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Synthesis, characterization and study electrical conductivity of New Poly 4-methoxy aniline\ manganese dioxide nano composite.

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Abstract

In the present paper, we synthesized Nano poly4-methoxy-aniline P (4-Man) and composites with Nano manganese dioxide (MnO2) in the various ratio (13, 26, 52 percentage) via polymerization oxidation. We Characterization it with the electronic scanning device and the FT-IR infrared spectroscopy, measuring spectra scope H.N.M.R, Differential scanning calorimetry and scanning electron microscope . The structure was confirmed by FT-IR and HNMR and characterized with a differential scanning calorimetry medium confirmed that the material had a crystalline nature. The surface morphology analysis of Poly 4-methoxy aniline /MnO2 (P (4-Man) \MnO2 Nanocomposite) shows that polymer capped with inorganic material which is MnO2. The electrical conductivity of the prepared polymer and its compound were also measured in different ratios was conductivity decreases with a percentage increase for MnO2.

Index Terms – *NanoMnO2, Poly 4-methoxyaniline, composite, polymerization, Polymers composites.*

تحضير وتشخيص ودراسة التوصيلية الكهربائية لبولي -4 ميثوكسي انلين جديد / نانو كومبوسايت ثنائي اوكسيد المنغنيز.

غفران حامد نايل , د.طارق عبدالجليل منديل
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الخلاصة :

في الورقة الحالية، قمنا بتحضير بولي 4 – ميثوكسي انلين ومتراكباتها مع نانو ثاني أكسيد المنغنيز بنسب مختلفة (13 ، 26 ، 52 ٪) عبر أكسدة البلمرة. قمنا بتشخيصها بجهاز المسح الإلكتروني و مطياف الأشعة تحت الحمراء FT–IR ، قياس H.N.M.R و قياس السعرات الحرارية للمسح التفاضليو المجهر الالكتروني الماسح . تم تأكيد الصيغة التركيبية بواسطة مطيافية FT–IR و HNMR و التشخيص بواسطة قياس للمسح التفاضلي أكد أن المادة ذات طبيعة بلورية. يوضح تحليل الشكل السطحي لمتراكب بولي 4 – ميثوكسي انلين / ثنائي اوكسيد المنغنيز نانو متراكب أن البوليمر مغطى بمواد غير عضوية وهو MnO_2. كما تم قياس الموصلية الكهربائية للبوليمر المحضر ومركبه بنسب مختلفة وكانت نقصان الموصلية مع زيادة النسبة المئوية لـ MnO_2.

1. Introduction

Electrically conductive polymers have the electrical properties of semiconductors and metals, and polymers' mechanical and chemical properties as a result of mixing polymer and semiconductor or conductive metals. Poly-pyrrole, polyacetylene, poly-pyrrole, and poly-aniline (PANI) are some of the major conductive polymers commonly used for a variety of applications. Nanocomposites (inorganic-organic) hybrid materials have gained considerable interest because they can combine the advantages of both components and offer different properties during modification or strengthening (Bekhoukh et al., 2017). Their future applicability in the manufacture of various sensors, photovoltaic devices, organic light-emitting diodes (OLEDs), organic area effect transistors (O-FETs), and electro chrome devices Conductive polymers have been extensively studied in academia and industry since their discovery(Pandule et al., 2018). Despite these advantages was the practical application of polyaniline has been limited due to its insolubility in common organic solvents and infusibility(Chouli et al., 2017). PANI solubility can be handled by adding substitution groups on the aniline ring Leading aniline polymers which include substitution groups are slightly less conductive to electricity but more soluble in organic solvents than PANI(Vani & JhancyMary, 2019). What defines electronic characteristics of aniline derivatives is the existence of the aniline ring substitutions(Mateos et al., 2019). That there are electron-donating substituents groups present together with the aromatic rings strongly influences Conformational modifications of conjugated polymers(Veras et al., 2020). PANI and its derivatives characterized as promising conducting polymers result in their controllable conductivity, environmental stability, and easy prepare(Zhao et al., 2016). By chemical oxidative polymerization was made organic soluble poly (substituted-aniline) samples (Liu et al., 2017). In our study, P (p-4Man) was prepared by chemical oxidative polymerization method utilized hydrochloric acid and Potassium iodate (as an oxidative) and P(p-Man) \MnO2 Nanocomposite with various amount of MnO2 (13, 26 and 52%) were prepared .The resulting samples were characterized via FTIR, SEM, DSC, H.N.M.R.

