

Structural and Morphological Characterization of MEH-PPV Nanocomposite Doped with FeCl₃

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Abstract

Poly [2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinyl] (MEH-PPV) thin films were created in this study using both spin coating and drop casting processes. MEH-PPV thin films generated by Ferric Chloride (FeCl₃) doping (0.03, 0.06, 0.09, and 0.12 wt%) were studied for some physical features using Fourier-Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FE-SEM), and Energy Dispersive X-ray Spectroscopy (EDX). An FTIR test showed that there was no chemical reaction that occurred between Ferric Chloride (FeCl₃) and MEH-PPV, but rather a physical one, that is, an organic material composite occurred. As for FE-SEM, the pure sample MEH-PPV formed uniformly, but when FeCl₃ was added by weight, we have different circles that indicate the formation of adsorption energy and that the highest adsorption energy appears at MEH-PPV/FeCl₃ (0.06%), as well as EDX, which indicates the absence of undesirable elements and indicates the presence of small peaks for iron (Fe) and chlorine (Cl). Peaks of carbon(C) and oxygen (O) types indicate the presence of the chemical elements of MEH-PPV.

Article Info.

Keywords:

Thin film, drop casting, spin coating, MEH-PPV, FeCl₃

Article history:

Received: Jun. 25, 2022

Accepted: Aug. 8, 2022

Published: Sep. 01, 2022

1. Introduction

Through the earliest research in polymeric light-emitting diodes [1], accurate measurement was made for a group of conjugated polymers in order to form devices for industrial applications [2-5]. Among these polymers, PPV (polyphenylene vinylene) and its derivatives have witnessed a great deal of interest recently due to their amazing electrical properties [6]. Various models of conductive as well as electroluminescent polymers have been selected as a promising group of materials for organic electronic applications such as organic phototransistors, organic light-emitting diodes (OLEDs), and organic photovoltaics, organic photodetectors [7]. Light-emitting polymers contain a polymer that conducts electricity when it is exposed to an external voltage. A. Bernanos and coworkers at Nancy University in France noted electroluminescence in organic materials in the early 1950s when materials such as acridine orange were exposed to a high alternating voltage [8]. In 1960, M. Pope and some of his co-workers at New York University produced contacts for an Ohmic electrode with a dark injection of organic crystals [9]. One of the prominent landmarks in history is the invention of the organic luminescent device with a thin green double-layer film [10]. This work incorporates carbon nanotubes into a conductive polymer called poly[2-methoxy,5-(2-ethylhexoxy)-1,4-phenylenevinylene] (MEH-PPV) to improve gas sensing capacity [11]. The two solutions, MEH-PPV and MWCNTs, were combined to create simple and inexpensive sensors. According to the FTIR measurements, an ester bond connects MEH-PPV to the carbon nanotube surface. The average roughness increased with increasing MWCNT content, as

revealed by AFM. When the sensors were exposed to H₂S gas, the MEH-PPV: MWCNTs based sensors showed notable reactions [11]. The optical and optoelectronic properties of MEH-PPV hybrid thin films comprising different quantities of SiO₂/TiO₂ nanocomposites (STNCs) have been studied [12]. With increased STNC concentration, they discovered significant dampening of MEH-PPV emission intensity, which is due to more efficient charge transfusion. As compared to a pure MEH-PPV thin film, MEH-PPV/STNCs have shorter emission and decay lifetimes, indicating effective charge transfer as well as the absence of static quenching. The absence of any change in the absorption spectra with increasing STNC concentration, as well as the linear Stern–Volmer plot, reveal completely dynamic quenching in hybrid thin films. Increased STNC concentration allows for more effective charge transfer, which results in increased current and lower device turn-on voltage, resulting in improved OLED performance [12].

The aim of this work is to study the structural properties of pure MEH-PPV and MEH-PPV doped with FeCl₃ in different weight ratios (0.03%, 0.06%, 0.09%, and 0.12%). FTIR measurements also verified the occurrence of a physical reaction and the absence of a chemical reaction between MEH-PPV and FeCl₃.

2. Experimental work

2.1. Materials

Table 1 shows the materials that were used in this work.

Table 1: Chemicals that were used in this work.

Materials	Purity	Properties	Supplier
MEH-PPV	99.99%	Chemical formula (C ₁₇ H ₂₄ O ₂) _n , appearance(Yellow solid), solubility in water(insoluble).	American Dye source, Inc. Canada
FeCl ₃	98%	Odor (Slight HCl), solubility in (Methanol,Ethanol,Acetone), appearance(Green-black by reflected light, purple-red by transmitted light, yellow solid as hexahydrate, brown as aq. solution).	THOMAS BAKER-INDIA
Methanol	99.5%	Water 0.1%, acidity (Acetic Acid) 0.003%, alkalinity 5ppm, total sulphur 5ppm, aldehydes & ketones 0.005%, nonvolatile matter 0.001%.	England
toluene	99.7%	Acidity(as Acetic acid)0,002%, color(APHA)10, sulfur compounds (as S) 0.003%, water(KF) 0.03% w/w.	France

