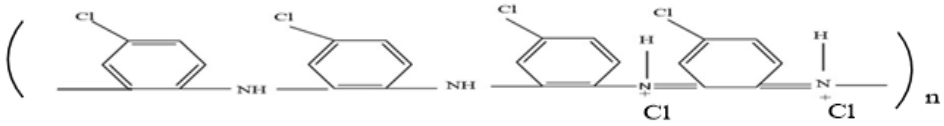


Fig. 2: Suggested chemical structure of the P(p-ClAn).

Preparation of MnO_2 in Nano-Size

By co-precipitation method, MnO_2 nanoparticles were synthesized by adding 25ml aqueous solution (8g, 0.2M) of sodium hydroxide drop by drop to 25ml aqueous (15g, 0.1M) of manganese sulfate $MnSO_4$. The solution was stirred continuously at 60ºC for 2h to precipitate the nanoparticles. Dark brown precipitates formed were then filtered and washed several times with deionized water and dry in a hot air oven at 100ºC for 14 h [16].

Preparation of P(p-ClAn) \MnO_2 nanocomposite

P(p-ClAn) \$MnO_2$ nanocomposite was synthesized by dissolving 2.5g of KIO_3 was dissolved in 100 ml of HCl [1M], kept at 5 ^{0}C, 1g from para chloro aniline was dissolved in 1 ml of HCl [1M] completed to 6 ml by ionized water. This solution was added drop by drop to the first solution with continuous stirring. After changing the color from colorless to purple we added 0,13g from MnO_2 to the solution, it stirs for 12 hours, after which showed a black precipitate, filtered and wash several times with deionized water and 3ml of methanol. It was dry in the oven from 40-50°C. Be the black precipitate of P(p-ClAn) \$MnO_2$ Nanocomposite. In the same way, it was prepared with different concentrations for MnO_2 0.26 and 0.52g. A figure 3 show suggested chemical structure P(p-ClAn)\ MnO_2 nanocomposites.

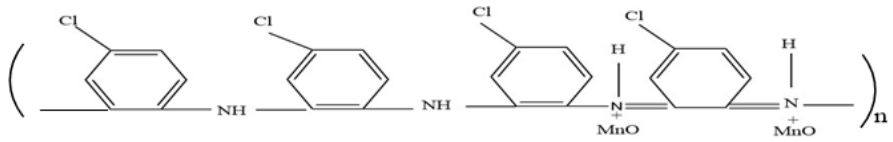


Fig. 3: Suggested chemical structure P(p-ClAn)\ MnO_2 nanocomposites.