2. Experimental Details

Chemicals: 4-methoxyaniline (Sigma-Aldrich), hydrochloric acid (GCC), and Potassium iodate (KIO_3) from Sigma- Aldrich, Ethanol, methanol (BDH) and Di ionized water

2.1 Synthesis of poly4-methoxyaniline

1.65 g [0,013M] from 4-methoxy aniline was dissolved in 50ml of HCL [0,1M] in a three-necked flask and was cooled at 5 °C for a second day. And 3.6 g [0,016M] of KIO3 was dissolved in 50 ml of HCL [0,1M] also cooled for a second day at 5°C. We stir the first solution using the magnetic stirrer, then the second solution was added in the form of drops to the first solution and the stirring continued for 6 hours at a temperature in the laboratory. It was washed several times by 3 ml of HCL acid supplemented with distilled water to 100 ml. then dry the precipitate in the oven at 50-60 °C. Be precipitate color blue -black and the conversion ratio was 71.6% (Ahmed et al., 2015).

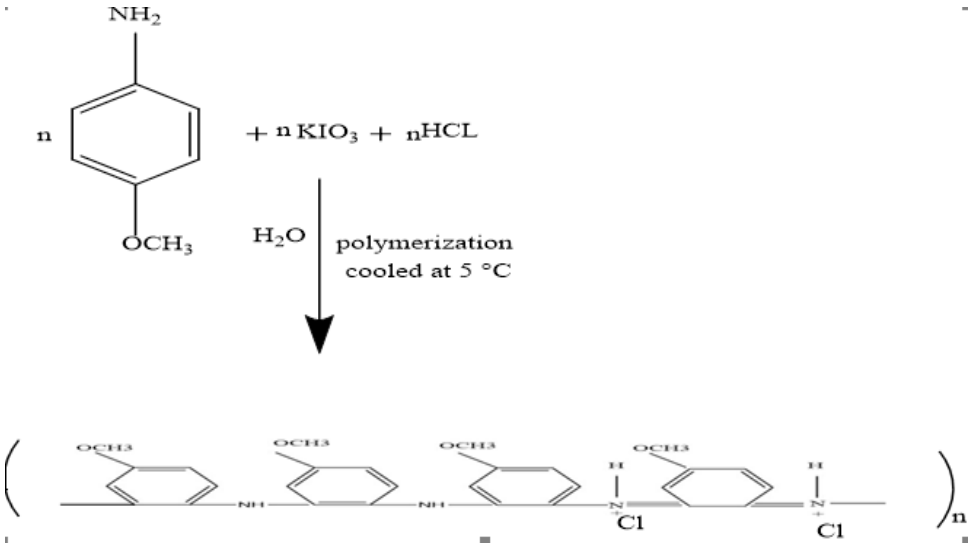


Chart 1 Show Synthesis of poly4-methoxyaniline.

2.2 Preparation of Poly 4-methoxy aniline –MnO2 nanocomposite

1g [0.008M] from 4-Methoxy aniline was dissolved in 1 ml of HCL completed to 6ml by distilling water. And 2,5g [0,011M] of KIO3 was dissolved in 100 ml of HCL [1M], the solution cooled at 0-4°C. The first solution was added to the second solution slowly with continuous stirring. When changing the color from colorless to purple we added 0.13 g [0,0015M] from MnO2 to solution. And it stir for 12 hours, after which showed a black precipitate was filtered and wash several times with deionized water and 3ml of methanol with 3ml di ionized water. It was dried in the oven from 50-60°C. Be poly 4-methoxy aniline \MnO2 Nanocomposite. With the same path it was prepared with various concentrations for MnO2 0.26[0,003M] and 0.52 [0.006M]. The conversion ratio for these concentrations was 63,65and 61%, respectively.

