Preparation of polyimides from linear low density polyethylene

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Abstract:

Polyethylene was known as an inactive polymer and cannot compatible or reacted with other polymers. In this paper proved that the inert linear low-density polyethylene (LLDPE) was converted to chemically active polymer by grafting with maleic anhydride moiety. The grafted polymer can be reacted with different amines in order to prepare the imides of LLDPE .To prepare polyamides of grafted LLDPE two types of amines were used (ammonium hydroxide and isobutylamine).The thermal properties were investigated. FTIR were used to study the chemical structure of the amide polymers and show enhancement different thermal characteristics according to the types of the amines used.The prepared polyamides show different crystalline regions with different crystals volume of the two types of amides according to XRD analysis.

Key words: polyethylene, polyamides ,maleic anhydride**,** grafting

تحضير البولي أميدات من البولي اثلين الخطي واطئ الكثافة

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الملخص: يُعرف البولي إيثيلين بأنه بوليمر غير خامل ولا يمكن أن يرتبط أو يتفاعل مع البوليمرات الأخرى. تم في هذا البحث تحويل البولي إيثلين الخطي الخامل منخفض الكثافة (LLDPE) إلى بوليمر نشط كيميائياً عن طريق تطعيمه بمجموعة أنهيدريد الماليك. يمكن للبوليمر المطعم ان يتفاعل مع أمينات مختلفة لينتج إميدات .LLDPE لتحضير LLDPE المطعم بالاميدات تم استخدام نوعين من الأمينات (هيدروكسيد الأمونيوم وأيزوبوتيل الامين). تم دراسة الخواص الحرارية للبوليمرات المحضرة و التركيب الكيميائي باستخدام تقنية FTIR. اظهرت الدراسة تعزيز للخواص الحرارية بنسب مختلفة حسب أنواع الأمينات المستخدمة، كما اظهر تحليل حيود الاشعة السينية XRD للبولي اميدات المحضرة مناطق بلورية مختلفة مع اختلاف حجم بلورات لنوعي الأميدات .

Introduction:

Polyethylene (PE) is the most used and essential polymer in our daily life. PE consists of several types, the major classes are: High- density polyethylene (HDPE), Low-density polyethylene (LDPE), Linear low- density polyethylene (LLDPE), and Cross- linked polyethylene (XLPE). This classification is according to different densities and degree of branching (1-3). LLDPE was grow globally in the market in the recent years (4). LLDPE has short branches (butane, hexane and octane) more than HDPE. This structure of LLDPE make its molecular arrangement not too tight and low crystallinity (1-3), so that it have

good elasticity, flexibility, transparency, toughness and good ability for molding (5). However, they can stay many years in the environment and contributing to environmental pollution due to their exceptional inert hydrocarbon backbone (6).The grafting technique were practiced to improve the morphology, chemical, and physical properties of the polymer.An insoluble polymer becomes soluble This modification is required to provide special properties to the modified PE, such as increased thermal stability, multiphase and physical responses, compatibility, flexibility, and rigidity. Through modification. It also improves the conditions for polymer processing (7). Maleic anhydride (MAn) grafted polyethylene is very important technique for application as a copolymer precursor in polymer blends(8,9). The MAn grafted to PE can improved the electrical resistance and dielectric break down strength (10). Thermoplastic polyurethane form with PE immiscible blends with an extremely low compatibility. In order to overcome this problem an improve the dispersion and properties of these blends, PE was grafted with MAn(11). The results show that the morphological properties of the blends was improved. LDPE was known as a thermoplastic material, renders processing flexibility and high chemical stability, but has poor thermal resistance and low mechanical strength(12). The mechanism of grafting MAn to LLDPE was studies by many researchers (13-15). They suggest that MAn can form branched graft or bridge graft with the polyethylene chain. The fraction of the bridged graft is less than that of the branched graft. Within the frame of this work, the solubility and thermal properties of LLDPE was improved through grafting with MAn. The grafted MAn moiety was amidified with different type of amines to get soluble polymer at room temperature in organic solvents.