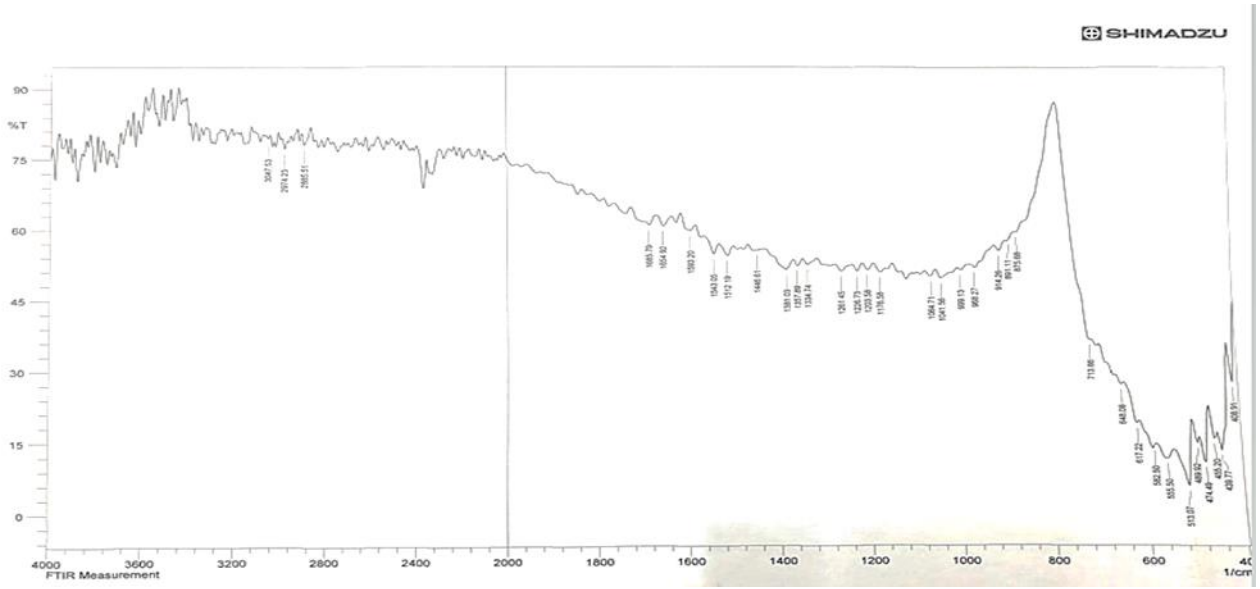
Characterizations

The morphology of the prepared P(p-ClAn) and their composites were examined using a scanning electron microscope (SEM) Hitachi-S 4160. The chemical structure of P(p-ClAn) and P(p-ClAn)\MnO_2 nanocomposite were characterization by FT-IR using (8300 FT-IR Shimadzu– spectrometer of 400 to 4000 cm^{-1}) for samples in the KBr disc form, and spectroscopy H.N.M.R using DMSO as a solvent carried out on a 500MHz Bruker NMR spectrometer. Differential scanning calorimetry (DSC) Mettler Toledo Thermal Analysis using nitrogen gas and rate 20 °C\ m. The electrical conductivity measured by LCR meter (HEWLETT-PACKARD).

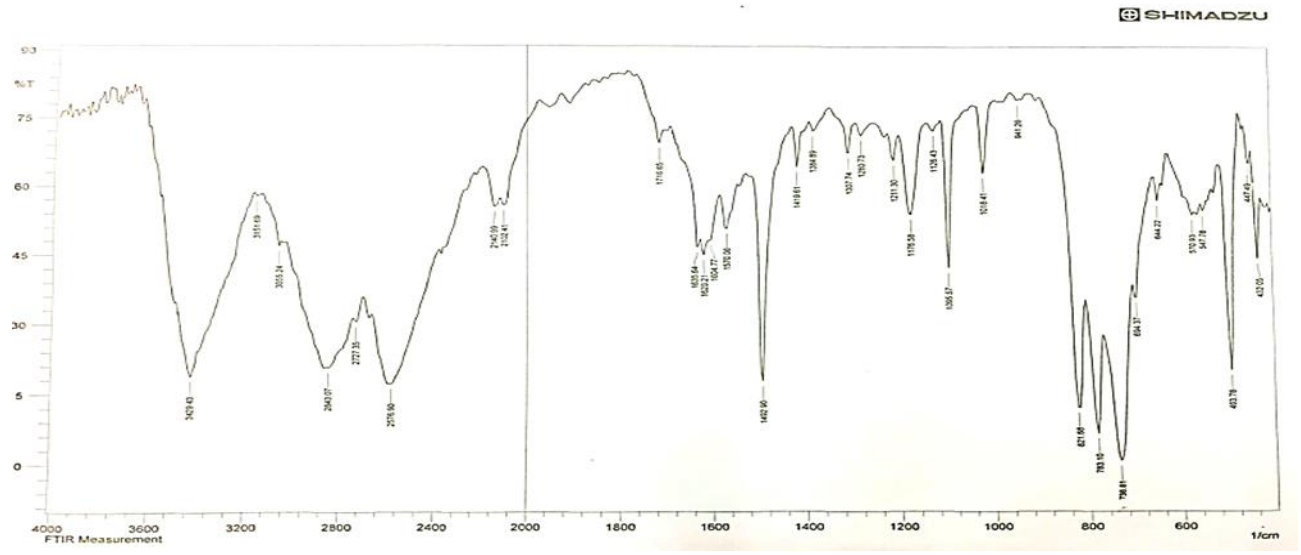
Results and Discussion

Result FT-IR

The FT-IR Spectra of the P(p-ClAn)- ES and MnO_2 Nano particles under bend the like conditions were shown in figure 4. The vibration frequencies of the main infrared bands and their assignment for poly P(p-ClAn) –ES summarized in Table 1. The disappearance of the binary signal between 3100 - 3500 indicates the occurrence of a substitution reaction with one of the hydrogen atoms on N and the formation of a polymer, a change in frequencies occurred due a reaction the polymer formation. These results in table 1 are identical to the result of the following search [1].