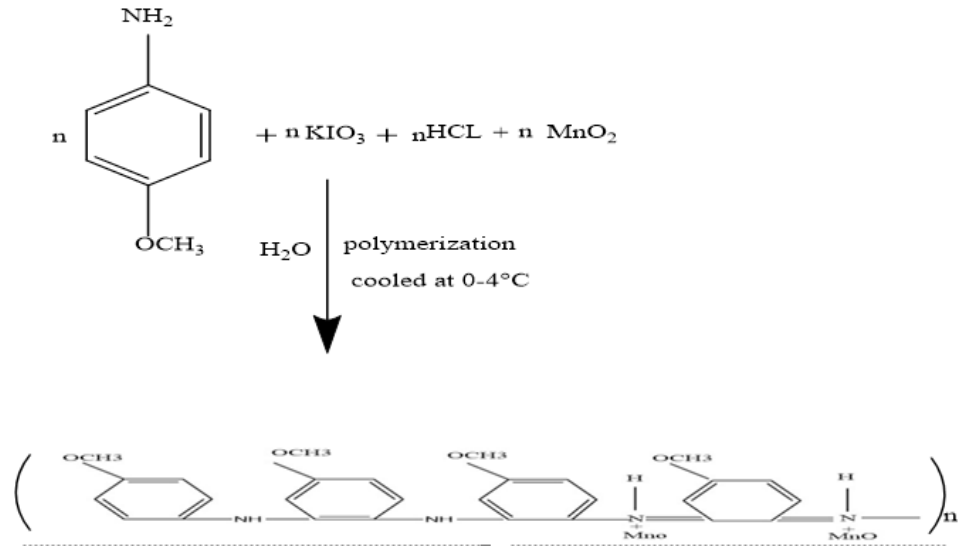


Chart (2) Show Preparation of Poly 4-methoxy aniline –MnO2 nanocomposite.