2.2. Preparation of specimens and thickness measurement

In this study, a glass slide was used as a base material for the thin films produced. The glass slides were cut into sizes of (2.5 * 2.5) and (1 * 1) cm² and cleaned by following the necessary procedure (rinsing with distilled water, washing in an ultrasonic organic solvent, and drying with hot air) and making them suitable for film coating. A homogeneous aqueous solution of (210 mg) MEH-PPV was prepared by dissolving it in a solution (25 ml) of toluene, and also the substance with which the doping was done (80 mg). FeCl₃ was prepared by dissolving it in a solution of toluene and methanol solution together. FeCl₃ was added in different weight percentages (0.03%, 0.06%, 0.09%, and 0.12%) to the MEH-PPV solution. The prepared solutions were stirred at room temperature for 10 hrs and allowed to be homogeneous for 5 days. After the solution preparation step was completed, the

drop-casting step was started to check the FTIR and the spin coating step to check SEM and EDX on clean glass bases in order to produce thin films homogeneously on the slides. As for the thin films prepared by the drop-casting method, they were placed in the oven at a temperature of 60 °C for an hour to dry. As for the thin films prepared by the spin coating method, the glass substrates were appropriately placed on the magnetic platform that can rotate at high speeds. The specified amount of solution was drawn by a micropipette to the center of the glass base and began to rotate at a speed of 1000 rpm. When the rotation time is complete, the glass substrates are removed from the device. As shown in Fig.1 the spin coating device has been worked on.



Figure 1: The spinning device that has been worked with.

To measure the thickness of the film, the weight difference method was used, Eq. (1). The mass of the film was measured before and after deposition. The difference will give the mass of the film (m). We know the area of the film (A) and the density (d) of the film material. So, the thickness of the films was found to be about 700 nm.

$$t = \frac{m}{Ad} \quad (1)$$

3. Results and discussion

3.1. Fourier Transform Infrared Spectroscopy (FTIR)

The goal of FTIR spectroscopy is to look at multicomponent functional groups in order to learn more about the reaction process and to determine the substance phase composition in a variety of bond types seen in all samples. Fig.2 shows FTIR spectra for pure MEH-PPV, MEH-PPV/FeCl₃ (0.03%), MEH-PPV/FeCl₃ (0.06%), MEH-PPV/FeCl₃ (0.09%), and MEH-PPV/FeCl₃ (0.12 %). As can be seen in Table 2, the spectra indicated separate bands. According to pure MEH-PPV, peaks at 3447.79 cm⁻¹ correspond to O-H stretching vibration. Peaks at 3053.31 cm⁻¹ correspond to C-H (aromatic stretching). Peaks at 2960.73 cm⁻¹ correspond to CH₃ (asymmetric stretching). Peaks at 1641.42 cm⁻¹ correspond to C=O (ester). These results are in agreement with I. M. Ibrahim et al [11]. Peaks at 1512.19 cm⁻¹ correspond to C-C aromatic (semicircular phenyl stretch) and this agrees with E. S. Bronze-Uhle et al [13]. Peaks at 1346.31cm⁻¹ are only observed in nanocomposites and are due to CH₂ deformation. 1207.43 cm⁻¹ and 975.98 cm⁻¹ respectively, which correspond to vinyl oxygen expansion and alkyl oxygen expansion and this is consistent with J. S. Shankar et al [9]. As for adding FeCl₃ in different weight ratios, there is a great similarity between the peaks that appeared in pure with the appearance of a new peak at 618 cm⁻¹. This agrees with M. A. Inam [14]. This means that the Fe-C bond does

not appear and there is stress in the C-Cl bond, and this indicates that there is no chemical reaction between FeCl_3 and organic material, but rather it should be a physical composite. And table (2) shows the types of bonds that have appeared.