Experimental:

All the used chemicals are used as received from the sources except MAn was purified by heating the molten row MAn in dry space at 120^0C for 15 min.

Equipment:

FT.IR spectra were accomplished by using (BRUKER FT.IR Infrared. Thermal analyses were measured by using Q 600 /TA Thermo gravimetric Analysis (the temperature range was 25-800^0C the heating speed of measuring TGA and DTA of the prepared samples was 20^oC \ min. X- ray diffraction was carried out by using XRD- 6000 Shimadzu. CHN was carried out by using Perkin-Elmer 2400 II.

Methodology:

Grafting of LLDPE by MAn:

10g of LLDPE with certain amount of MAn, 0.1 g of initiator dicumyl peroxide in 50ml dry xylene was reflexed for 2hrs.The produced grafted polymeric was precipitated from methanol, filtered, washed with acetone and dried under vacuum at 50^0C. Another experiments were followed by adding two portions of

the initiator. The second portion (0.1g) was added after a period of 2hrs.(16) (Table 1).

Table 1: grafting of LLDPE with MAn

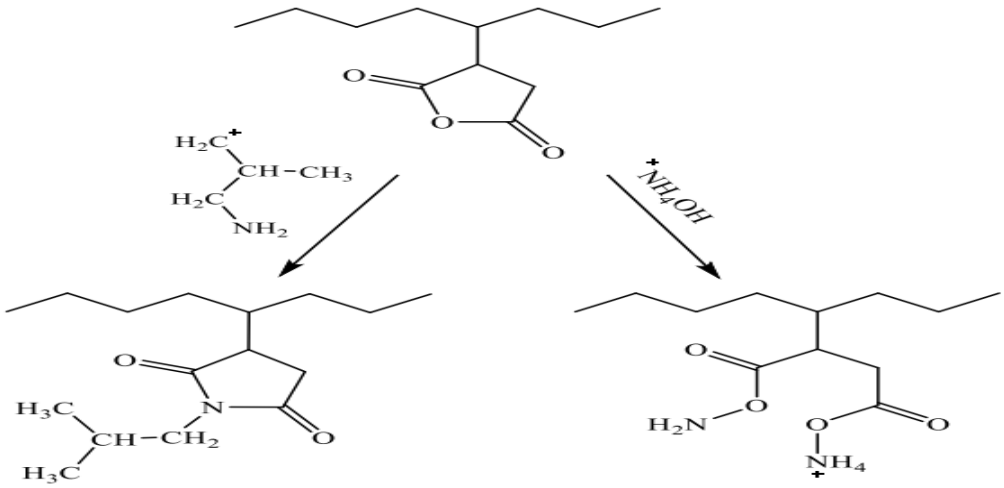
NO.	MAn/ gm added	Dicumyl peroxide/g	LLDPE/gm	MAn/ gm Grafted
1	5	0.1	10	1.8
2	10	0.1	10	4.2
3	15	0.1	10	7.4
4	15	0.1+0.1	10	8.8
5	20	0.1	10	12.2
6	20	0.1+0.1	10	15.3
7	25	0.1	10	15.2
8	25	0.1+0.1	10	15.3

Evaluation of grafting degree:

The degree of grafting of LLDPE with MAn was determined by titrating the acid groups with NaOH according to the published work (17)**.**

Amidification of the grafted polymer:
Dissolving 1g of the grafted LLDPE (sample 6) in 50ml of toluene and equivalent mole of amine to the grafted Man was added .The mixture was refluxed for a period of 2hrs.

The resulted product is soluble in the toluene until even at room temperature. Half amount of the solvent was distilled off under vacuum and the resulted polymer was precipitated from methanol.