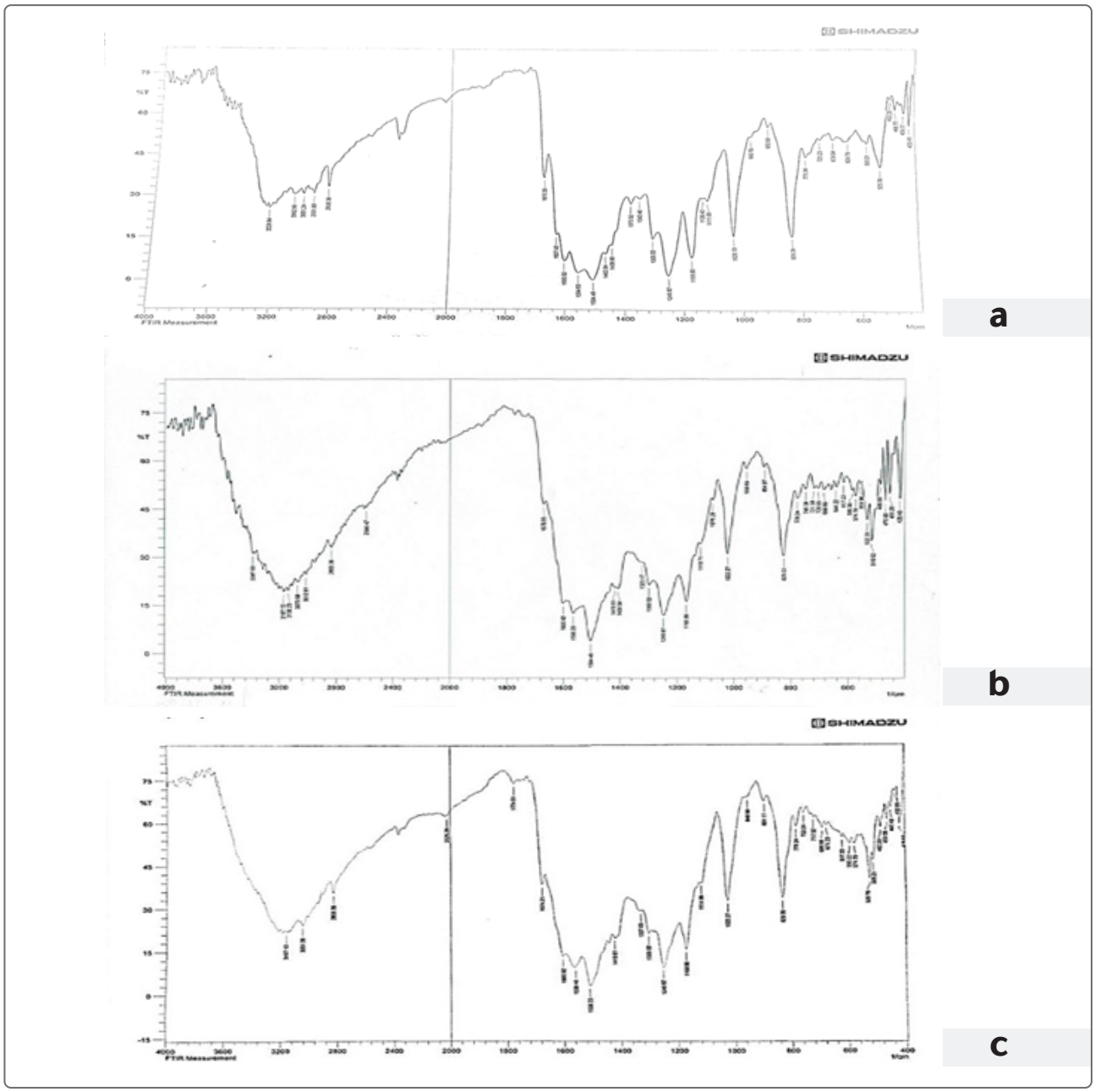
2.3 Characterizations

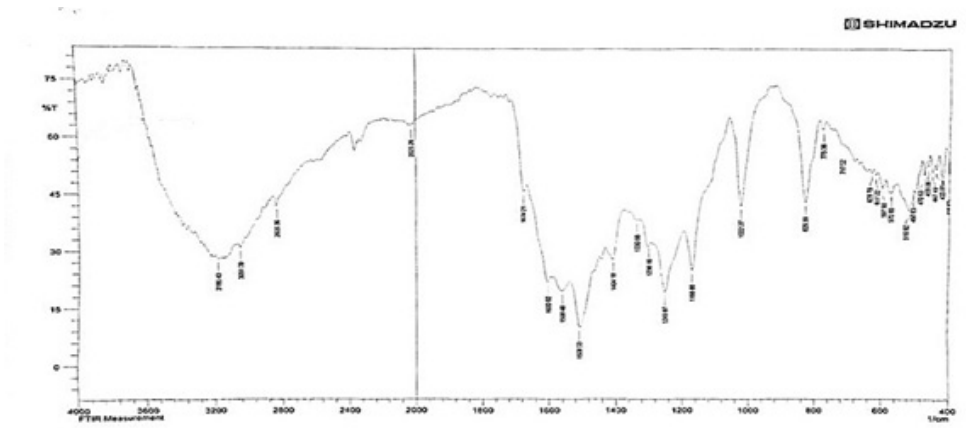
FTIR spectra were recorded on Nicoletir 100 FT-IR - spectrometer of 400 to 4000 cm^{-1} for samples in the KBr disc form. A scanning electron microscope (SEM) in the Iran\ university of Tehran Zeiss, Differential scanning calorimetry (DSC) using nitrogen gas and rate 20 C \ m, Spectra scope H.N.M.R using DMSO as a solvent carried out on a 500MHz Bruker NMR spectrometer.

3. Results and Discussion

3.1 Result for FT-IR

The FTIR spectra of the poly (4-Methoxy aniline) ES and Poly (4-Methoxy Aniline)-ES with HCL under bend the like conditions were appear in Figures a, b, c and d. The vibration frequencies of the main infrared bands and their assignment for poly 4-methoxy aniline -ES and poly 4-methoxy aniline -Cl are summarized in Table 1





d