a


SHIMADZU
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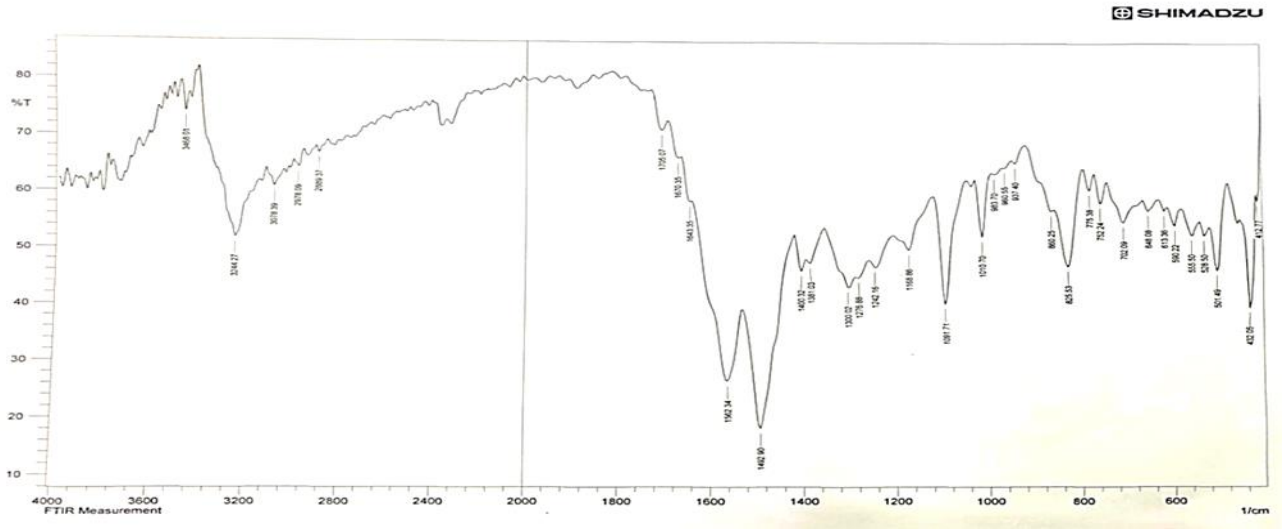
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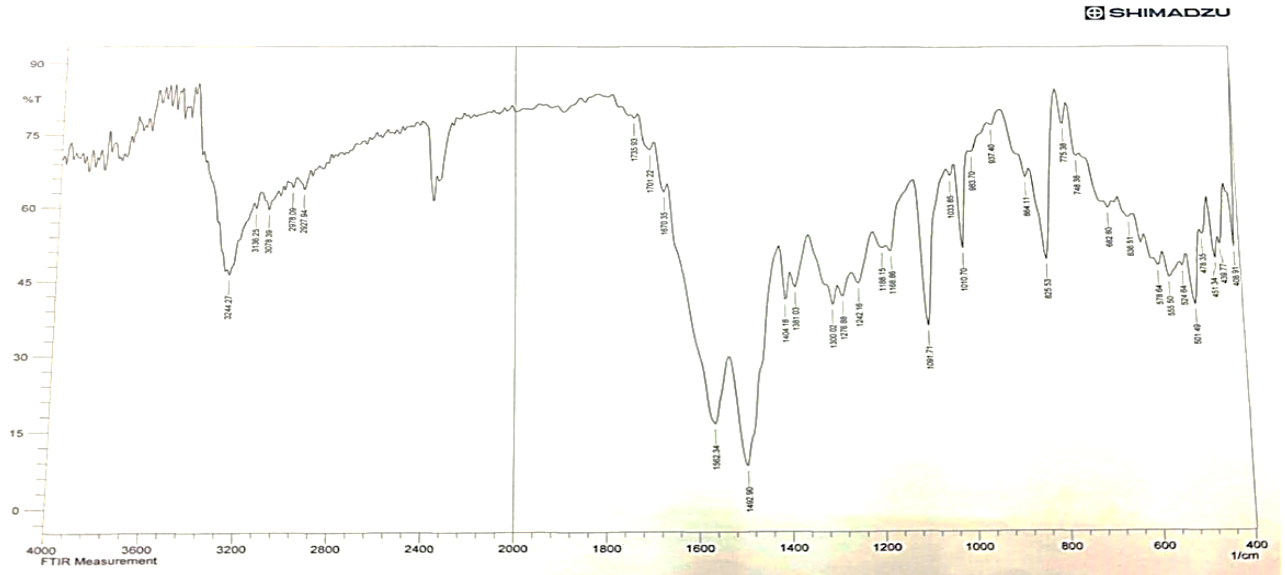
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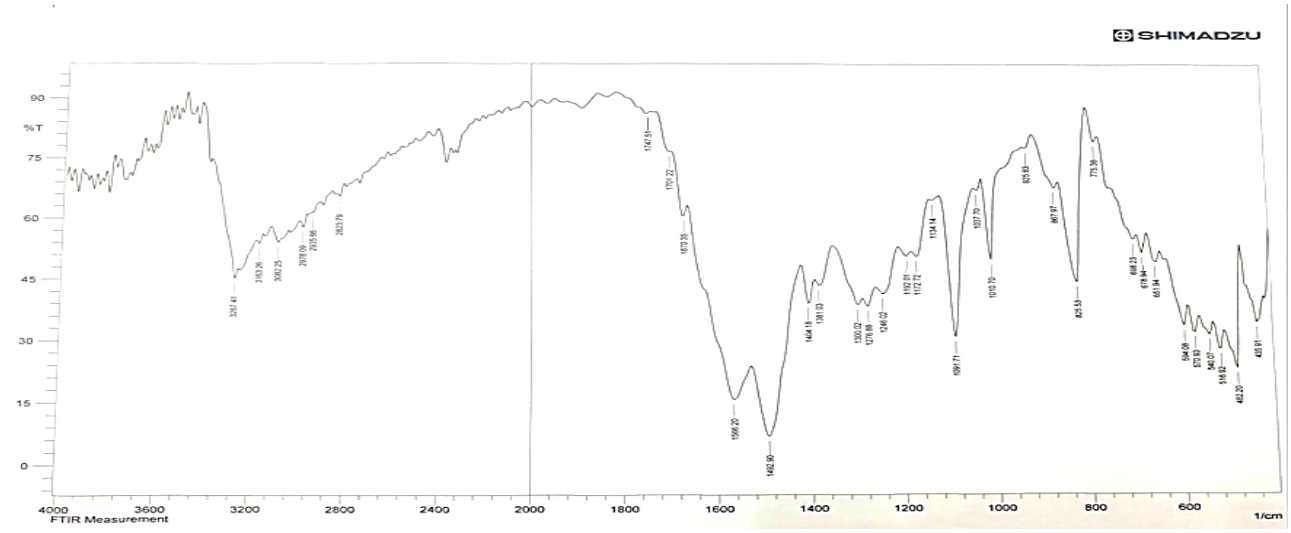


