Synthesis and Characterization of New Copolymers as Asphalt Additives

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Abstract

Rheological properties of asphalt S_{50} were improved by adding different prepared copolymers as additives with high homogeneity of asphalts samples. Three types of copolymers were prepared Poly (Indene –Co- maleic anhydride)**(A_1)** Poly (Acrylonitrile –Co- Maleic anhydride) **(A2)** and Poly (Dipentine –Co-Maleic anhydride) **(A_3),** the cross linking of (**A3)** to (**A3d**). by using sulfur.

These copolymers were designed by inserting Maleic anhydride as rings containing through backbone of polymer chains to be high potentially to react with water to protect the crack of pavement .And moisture with inhibit bonding of crack of pavement, Many factors should be considered when prepared the additives to enhanced performance to be convenience cost, beneficial thermal safety , extended life of the asphalt, preparing conditions which gave high thermal resistance with more stabilities, all these prepared copolymer have been characterized by FTIR and H-NMR spectroscopies .Intrinsic viscosities were calculated. softening point and penetration were observed for all asphalts blends which were compared with the asphalt samples, which gave high thermal resistance with more stabilities.

The results showed high properties of these blends when compared with the original asphalt. The physical properties of a specific polymers are determined by the sequence and chemical structure , When polymers are added to asphalt , the properties of the modified asphalt cement depend on polymer characteristic of asphalt and compatibility of polymer with asphalt.

All these prepared copolymers were tested by softening points and penetration for all asphalt blends which were compared with the asphalt sample. All the Improvements made by adding polymers to asphalt included the Increasing the viscosity of the binder service, the thermal susceptibility of the binder, increased the cohesion of the asphalt, Increasing the resistance to permanent deformation, and Improved the resistance to fatigue at low temperatures, improved binder adhesion (higher viscosity of the binder),

Key word : Asphalt , Additives, copolymer

الخلاصة

تم تحسين خصائص الانسيابية من الاسفلت S_{50} بإضافة بوليمرات متعددة مختلفة كإضافات مع تجانس عالية من عينات الإسفلت. تم إعداد ثلاثة أنواع من بوليمرات بولي (أندين –Co– أنهيدريد الماليك) (A1) بولي (أكريلونتريل –Co– أنهيدريد ماليك) (A2) وبولي (أنهيدريد Dipentine -co–المالئيك) (A3)، وعبر ربط من (A3) إلى (A3D). باستخدام الكبريت.

وقد صممت هذه بوليمرات عن طريق إدراج أنهيدريد المالئيك كما عصابات تحتوي من خلال العمود الفقري لسلاسل البوليمر لتكون مرتفعة يحتمل أن تتفاعل مع الماء لحماية الكراك من الرصيف. والرطوبة مع الرابطة تمنع من صدع من الرصيف، وينبغي النظر في العديد من العوامل عند إعداد الإضافات لتحسين الأداء لتكون تكلفة الراحة والسلامة الحرارية مفيدة، حياة طويلة من الأسفلت، وإعداد الشروط التي أعطت مقاومة حرارية عالية مع أكثر بثبات، وقد تميزت كل هذه أعدت من البوليمرات التي FTIR ومطيافية H-NMR حسبت اللزوجة .Intrinsic. وقد لوحظت نقطة تليين والاختراق لجميع خلطات الإسفلت التي تمت مقارنة مع عينات الأسفلت، والذي أعطى المقاومة الحرارية العالية مع مزيد منة بثبات.

أظهرت النتائج خصائص عالية من هذه الأخلاط إذا ما قورنت مع الأسفلت الأصلي. يتم تحديد الخصائص الفيزيائية للبوليمرات محددة من تسلسل والكيميائية هيكل، عند إضافة البوليمرات سفلتة وخصائص الاسمنت الأسفلت تعديل تعتمد على خاصية البوليمر من الاسفلت والتوافق من البوليمر مع الأسفلت.

تم اختبار كل هذه بوليمرات التي أعدها تليين نقطة والاختراق لجميع خلطات الأسفلت التي تمت مقارنة مع العينة الأسفلت. شملت جميع التحسينات التي أدلى بها مضيفا البوليمرات إلى الأسفلت وزيادة لزوجة خدمة الموثق، الحساسية الحرارية من الموثق، وزيادة تماسك الإسفلت، زيادة المقاومة للتشوه دائم، وتحسين مقاومة التاثر في درجات حرارة منخفضة، تحسين التصاق الرابط (اللزوجة أعلى من الرابط).

الكلمات المفتاحية: اسفلت، اضافات، متشابك.