Results and discussions:
FTIR,TGA,DTA and XRD were measured for the grafted LLDPE with MAn and all their amic acids. According to table (2), it was shown that the maximum

grafting of LLDPE with MAn was observed with the sample 6. This result was confirm with the previous study that shows the maximum grafting degree can be obtained when the initiator was added as two portions (16,17). The amidification of sample 6 (table 1)with amines was proved by elemental analysis, whereby the results approved the success of amidification process and revealed that every 12 carbon atom on the polyethylene chain can be bonded with one MAn moiety (table 4). Table 3 shows the signs of the LLDPE and the their imides(18)

Sign	Recipes
P	Linear low density Polyethylene Pure
MP	Maleic anhydride grafted Linear low density Polyethylene
I	polyimide with iso butyl amine
M	Polyimide with ammonium hydroxide

Table 2: Signs of the prepared recipes

Table (3): CHNS elemental analysis of prepared polymers.

Sample	Calculated			Measured		
	N%	C%	H%	N%	C%	H%
I	4.43	74.53	11.18	2.82	78.1	9.11
M	9.3	63.78	10.96	8.41	60.92	8.4

FTIR analysis:

Figure 1 shows the IR spectrum of LLDPE, whereby the bands appeared at 2914 cm^{-1} and 2847 cm^{-1} are related to the stretching vibration of aliphatic CH group, while the vibrations appeared at 1462cm^{-1} and 1472 cm^{-1} are belong to the bending vibrations of aliphatic CH group. The peak at 718 cm^{-1} is belong to C-C vibration.

Figure (2) represent the IR spectrum of sample 6. In addition to the main frequencies of MP, new bands were appeared at 1707cm^{-1} and 1632 cm^{-1} which are belong to the stretching vibration of carbonyl group and the bands at 1170-1219 cm^{-1} attributed to C-O-C vibration. These observations prove the success of grafting.

The modified samples show broad bands at 1735 and 1732cm^{-1} indicating the presence of amic acid. In addition M sample show weak band at (3424 cm^{-1})

which are attributed to the probability of primary and secondary amine groups of the amic acid (18). The reaction of the MAn- g- LLDPE with different amines produce the imides. Figures (3) represent the IR spectra of the imides I, M. Table (4) indicates the absorption bands of the different groups of the prepared imide.

. This explain the reaction of the grafted MAn with one molecule of amine to form imide and the other part of MAn produce the carboxylic acid (18).

Table (4): Assignment of the IR-absorption of different ester of LLDPE

Groubes / Sample	O−H	C─H Stretche	C─H Bend	C═O	C─O	C─C	OTHERS
I		2915 2848	1463 1471	1735	1010	719	C-N-C (1166)
M	3424	2916 2848	1461	1732	1087 1003	719	N-H (3216)

Thermal analysis:

The DTA, TGA and DSC of the prepared polyamides are accomplished at a heating rate of 20^0C/ min. The results show different thermal behaviors of the prepared imides than the origin polyethylene.

DSC Thermogram of the amide I shows Tg at 442.2 ^{0}C, while the TGA and DTA reveal the thermal history. The sample lose5.811% of its weight at 125^0C . The start pyrolysis loss 86.821% of its weight $260C^0$ and complete decomposition at 505^0C (figure 5).

In the other hand, the polyamide of M gives small different thermal characteristics than I. TGA and DTA (figure 6) indicate that the sample lose about 14.44% of its weight at 225^0C, and start complete decomposition at 505^0C. while the DSC shows the TG is about 136.89^0C

X-ray diffraction analysis:

It is well known that the LLDPE is an amorphous material; its degree of crystallinity can be changed when grafting with some different moieties. Figure (7) illustrate the XRD diagram of E1. It shows six region of crystallinity. Table(5) explain the analysis of these region where by the main region appeared at 2θ= 21.9309

Table (5): XRD analysis of I

V (value)	λ	FWHM (20Th.)	d-spacing (A)	2θ
1.449	1.54	0.9741	4.04958	21.9309
2.6872	1.54	0.5278	3.65848	24.3094
0.9883	1.54	1.4779	2.44882	36.6684
1.202	1.54	1.2279	2.23757	40.2729
1.01	1.54	1.4706	2.08853	43.2861
0.951	1.54	106295	1.71998	53.212

M imide with ammonium hydroxide have eight region of crystal, two more than imide of iso butylamine but still the major region at the same place (figure 8 and table 6).