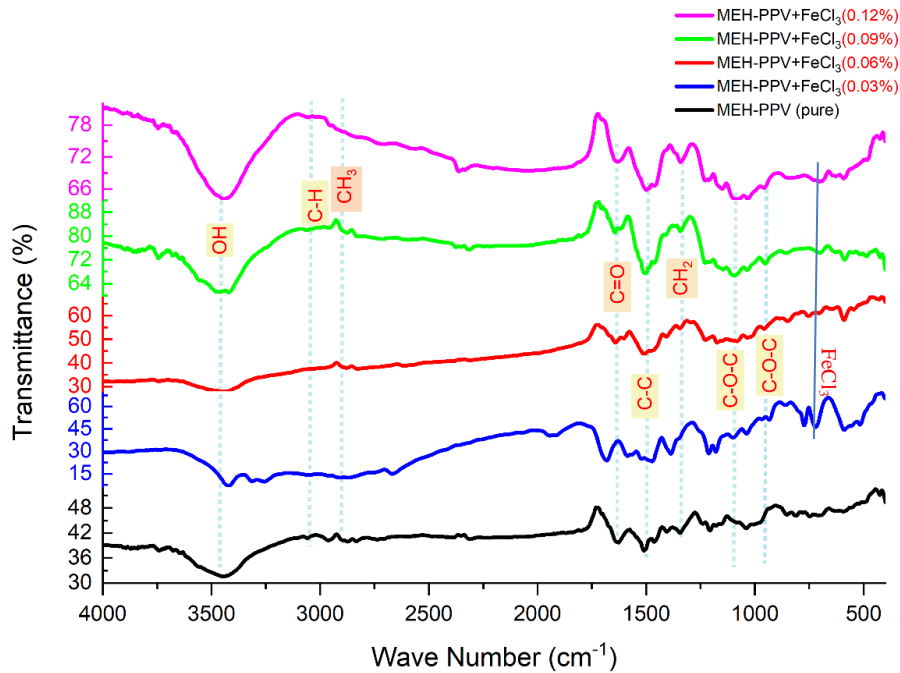


Figure 2: FTIR for pure MEH-PPV, MEH-PPV/ FeCl_3 (0.03%), MEH-PPV/ FeCl_3 (0.06%), MEH-PPV/ FeCl_3 (0.09%) and MEH-PPV/ FeCl_3 (0.12%).

Table 2: List of FTIR peaks for all samples.

Band type	Wave Number (cm^{-1})				
	MEH-PPV (pure)	MEH-PPV+ FeCl_3 -(0.03%)	MEH-PPV+ FeCl_3 -(0.06%)	MEH-PPV+ FeCl_3 -(0.09%)	MEH-PPV+ FeCl_3 -(0.12%)
OH	3447.94	3414.604	3452.58	3458.367	3446.794
C-H	3053.31	3051.38	no	3055.24	3059.102
CH ₃	2960.73	2912.51	2879.72	2873.93	no
C=O	1641.422	1681.92	1637.56	1651.0665	1634.9
C-C	1512.19	1523.764	15010.26	1506.4	1504.47
CH ₂	1346.31	1344.38	1342.455	1338.59	1340.52
C-O-C	1207.43	1176.57	1170.79	1151.5	1145.716
C-O-C	975.98	966.336	958.621	948.977	956.96
FeCl ₃	no	618	618	618	618

3.2. Field-Emission Scanning Electron Microscopy (FE-SEM)

Figs.3-7 show pure MEH-PPV and MEH-PPV/ FeCl_3 with different weight percentages. As shown in fig.3, the MEH-PPV film shows uniformly homogeneous growth. Detailed FE-SEM observations have revealed that the heat-checking pattern is composed of thin interconnected cracks of different lengths and orientations, due to the oxide-scale cracking under the thermal stresses. This is due to cyclic transition thermal gradients, induced by repeated heating and cooling of the surface. When adding doping material FeCl_3 in different weight percentages (0.03%, 0.06%, 0.09% and 0.12%) to MEH-PPV, the shapes appear the formation of prominent or clear circles, which indicate the presence of adsorption, with the increase in the amount of

dopants, the adsorption increases and the highest adsorption energy appears in the MEH-PPV/ FeCl_3 (0.06%) sample.

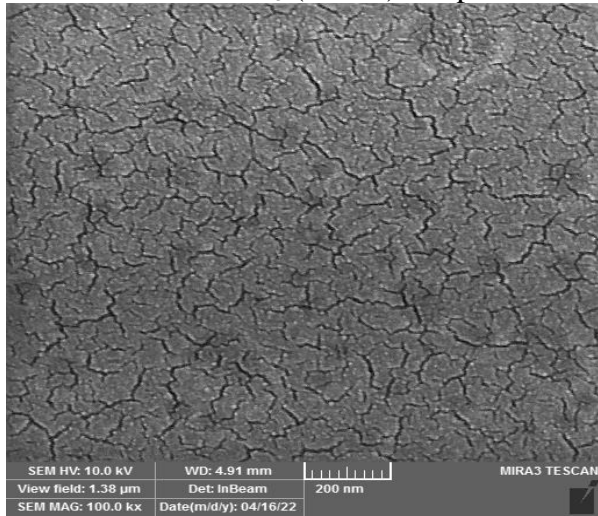


Figure 3: FE-SEM images of pure MEH-PPV.