e

Fig. 4: FT-IR for (a) pure MnO_2, (b) P(p-ClAn) doped HCl, (c) P(p-ClAn)\$MnO_2$ nano composite at 13%, (d) P(p-ClAn)\$MnO_2$ nano composite at 26%, and (e) P(p-ClAn)\ MnO_2 nano composite at 52%.

Table 1: Appear FT-IR for P(p-ClAn) doped HCl, P(p-ClAn) \MnO_2 nanocomposite at 13, 26 and 52%.

			p(p-ClAn)\Mn-O at concentration		
Peak assignment	Mn-O	P(p-ClAn)	13%	26%	52%
Quinonoid	\\	1570cm^{-1}	1562cm^{-1}	1562cm^{-1}	1566cm^{-1}
Benzenoid	\\	1492 cm^{-1}	1492 cm^{-1}	1492 cm^{-1}	1492 cm^{-1}
B-N+H-B\Q=N+H-B	\\	1176cm^{-1}	1168 cm^{-1}	1168 cm^{-1}	1172 cm^{-1}
C-Cl	\\	694cm^{-1}	648cm^{-1}	682cm^{-1}	698cm^{-1}
C-N	\\	1307cm^{-1}	1300,1242 cm^{-1}	1300,1242 cm^{-1}	1300,1246 cm^{-1}
_NH st	\\	3429, 3151 cm^{-1}	3244cm^{-1}	3244.3136 cm^{-1}	3267,3163cm^{-1}
1,2,4 tri substitution	\\	821cm^{-1}	825cm^{-1}	825cm^{-1}	825cm^{-1}
Mn-O	513cm^{-1}	\\	528 cm^{-1}	524 cm^{-1}	516cm^{-1}