Table (6): XRD analysis of M

V (value)	λ (value)	FWHM (2^0Th.)	d-spacing (A)	2θ
0.352	1.54	4.0000	4.08478	21.7396
2.88	1.54	0.4920	3.68766	24.1141
4.13	1.54	0.3496	2.72527	32.8369
1476.18	1.54	0.0010	2.24462	40.141
16.606	1.54	0.0900	2.06338	43.8410
16.808	1.54	0.0900	1.92634	47.1410
17.232	1.54	0.0900	1.71911	53.2410
17.395	1.54	0.0900	1.65875	55.3410

Conclusion:

1-Different polyamides are prepared from grafted LLDPE by used as reactive compound.

2-By using grafting LLDPE with MAn can be converted to reactive compound.

3-Grafted LLDPE has less thermal stability than polyamide.

4- The LLDPE can be converted to soluble polymers in organic solvent (toluene) at room temperature.

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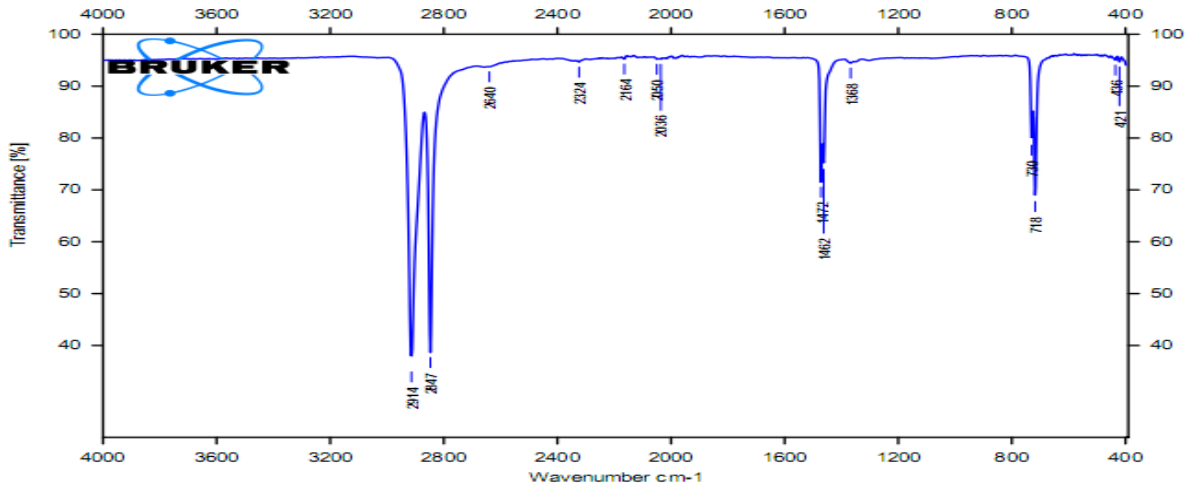
Figures:



Figure(1): FTIR spectrum of P

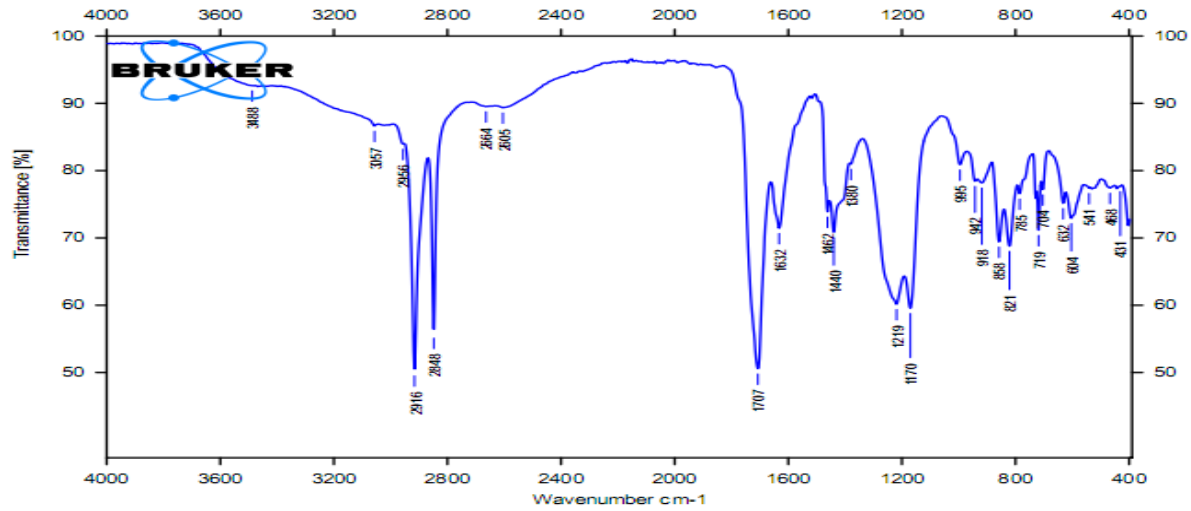


Figure (2): IR spectrum of MP (sample 6

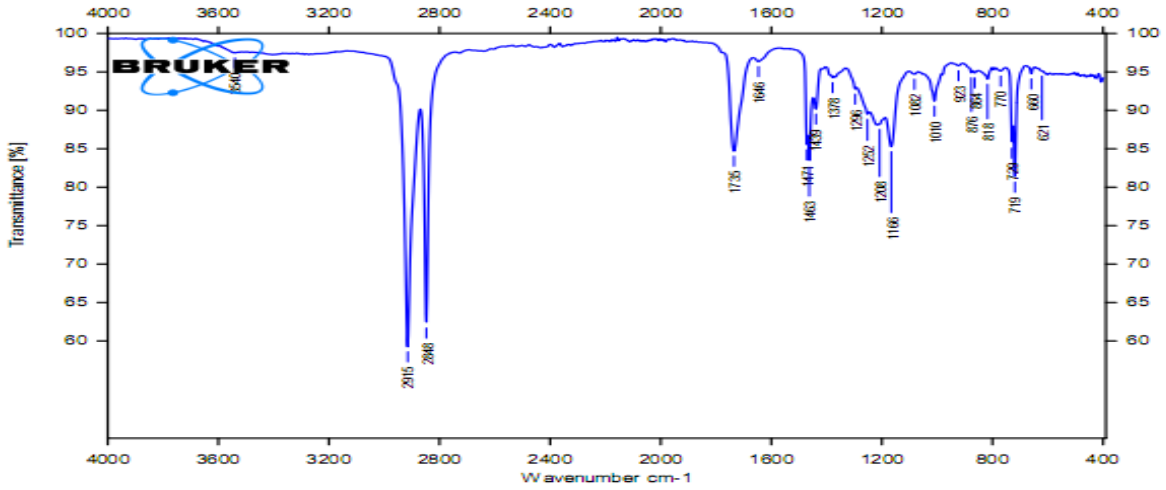