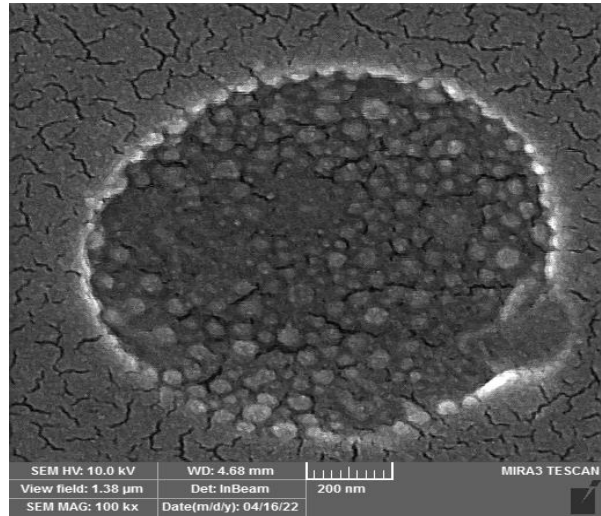


Figure 4: FE-SEM images of MEH-PPV/ FeCl_3 (0.03%).

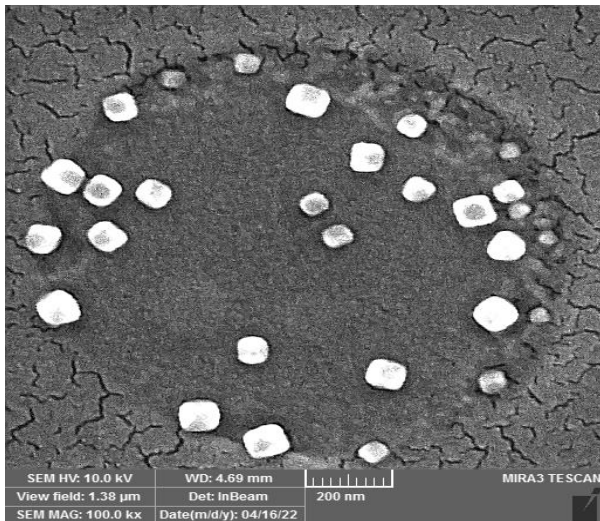


Figure 5: FE-SEM images of MEH-PPV/ FeCl_3 (0.06%).

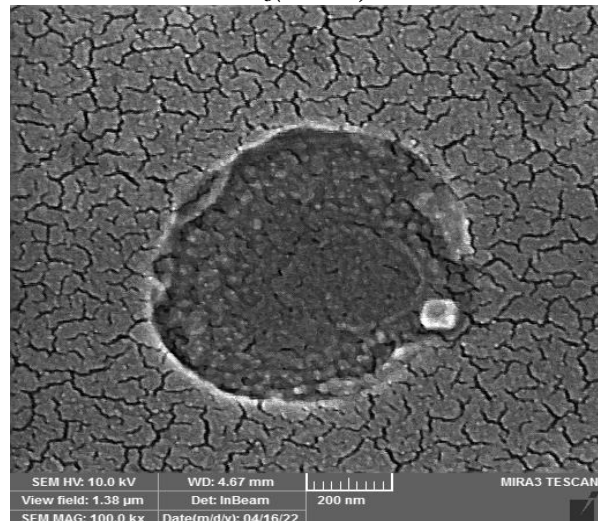


Figure 6: FE-SEM images of MEH-PPV/ FeCl_3 (0.09%).

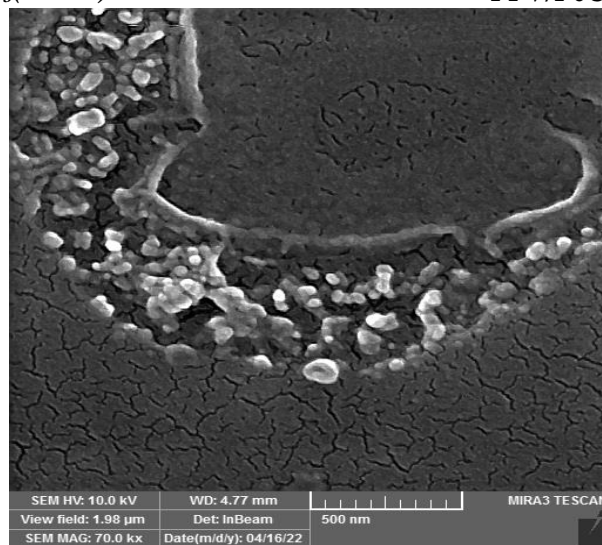


Figure 7: FE-SEM images of MEH-PPV/ FeCl_3 (0.12%).

3.3. Energy-Dispersive X-Ray (EDX) Spectroscopy

Energy dispersive X-ray (EDX) spectroscopy is a technique for elemental analysis and chemical composition determination, associated with electron microscopy. The method relies on the generation of characteristic X-rays, that reveal the identity of the elements present in the sample. Typically, this technique is used in conjunction with SEM. The X-ray emissions from the prepared nanoparticles at different wavelengths are measured by a photon-energy-sensitive detector. These X-rays are characteristic of each element and allow the determination of the nanoparticle's elemental composition. EDX spectrum analysis can offer both semi-quantitative and semi-quantitative information. The composition of the sample was determined by analyzing the EDX spectrum shown in Fig.8 (a-e), which showed the initial distribution in the samples (pure MEH-PPV, MEH-PPV/FeCl₃ 0.03%, 0.06%, 0.09%, and 0.12%). The results show that there are no unwanted elements in the samples. Some items were found to be due to contamination agents that were used for testing. The EDX spectrum of the surface of the samples reveals the presence of small peaks of iron (Fe) and chlorine (Cl), which confirms the presence of the substance that has been doped with it, which is iron chlorides, and also reveals the presence of large peaks of silicon as shown in Fig.8. A series of peaks related to carbon (C) and oxygen (O) types were observed in the spectrum survey, and this also confirms the presence of chemical elements in MEH-PPV.