Introduction

Rheology is the main science to characterize asphalt as it deals with flow and deformation at various rates and temperatures. Rheological properties of asphalt depend on the physical arrangement of the constituent molecules and this change rapidly with temperature [Hui *et al.*, 2013; ASTM. 2010].

Asphalt is a highly complex material that has yet to be characterized compounds with up to an estimated 150 carbon atoms [Henry and Michel 2007]. Usually the composition of the asphalt depends a great deal on the type of crude oil from which it is derived. Generally, the molecular compounds within asphalt contain oxygen, nitrogen, sulfur and other heteroatoms. However, asphalt largely consists of 80 percent by weight of carbon, up to 10 percent by weight of hydrogen, and 6 percent by weight of sulfur, small 10 percent by weight of hydrogen, and 6 percent by weight of sulfur, small amounts of oxygen and nitrogen, and traces of metals like iron, nickel and vanadium [John and Speight, 2000]. The constituent compounds possess molecular weights that range from several hundred to many thousands. The detailed composition of asphalt still obtains a significant amount of attention from several research groups around the world [(ASTM) D 4124 – 01,(2009)] . Due to its complex composition, asphalt is often separated in two different chemical classes of constituents called Asphaltenes and maltenes. Maltenes can further be divided in three groups: saturates, aromatics, and resins. In this study, a solvent precipitation method was used to separate Asphaltenes and maltenes [Speight, 1999; Freddy& Fabrice, 2013, Freddy & Fabrice, 2013, Juan *et al.*1998)]

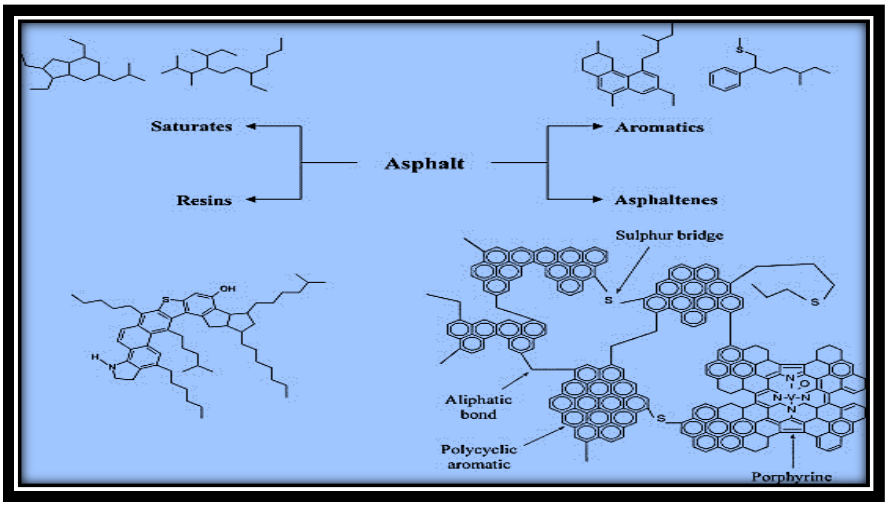


Figure (1) structure of asphalt

Polymer Modified Asphalt

The addition of polymers, chains of repeated small Pavement with polymer modification exhibits greater resistance to rutting and thermal cracking and decreased fatigue damage, stripping and temperature susceptibility. Polymer modified binders have been used with success at locations of high stress, such as intersections of busy streets, airports, vehicle weigh stations, and race tracks [Bates & Worch, 1987, Zhu, *et al.* 2014].

There are three types of polymers which can be used in treating asphaltic materials for different applications of road paving field. These includes elastomers, elastomers, and thermosetting resins [Asahi Kasei Chemical Corporation, 2005]

Blending of Polymers with Asphalt

A good asphalt binder modification with polymers is in trying to improve the rheology of the binder and to make it behave more stable in different weather conditions. The polymers are added to asphalt binder in order to: Increase elasticity. Increase tensile strength. Reduce temperature susceptibility. Increase water resistance [Polacco *et al.* 2005; Chen *et al.*, 2002)].

Addition of polymers to the asphalt binder can be applied by two ways , the first way includes addition of polymers in the form of "simple" mixture involving no chemical interaction between the asphalt constituents and the polymer molecules where the polymer is dispersed in the maltene phase while the second way includes addition of polymers in the form of "complex" mixtures involving a chemical interaction between the polymer molecules and certain constituents of asphalt binder where the polymer is dispersed in the maltene phase and then reacts with asphaltenes to form higher molecular weight molecules .Chemical compatibility of polymer with asphalt binder components and blending process conditions are critical to obtain acceptable rheological properties, where some polymers are incompatible with asphalt binder components so that phase separation may result [Becker *et al.*, 2003; Perez-Lepe. *et al.* 2006].