Result for SEM

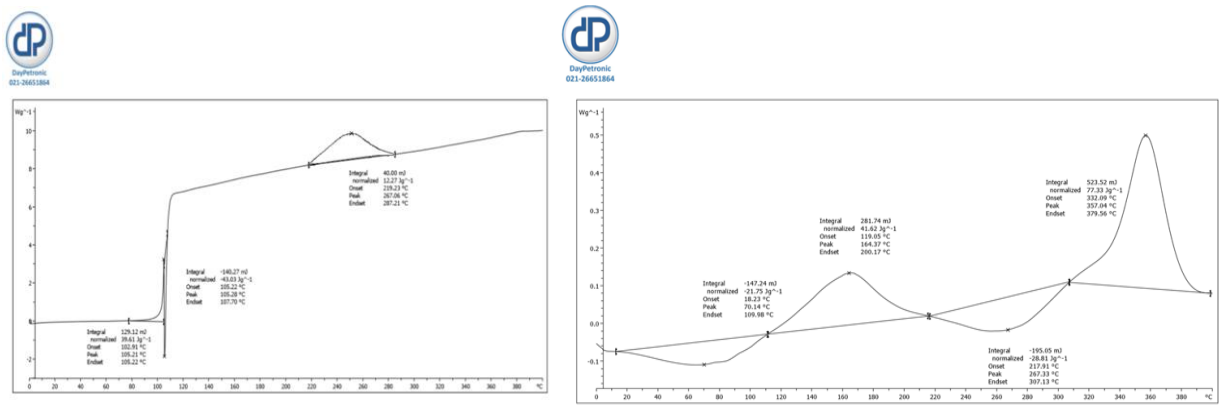
A figure 5 shows the SEM micrographs of P(p-ClAn), MnO_2 nanoparticles and P(p-ClAn)\MnO_2 composite. Figure 5a shows the SEM image of the MnO_2 in form nanoparticles with sizes less than 100 nm. The SEM image of P(p-ClAn) clearly indicates that this polymer does not contain MnO_2 on surface. The SEM image of the P(p-ClAn) \ MnO_2 nanocomposite (c,

d, and e) shows that the polymer surface includes nanoparticles in nanocomposites at different concentrations of MnO_2. These figures of nanocomposite showed high agglomeration and differences in surface morphology form, due to strong interaction of polymer chains with MnO_2 nanoparticles lead to increase in agglomeration due to bond between organic group of polymer with doped MnO_2 surface.

Fig. 5: SEM for (a) Nano MnO_2, (b) P(p-ClAn), (c) P(p-ClAn) \$MnO_2$ Nano composites at 13%, (d) P(p-ClAn) \$MnO_2$ Nano composites at 26%, (e) P(p-ClAn) \$MnO_2$ Nano composites at 52%.

Result thermal analysis of polymer and composites using DSC

DSC Measurement for P(p-ClAn) appears a value of 102.91° C attributed to onset crystallization. An exothermic peak at 105.22° C appears to denote Temperature Crystallization. The endothermic peak at 267.06 ° C indicates the Temperature melting. As shown in figure 6a. DSC for P(p-ClAn)\MnO_2 nanocomposite 0,52g appears in figure 6b. An exothermic peak at 70.14 ° C appears to be denotes temperature crystallization. The endothermic peak at 164.37 ° C is denoted thermal temperature melting in the polymer matrix. The exothermic peaks at 267.33° C indicate cross- linked or oxidation of composite. The endothermic peak at 357.04°C degradation.



a b

Fig. 6: DSC for (a) P(p-ClAn) and (b) P(p-ClAn) \MnO_2 Nanocomposite.

Result HNMR

As shown in figure 7, the weak signal when 3.73 ppm it indicates absorbed water in DMSO, strong signs appeared at 2.51 and 2.52 ppm indicating to DMSO, value for -NH- (second amine) single signs show at 9.89 ppm, the base value for =N⁺H- sharp peak is shown at 6.74 and 6.75 ppm, as for signs to aromatic rings show for Ha 7.33 ppm, Hb 7.19 ppm , Hc 7.07 ppm, Hd 7.35 ppm , He 6.98 ppm , Hf 7.08 ppm, Hg 7.23 ppm, Hh 6.87ppm, Hi 7.14 ppm, Hj 6.62ppm, Hk 7.93 ppm and single signs at 5.71 ppm indicating Hl . Note No signs of weak signal between (3.4 -4) for NH_2 [17].