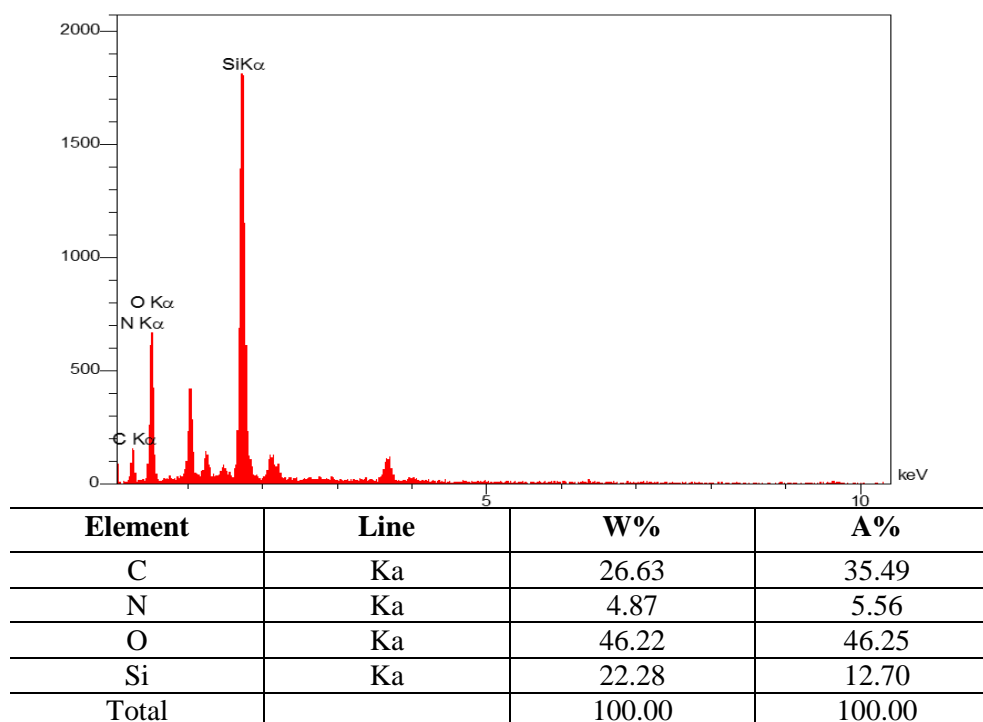
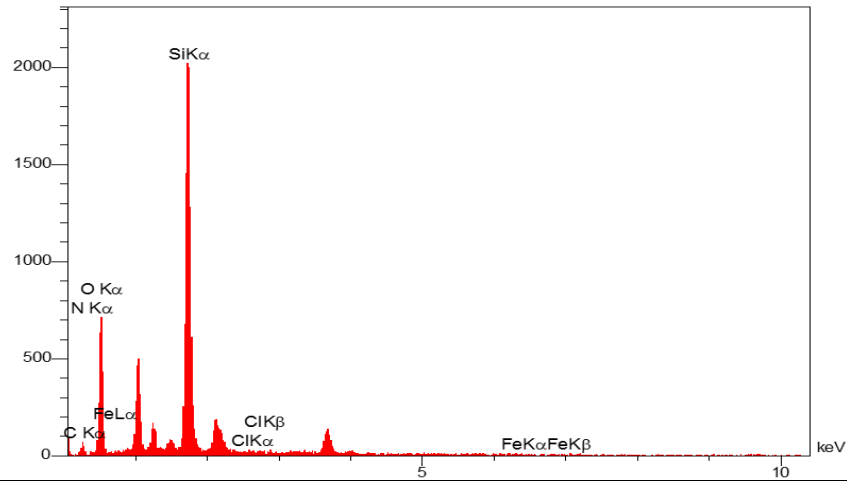
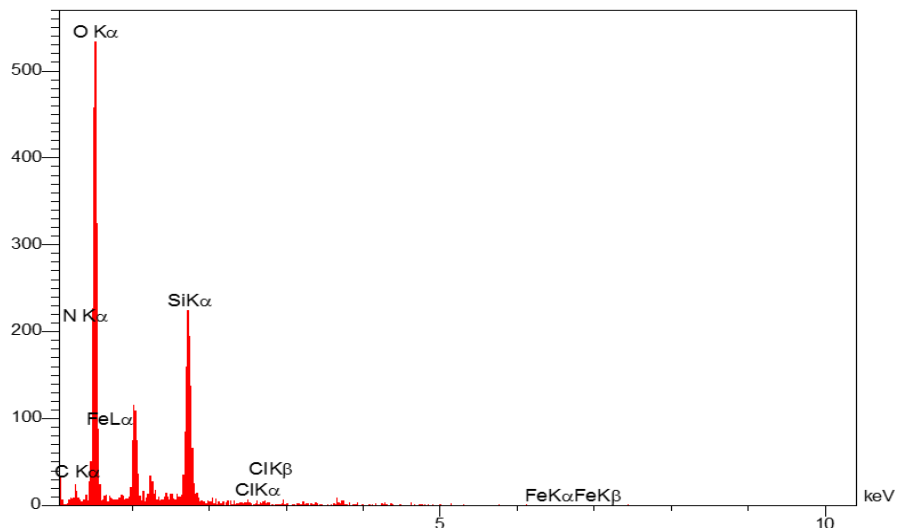