Experimental

Materials and Instruments

The following chemicals were used as received from suppliers; Indene was purchased from Fluka. Maeic anhydride was purchased from Sigma-Aldrich (St. Louis, MO, USA ,Dipentene and DMF (CF) were obtained from BDH .Ammonium Per Sulfate APS was obtained from Merck, Acrylonitril was purchased from Fluk ,asphalt S50 was obtained from Aldura refineries. ^{1}H-NMR spectra were recorded on a Shimatzu spectrophotometer in Dimethylsulphoxide (DMSO). The FTIR spectra were recorded by (4000-400cm^{-1}) on a Shimatzu spectrophotometer. Melting points were determined on callenkamp MF B-600 Melting point apparatus. Electronic spectra measurement using CINTRA5-UV.Visble spectrophotometer.

Poly (Indene –Co- maleic anhydride)(A$_1$)

In a screw capped polymerization bottle (3g.), of (20gm.0.2 ml) Of Maleic anhydride dissolved in (12ml) of Acetone and (17gm,0.2ml) of Indene .(0.05gm) of dibenzoylperoxide were introduced in the bottle .it was flashed with nitrogen for few minutes inside a glove and firmly stopped. The solution was maintained at 70℃, using water bath for 1 hr. The solvent was evaporated under vacuum; the product was obtained, washed three times with ether. Dried in a vacuum oven at 50°C, produced 95% of polymer with $\mu_{in} =$ 0.84 dL /g.

Poly (Acrylonitrile –Co- Maleic anhydride) (A2)

(2.2gm.0.02 ml) Of Maleic anhydride dissolved in (7 ml) of Acetone and (2gm,0.02ml) of Acrylonitrile.0.05gm of dibenzoylperoxide was added ,the mixture was introduced in polymerization bottle , the bottle was flashed with nitrogen for few minutes inside a glove and firmly equipped and stopped. The solution was maintained at 70℃, using water bath for 1 hr. The solvent was evaporated under vacuum; the product was obtained, washed three times with ether. Dried in a vacuum oven at 50°C, produced 95% of polymer with $\mu_{in} =$ 0.86 dL /g.

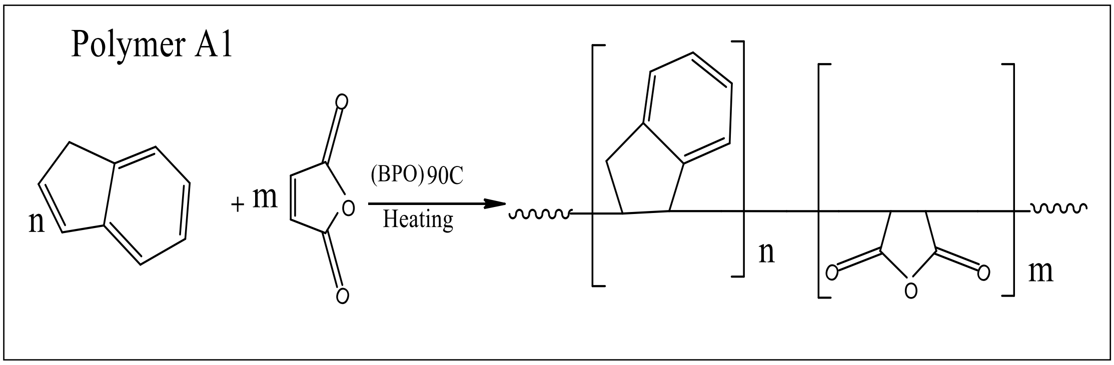
Poly (Dipentine –Co-Maleic anhydride) (A_3)

(10gm.0.1 ml) of Maleic anhydride dissolved in (4 ml) of acetone than the (10 gm 0.07ml) of dipentene (0.05gm) of dibenzoyl peroxide added to the mixture. the mixture was introduced in polymerization bottle and it was flashed with nitrogen for few minutes inside a glove box and firmly equipped and stopped. The solution was maintained at 70°C, using water bath for 1 hr. The solvent was evaporated under vacuum; the product was obtained, washed three times with ether. Dried in a vacuum oven at 50°C, produced 95% of polymer with $\mu_{in} =$ 0.89 dL /g.