Figure (3): FTIR spectrum of I

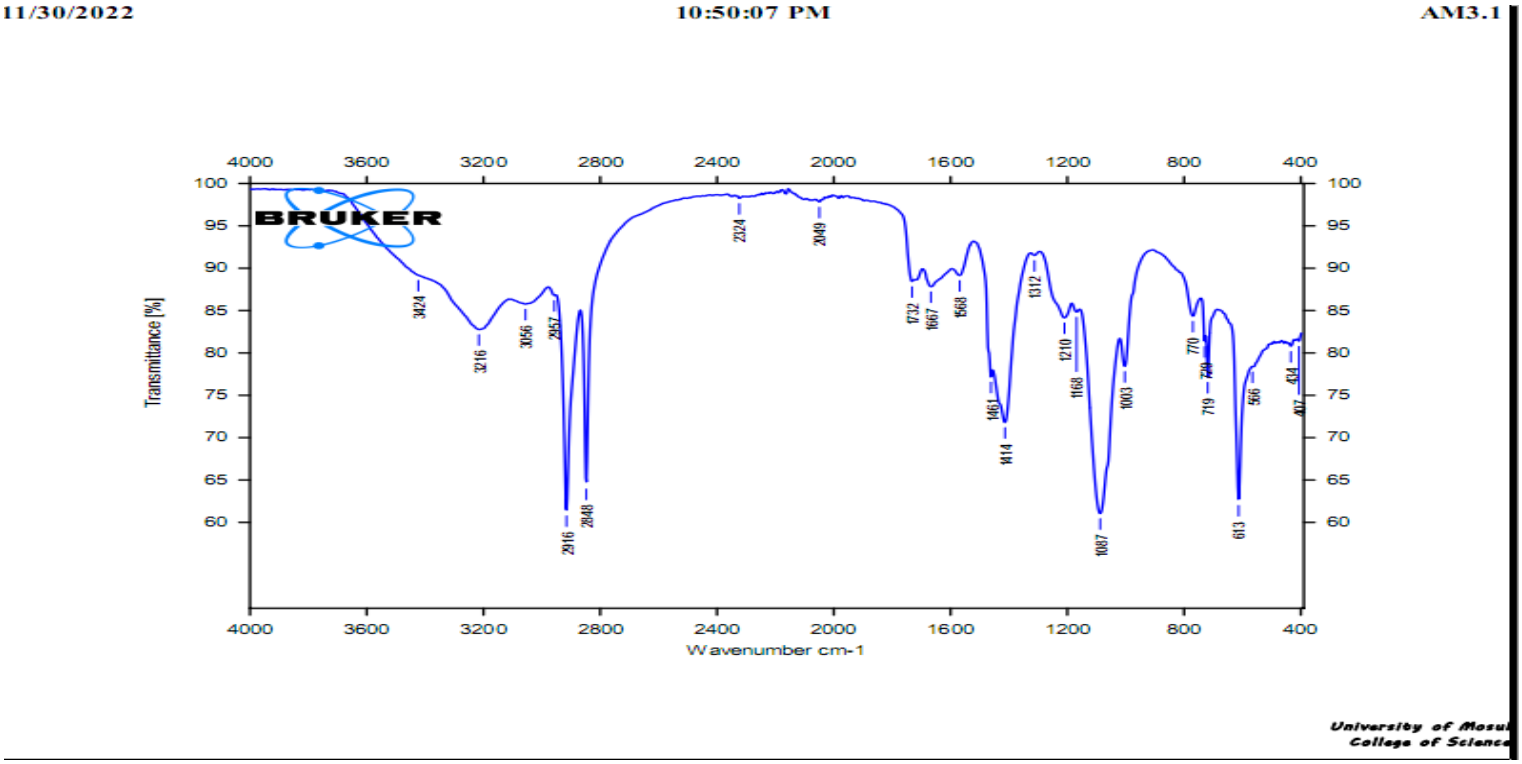


Figure (4): FTIR spectrum of M