Figure 8(a): A typical EDX for pure MEH-PPV.



Element	Line	W%	A%
C	Ka	15.99	22.74
N	Ka	5.75	7.01
O	Ka	49.55	52.90
Si	Ka	28.24	17.18
Cl	Ka	0.18	0.09
Fe	Ka	0.28	0.09
Total		100.00	100.00

Figure 8(b): A typical EDX for MEH-PPV/FeCl₃ (0.03%).



Element	Line	W%	A%
C	Ka	9.39	12.65
N	Ka	4.71	5.44
O	Ka	74.89	75.78
Si	Ka	10.16	5.86
Cl	Ka	0.15	0.07
Fe	Ka	0.71	0.21
Total		100.00	100.00

Figure 8 (c): A typical EDX for MEH-PPV/FeCl₃ (0.06%).

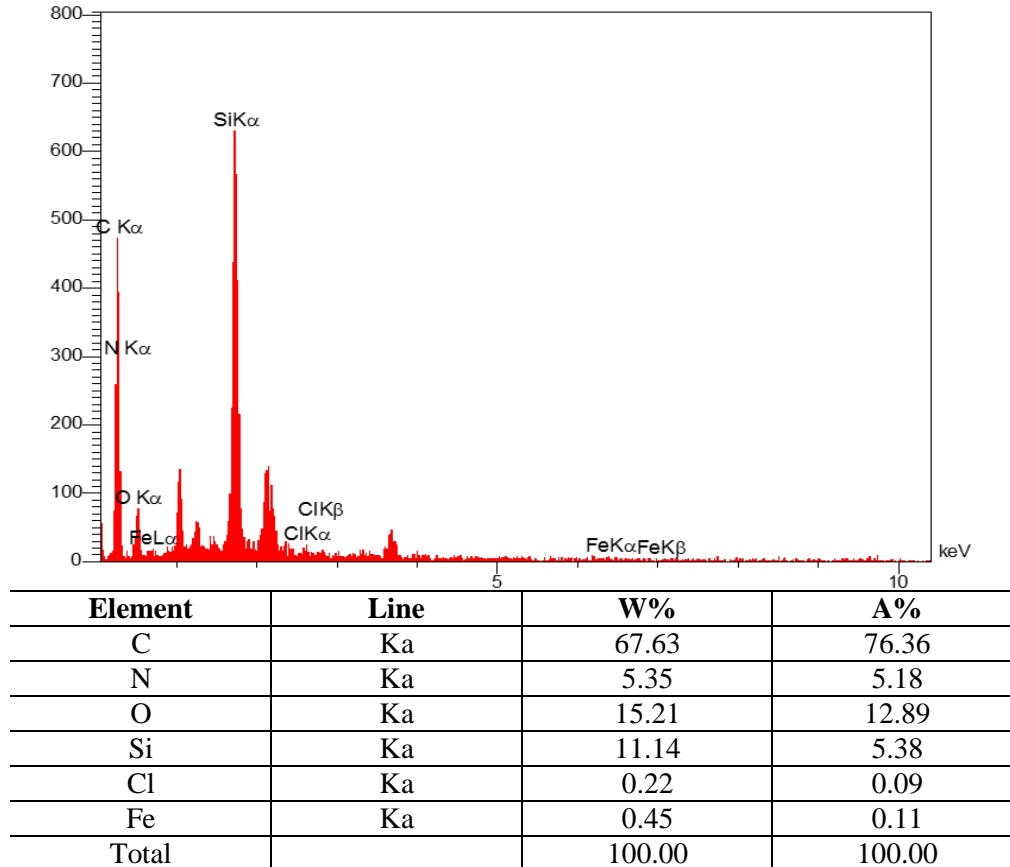


Figure 8 (d): A typical EDX for MEH-PPV/FeCl₃ (0.09%)