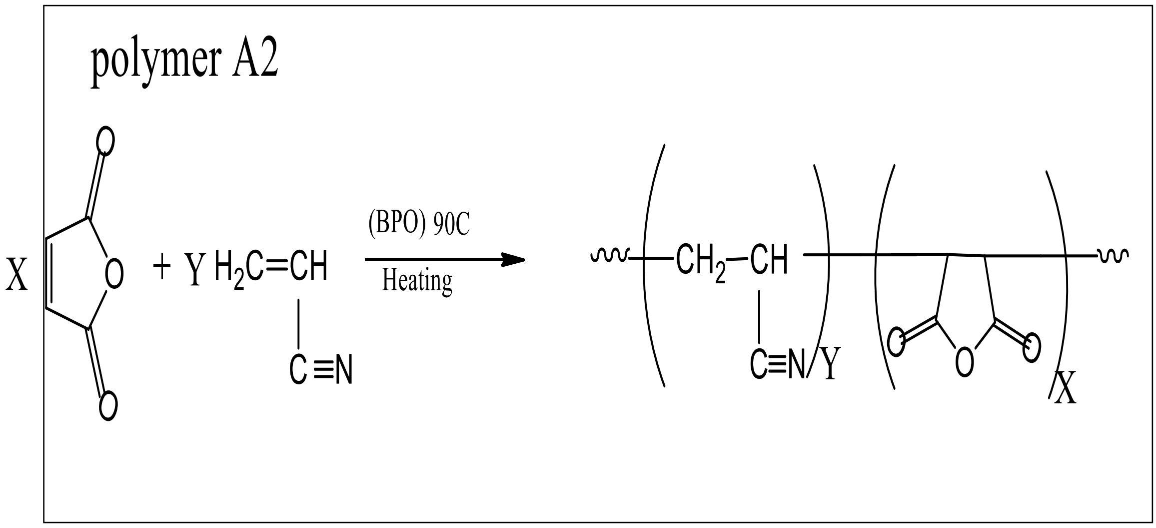
Results and Discussion

We described that to modify asphalt that the main reasons to modify asphalt materials with different types of prepared copolymers additives to obtain different blends with improvement Rheological properties of Iraqi asphalt and reduce cracking, to reach stiffer blends at high temperatures and reduce rutting, to increase the stability and the strength of mixtures to improve fatigue resistance of blends, and to reduce structural thickness of pavements. Rheological properties of Iraqi asphalt was improved by different prepared copolymers additives with high homogeneity of asphalts samples .Three types of copolymers were prepared a- Indene –Maleic anhydride copolymer A1

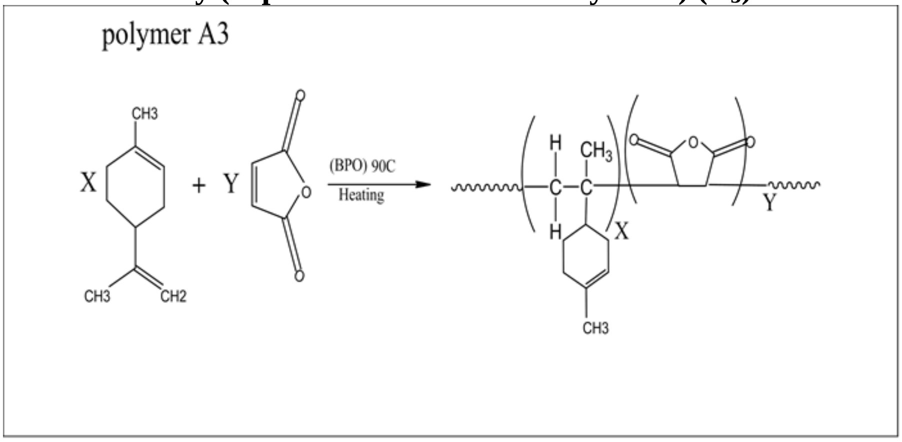
Poly (Indene –Co- maleic anhydride)(A_1)