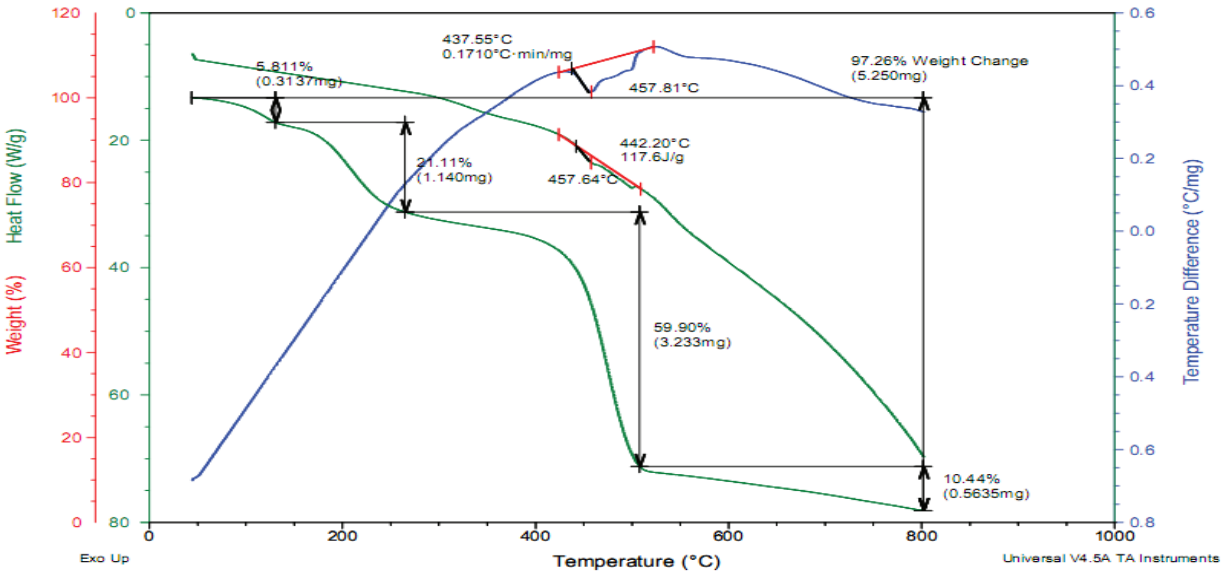


Figure (5): Thermograme of I

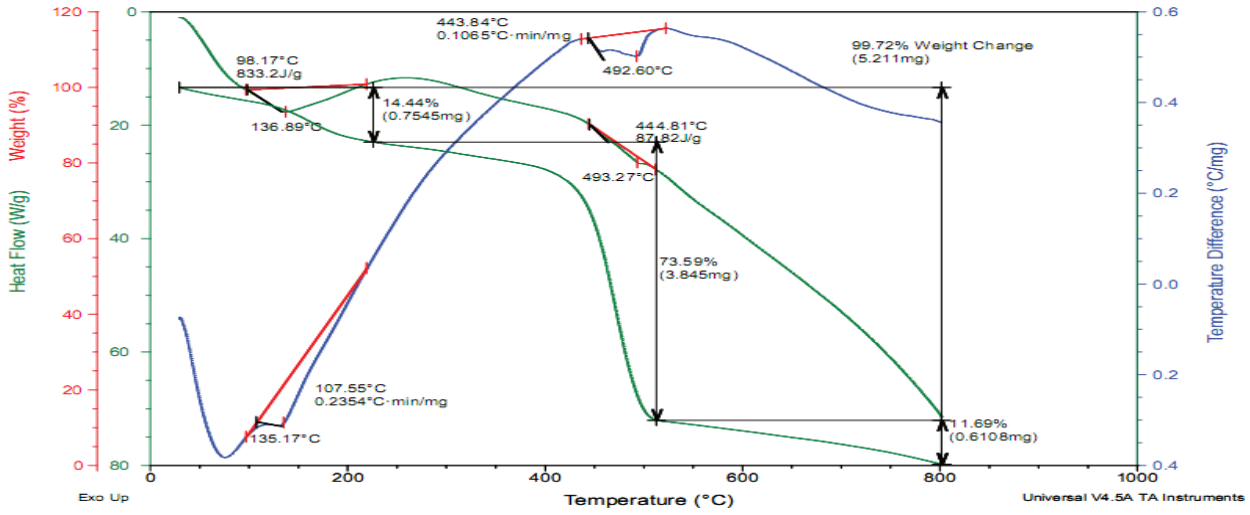
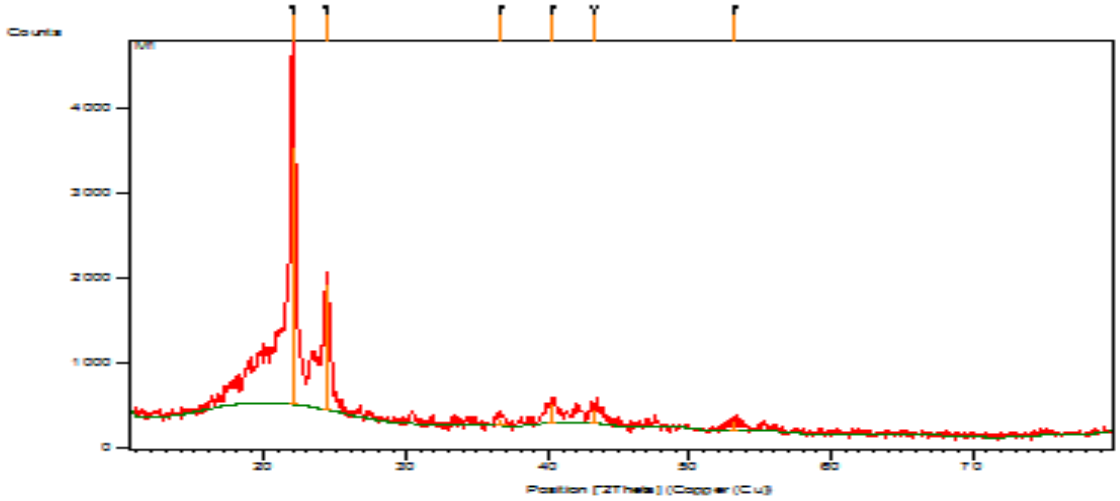