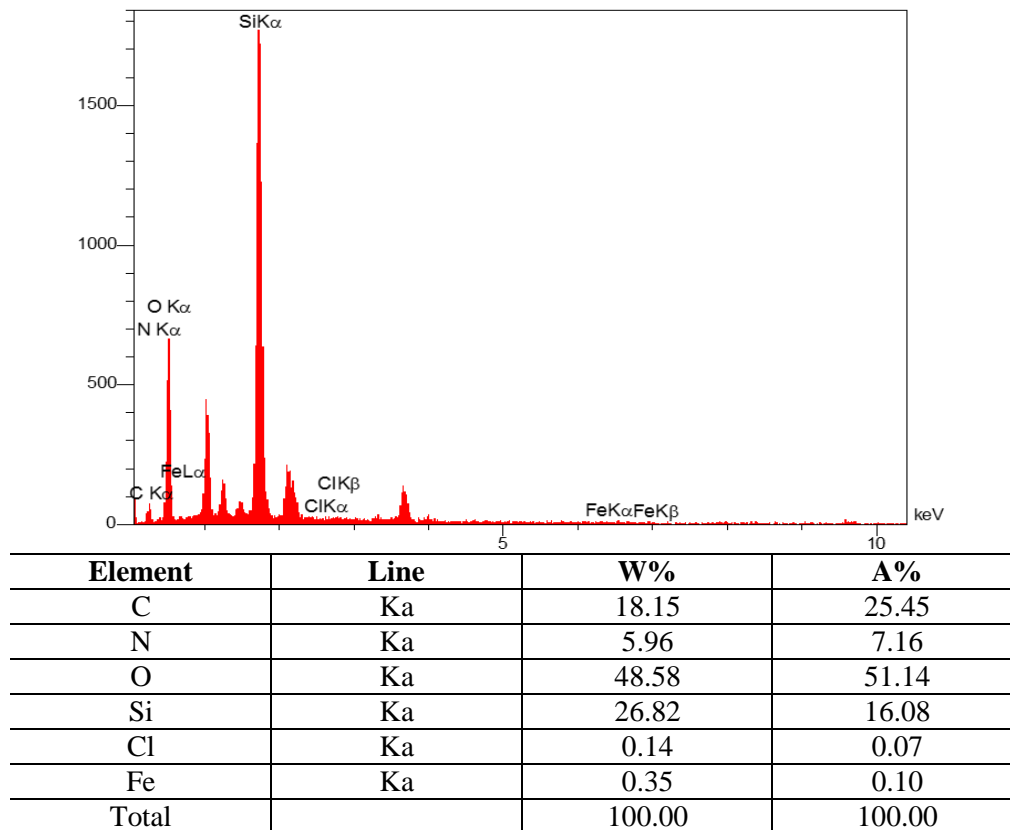


Figure 8 (e): A typical EDX for MEH-PPV/FeCl₃ (0.12%).

4. Conclusion

Thin films of pure MEH-PPV and MEH-PPV/FeCl₃ with different weight ratios were successfully prepared by spin coating and drop casting methods. FTIR samples show the presence of peaks of MEH-PPV in all samples. Also, a new peak of 618cm⁻¹ appeared when FeCl₃ was added with different weight ratios, and this peak belonged to FeCl₃, and this indicates that it is not chemically formed, but rather that it is composite. As for the FE-SEM assay, the pure MEH-PPV films showed a homogeneous and regular shape, and when FeCl₃ was added in different weight ratios, prominent circles appeared, indicating the presence of adsorption energy, with the highest adsorption energy formed at MEH-PPV/FeCl₃ (0.06%). The presence of undesirable elements also confirms the presence of small peaks of C and O chemical elements in MEH-PPV.

Acknowledgments

The authors acknowledge their thanks to the Environmental Laboratory in the College of Science, Department of Chemistry, for completing this research work.

Conflict of interest

Authors declare that they have no conflict of interest.