Figure (1) show FT-IR for (a) P(4-Man) doped HCL,(b) P(4-Man) \MnO2 nano composite at 13%, (c) P(4-Man) /MnO2 nano composite at 26% and (d) P(4-Man) \ MnO2 nano composite at 52%.

Peak assignment	P(4-Man)	P(4-Man) \ MnO2 Nanocomposite at 13%	P(4-Man) \ MnO2 Nanocomposite at 26%	P(4-Man) \ MnO2 Nanocomposite at 52%
Benzenoid	1462 cm^{-1}	1504 cm^{-1}	1508 cm^{-1}	1508 cm^{-1}
Quinonoid	1554 and 1504 cm^{-1}	1566 cm^{-1}	1558 cm^{-1}	1558cm^{-1}
C-H aromatic	3062 and 3001 cm^{-1}	3070 and 3012 cm^{-1}	3051 cm^{-1}	3051 cm^{-1}
_NH st	3228 cm^{-1}	3387,3167 and 3136 cm^{-1}	3167 cm^{-1}	3186 cm^{-1}
1,2,4 tri substitution	829 cm^{-1}	825 cm^{-1}	829 cm^{-1}	829 cm^{-1}
B-N+H-B\Q= N+H-B	1168 cm^{-1}	1168 cm^{-1}	1168 cm^{-1}	1168 cm^{-1}
C-O-C	1026 cm^{-1}	1022cm^{-1}	1022cm^{-1}	1022cm^{-1}
C-N	1300 and 1249 cm^{-1}	1300 and 1249 cm^{-1}	1300 and 1249 cm^{-1}	1296 and 1249 cm^{-1}
Mn-O	//	516 cm^{-1}	520 cm^{-1}	516 cm^{-1}

Table 1.