Figure (6): Thermograme of M

Graphics: (Bookmark2)



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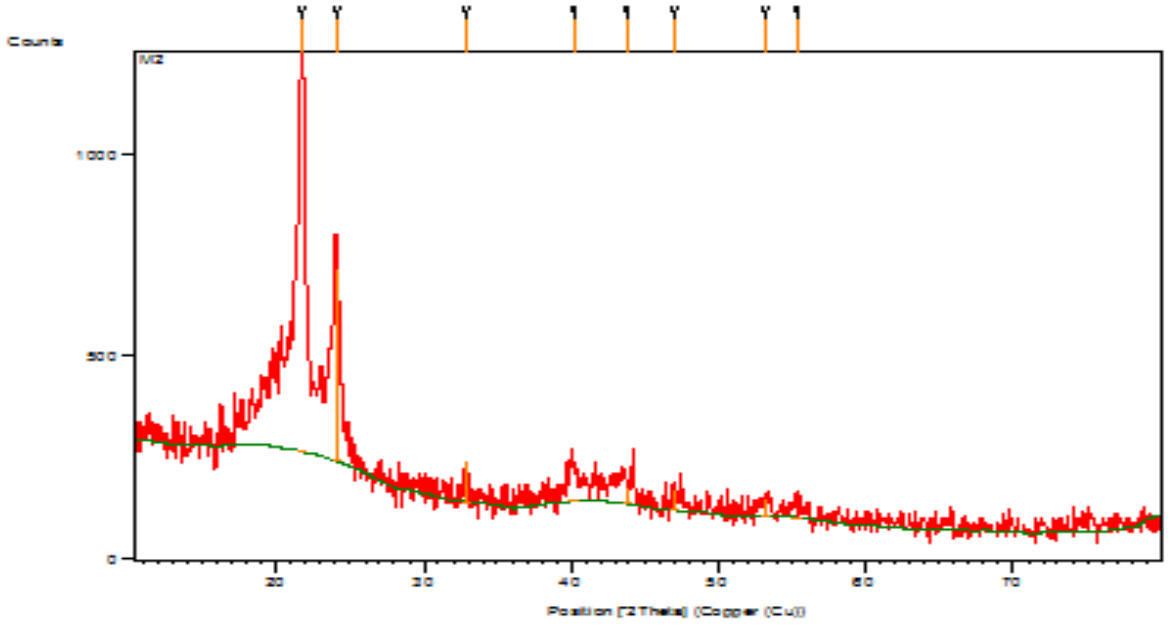

Figure (8): XRD of M