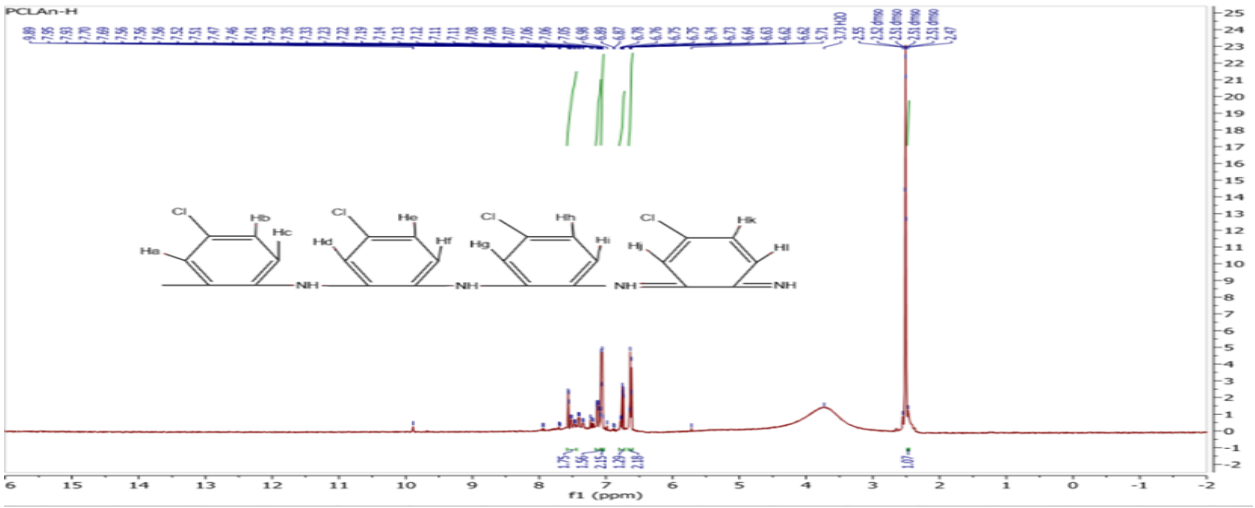


Fig. 7: ^{1}H-NMR spectrum of the P(p-ClAn).

Electrical conductivity

The electrical conductivity of the synthesized P(p-ClAn) and their nanocomposites was measured via weight ratios (13 and 52 %). Measured by the LCR device at a range frequencies of 100-100000 Hz. Conductivity values decrease with increasing frequency gradually at (100-4000Hz). The conductivity decreased with a percentage increase of MnO_2, the reason for this is that MnO_2 is a semiconductor material that has a lower conductivity than a basic polymer. The results are shown in the following table.

Table 2: Show a conductivity value for polymer and polymer composite.

Compound	Conductivity $S.cm^{-1}$
P(p-ClAn)	$2.29 .10^{-4}$
P(p-ClAn)\NanoMnO2 13%	$7.19 .10^{-3}$
P(p-ClAn)\NanoMnO2 52%	$5.5 .10^{-3}$

Conclusions

P (p-ClAn) and P (p-ClAn) \MnO_2 nanocomposites were synthesized via using the oxidative polymerization method. A polymer and their composites were characterized by FT-IR and ^{1}HNMR in order to show doping with MnO_2. It was characterization by SEM for surface morphology analysis, that the materials had a crystalline nature characterization by DSC confirmed. The electrical conductivity of the prepared polymer and its composites were also measured in various percentages, conductivity decrease little with a ratios increase for MnO_2.

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تحضير وتشخصيص ودراسة خصائص بولي بارا-كلورو انلين و بولي بارا- كلوروانلين/ ثنائي اوكسيد المنغنيز نانومتراكب

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البحث مستل من رسالة ماجستير الباحث الاول

معلومات البحث:

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تأريخ القبــول: 18\10\2020

الكلمات المفتاحية:

نانو ثنائي اوكسيد المنغنيز, بولي بارا كلورو انلين, متراكب, بلمرة و متراكب بوليمر.

الخلاصة:

تم تحضير بولي بارا كلورو انلين ومتراكباته مع ثاني أكسيد المنغنيز النانوي (MnO_2) بنسب مختلفة (13، 26، 52٪) من خلال أكسدة البلمرة، شخصت المركبات المحضرة باستخدام جهاز المسح الإلكتروني ومطياف الأشعة تحت الحمراء FT-IR، وقياس مطياف H.N.M.R ومسعر المسح التفاضلي، وأيضا قياس الموصلية الكهربائية. بواسطة FT-IR و HNMR تم تأكيد هيكل المركب وتم تأكيد ان المادة بلورية بواسطة قياس مسعر المسح التفاضلي. كما تم قياس الموصلية الكهربائية للبوليمر المحضر ومركبه بنسب مختلفة ووجد أن الموصلية تقل مع زيادة نسبة MnO_2. يوضح تشخيص التشكل السطحي لمركب بولي بارا كلور انلين \ثنائي اوكسيد المنغنيز نانو كومبوزايت أن البوليمر مغطى بمواد غير عضوية وهي MnO_2.