3.2 SEM for P (4-Man)

This figures of nano composite showed agglomeration different in surface shape, due to polymerization of polymer chains with MnO2 surface lead to increase in agglomeration due to covalent bond between grafted MnO2 surface with organic group of polymer . The value was smaller size 27.91nm for NanoMnO2, small size 61.41nm for P(4-Man), Small size we obtained 44.66 nm for P(4-Man\MnO2 nano composite at 13%,we got small sizes 24,19nm. nm for P(4-Man\MnO2 nano composite at 26% and P(4-Man\MnO2 nano composite at 52%.

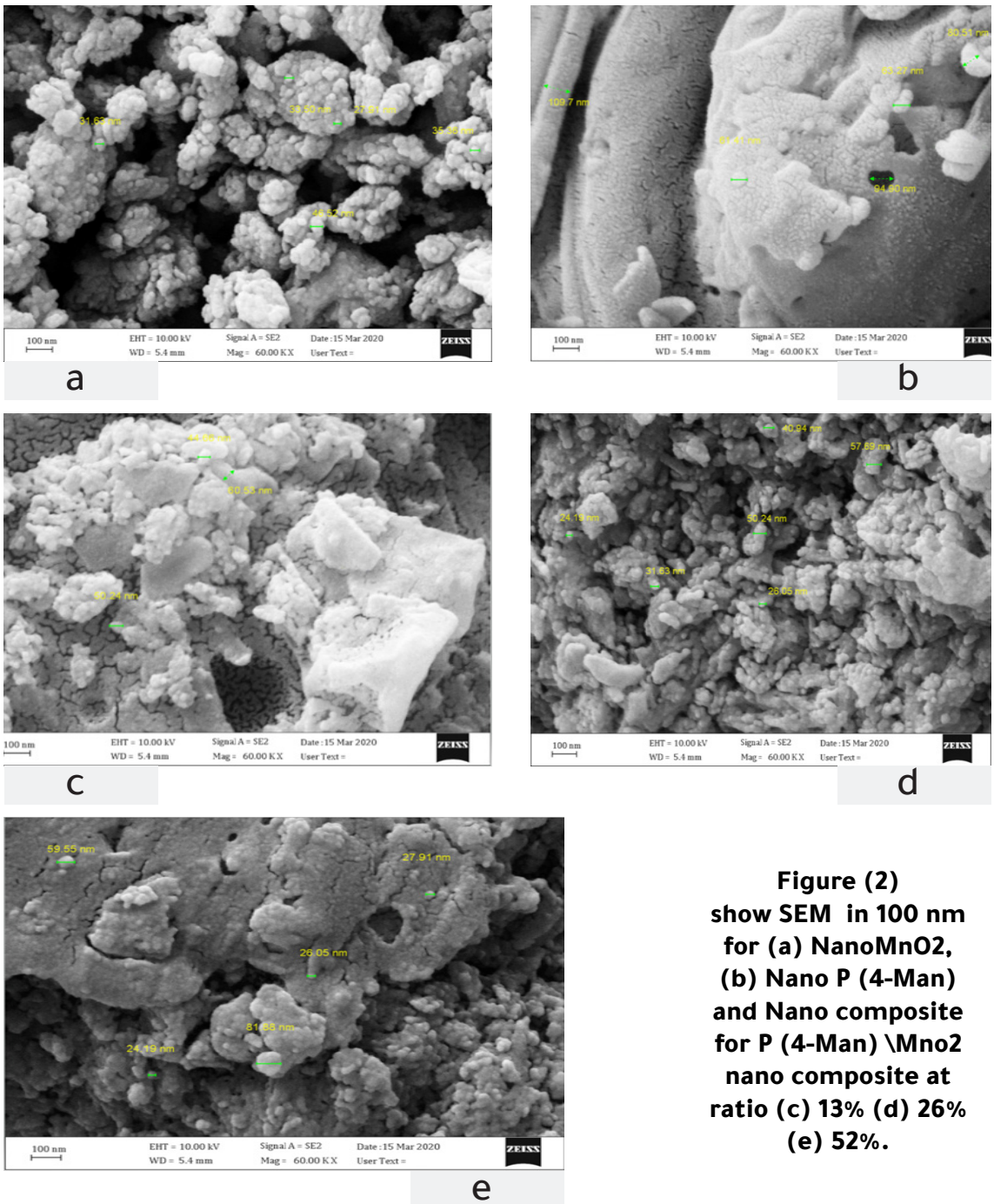


Figure (2) show SEM in 100 nm for (a) NanoMnO2, (b) Nano P (4-Man) and Nano composite for P (4-Man) \Mno2 nano composite at ratio (c) 13% (d) 26% (e) 52%.

3.3 DSC for P (4-Man) and P (4 -Man) \ MnO2 Nano composite

DSC for P (p-Man). Four peaks exothermic appears in figure (a). The first peak at 51.48° C denotes to Crystal transformation, the second peak at 120.63 °C signify Tc1, the third peak at 233.57° C denote to Tc2 and the fourth peak at 362.09° C indicate to Tc3 higher temperature crystallization exothermal (Müller & Michell, 2016). DSC for P (p- Man)/MnO2 Nano composite 0,52 as appears in figure (b) The first exothermic peak at 77.89 °C denote to Tc1 be higher temperature crystallization exothermal. The second endothermic peak at 120 °C refers to Tc_2. The third peak at 144.23 °C refers to removing small particles, the fourth endothermic peak at 247.54 °C indicate to Tm and the fifth endothermic peak at 325.59 °C denote to thermal degradation of composite. The self-doped polymer exhibits multiple crystallization temperatures (Tc1,Tc2 and Tc3 higher temperature crystallization). As for poly P(4-Man) \MnO2 Nano composites contains two peak of crystallization (Tc1 and Tc2) as a result of the presence of MnO2 Which acts as an area for the growth of the crystallization.

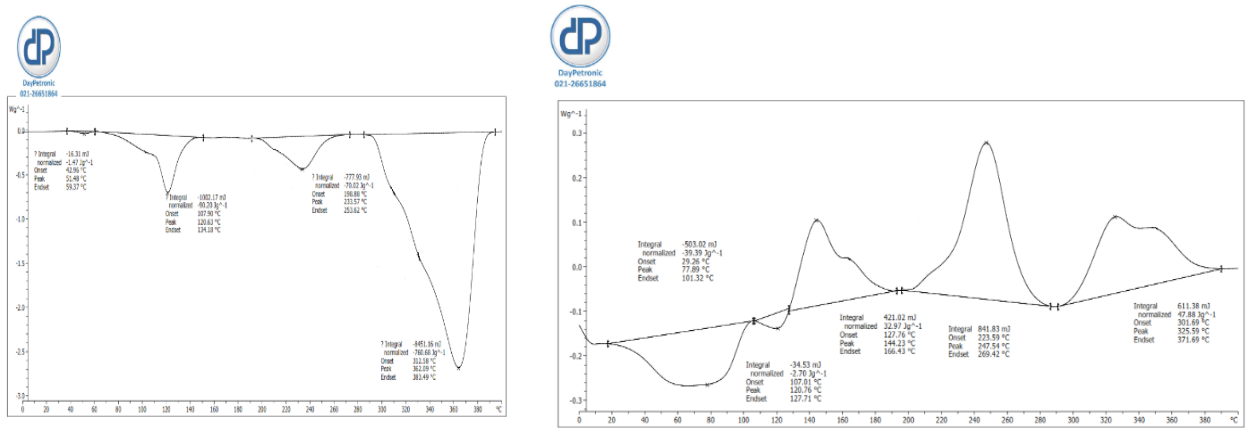


Figure (3) Show DSC for (a) P(4-Man) and (b) P(4-Man) \MnO2 Nano composites 52%.