References

1. Li Y., Wei Q., Cao L., Fries F., Cucchi M., Wu Z., Scholz R., Lenk S., Voit B., and Ge Z., *Organic light-emitting diodes based on conjugation-induced thermally activated delayed fluorescence polymers: Interplay between intra-and intermolecular charge transfer states*. *Frontiers in Chemistry*, 2019. **7**: pp. 1-12.
2. Peng Z., Bao Z., and Galvin M., *Oxadiazole-Containing Conjugated Polymers for Light Emitting Diodes*. *Advanced Materials*, 1998. **10**(9): pp. 680-684.
3. Bliznyuk V., Ruhstaller B., Brock P.J., Scherf U., and Carter S.A., *Self Assembled Nanocomposite Polymer Light Emitting Diodes with Improved Efficiency and Luminance*. *Advanced Materials*, 1999. **11**(15): pp. 1257-1261.
4. Bernius M.T., Inbasekaran M., O'Brien J., and Wu W., *Progress with light emitting polymers*. *Advanced Materials*, 2000. **12**(23): pp. 1737-1750.
5. Politis J.K., Curtis M.D., Gonzalez-Ronda L., and Martin D.C., *Poly (nonylbisoxazole): A member of a new class of conjugated polymer*. *Chemistry of Materials*, 2000. **12**(9): pp. 2798-2804.
6. Banerjee J. and Dutta K., *A short overview on the synthesis, properties and major applications of poly (p-phenylene vinylene)*. *Chemical Papers*, 2021. **75**(10): pp. 5139-5151.
7. Mishra R., *Light Emitting Polymers*. *International Journal of Chemistry*, 2014. **1**: pp.22-30.
8. Shire U.J. and Arbat A., *A Review Paper on: Organic Light Emitting Diode over Conventional Lead*. *International Journal of Advanced Research Computer Science and Software Engineering*, 2015. **5**: pp. 178-181.
9. Shankar J.S., Ashok K.S., Periyasamy B.K., and Nayak S.K., *Studies on optical characteristics of multicolor emitting MEH-PPV/ZnO hybrid nanocomposite*. *Polymer-Plastics Technology Materials*, 2019. **58**(2): pp.148-157.
10. Swayamprabha S.S., Nagar M.R., Yadav R.A.K., Gull S., Dubey D.K., and Jou J. H., *Hole-transporting materials for organic light-emitting diodes: An overview*. *Journal of Materials Chemistry C*, 2019. **7**(24): pp. 7144-7158.

11. Ibrahim I., Khalid A., and Wahid M.A. *Enhancement of MEH-PPV: CNT for H₂S gas sensor*. Journal of Physics: Conference Series. 2018. IOP Publishing.
12. Al-Asbahi B.A., Qaid S.M., Ghaithan H.M., and Farooq W., *Enhancing the optical and optoelectronic properties of MEH-PPV-based light-emitting diodes by adding SiO₂/TiO₂ nanocomposites*. Journal of Non-Crystalline Solids, 2021. **552**: pp. 120429.
13. Bronze-Uhle E., Batagin-Neto A., Lavarda F.C., and Graeff C.F.d.O., *Ionizing radiation induced degradation of poly (2-methoxy-5-(2'-ethyl-hexyloxy)-1, 4-phenylene vinylene) in solution*. Journal of Applied Physics, 2011. **110**(7): pp. 073510.
14. Inam M.A., Khan R., Park D.R., Lee Y.-W., and Yeom I.T., *Removal of Sb (III) and Sb (V) by ferric chloride coagulation: Implications of Fe solubility*. Water, 2018. **10**(4): pp. 418.

الخصائص التركيبية والشكلية للمركب النانوي بولي [2-ميثوكسي -5- (2-إيثيل-هيكسيلوكسي) -1،4-فينيلين-فانيلين المشوب بكلوريد الحديد الثلاثي

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الخلاصة

في هذه الدراسة تم انشاء اغشية رقيقة من المركب النانوي بولي [2-ميثوكسي -5- (2-إيثيل-هيكسيلوكسي) -1،4-فينيلين-فانيلين] باستخدام كل من عملية الطلاء الدوراني وعملية الصب بالتنقيط. تمت دراسة الاغشية الرقيقة للمركب النانوي بولي [2-ميثوكسي -5- (2-إيثيل-هيكسيلوكسي) -1،4-فينيلين-فانيلين] المشوب بكلوريد الحديد الثلاثي بنسب وزنية مختلفة (0.03% و 0.06% و 0.09% و 0.12%) لبعض الخصائص الفيزيائية باستخدام كل من تحويل فوربييه للطيف بالأشعة تحت الحمراء و المجهر الالكتروني الماسح والاشعة السينية المشتتة للطاقة. عندما تم قياس الخصائص الهيكلية (تحويل فوربييه للطيف بالأشعة تحت الحمراء) وجد انه لم يحدث أي تفاعل كيميائي بين كلوريد الحديد الثلاثي وبولي [2-ميثوكسي -5- (2-إيثيل-هيكسيلوكسي) -1،4-فينيلين-فانيلين]. اما بالنسبة الى المجهر الالكتروني الماسح تشكلت العينة النقية بشكل موحد ولكن عندما تمت إضافة كلوريد الحديد الثلاثي بنسب وزنية مختلفة تشكلت دوائر بارزة او دوائر واضحة تشير الى تكوين طاقة امتزاز وان اعلى طاقة امتزاز تظهر في (0.06%) وكذلك الاشعة السينية المشتتة للطاقة تشير الى عدم وجود عناصر غير مرغوب فيها وتشير الى وجود قمم صغيرة من الحديد والكلور. لوحظت سلسلة من القمم المتعلقة بانواع الكاربون والاكسجين وهذا يؤكد من وجود العناصر الكيميائية في بولي [2-ميثوكسي -5- (2-إيثيل-هيكسيلوكسي) -1،4-فينيلين-فانيلين].