3.4 Results of the HNMR

Spectra HNMR of a number of prepared polymers is shown in the following figure and using DMSO as a solvent carried out on a 500MHz Bruker NMR spectrometer equipped with a probe BB05mm, tetra methyl silane (TMS) was used as the internal standard in these cases. These spectra have been recorded at 25° C. HNMR for P (4-Man) The strong signs are shown at 2.51 and 2.52 ppm indicating to DMSO, the base value for $=N^{+}H-$ sharp peak has shown at5.97, 6.21 and 6.22 ppm, value signs for -NH- for the second amine shown at 9-9.8 ppm ,sharp and strong signs at 3.71-4.04 ppm assigned to OCH_3, as for signs to aromatic rings appear for Ha 7.30 ppm, Hb 7.19 ppm , Hc 7.07 ppm, Hd 7.35 ppm , He 7.01ppm , Hf 7.08 ppm, Hg 7.21ppm, Hi 7.05 ppm, Hj 7.14 ppm, Hk 7.03 ppm, Hl 7.37 and single signs at 5.96 ppm indicating Hm. Note No signs of weak signal between3-4 for NH_2(Sen et al., 2017)

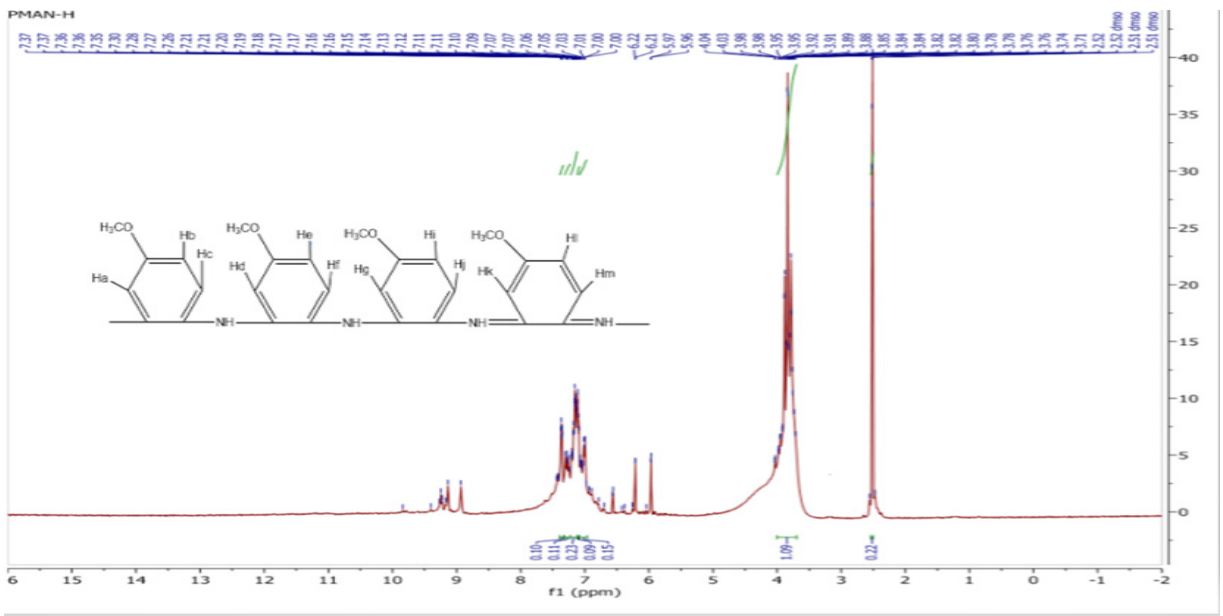


Figure (4) show HNMR for P (4-Man).

3.5 Measurement of electrical conductivity

The electrical conductivity of the prepared polymer and its Nano composites was measured by weight ratios (13 and 52 %). It was found that the value of the highest electrical conductivity was for the composites 52%, that is, the conductivity decreased with a percentage increase MnO2.

Name compound	Conductivity $S.cm^{-1}$
P(4-Man)	$5.9 .104^{-4}$
P(4-Man)\Mno2 13%	$8.6 .10^{-3}$
P(4-Man)\Mno2 52%	$5.2 .10^{-3}$

Table (2)

4. Conclusion

In this work, P(4-Man) and P(4-Man)\ MnO2 Nano composites synthesized by using via polymerization oxidation method and the results were The structure was confirmed by FT-IR and HNMR and Characterized with a DSC medium confirmed that the material had a crystalline nature. The surface morphology analysis of P (4-Man) /MnO2 Nanocomposite shows that polymer capped with inorganic material which is MnO2. The electrical conductivity of the prepared polymer and its compound were also measured in different ratios was conductivity decreases with a percentage increase for MnO2.

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