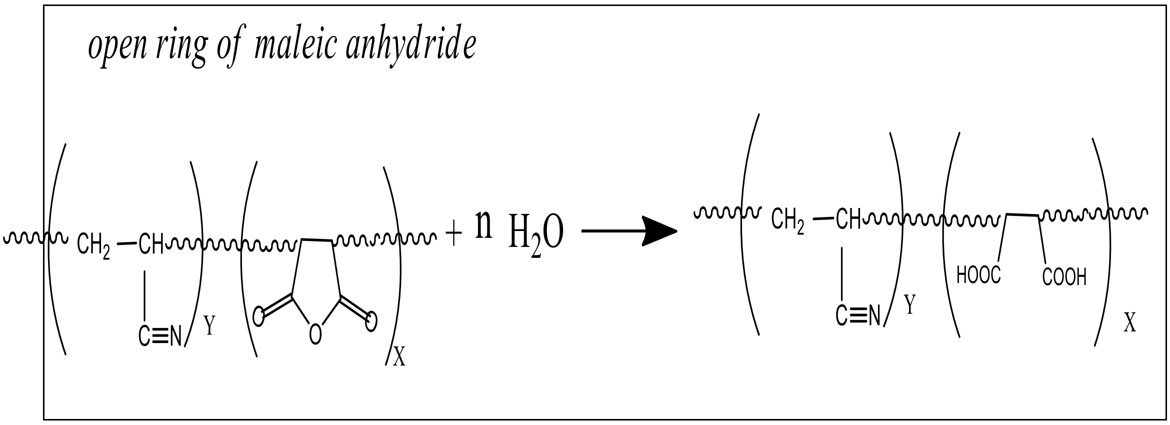
Poly (Acrylonitrile –Co- Maleic anhydride) (A2)



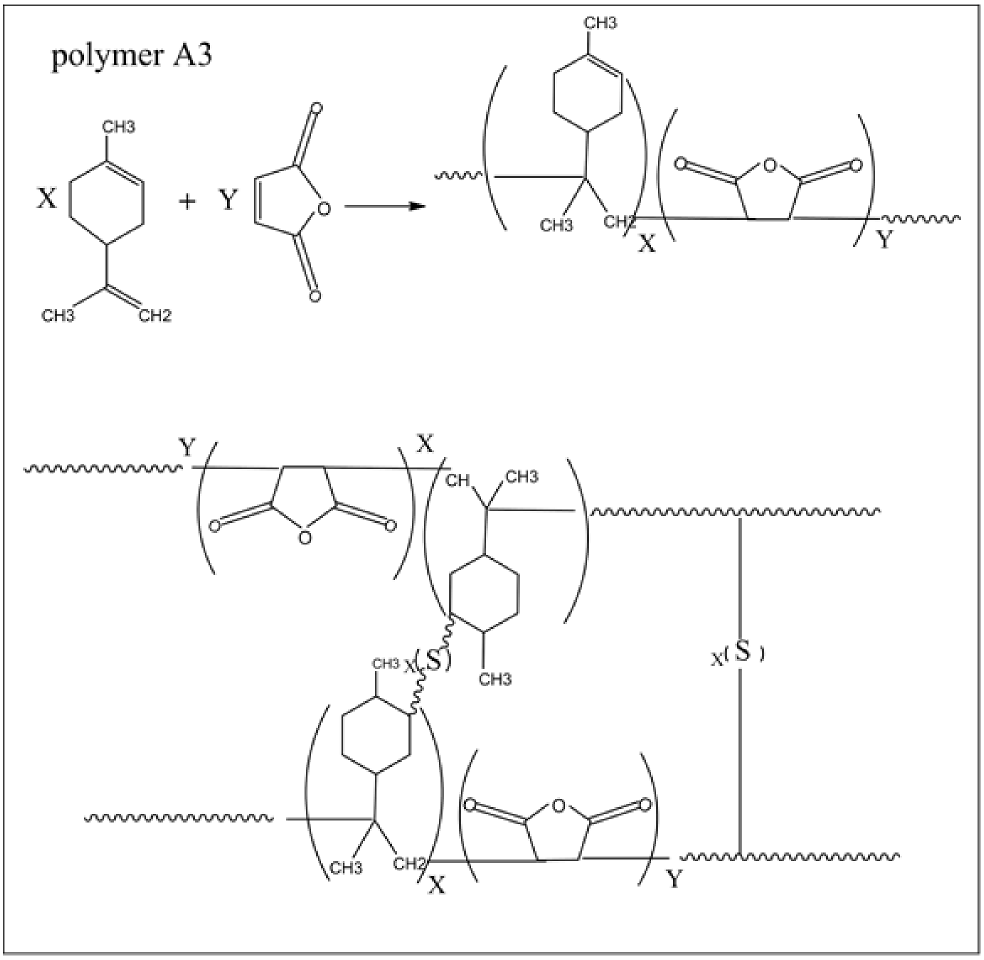
Poly (Dipentine –Co-Maleic anhydride) (A_3)



These copolymers were designed by inserting Maleic anhydride as rings contained through backbone of polymers chains to be high potentially to react with water to protect the crack of pavement .and moisture with inhibit bonding of crack of pavement, which could cured the bonding of crack of pavement, many factors should be considered when prepared the additives to enhanced performance to be convenience cost, beneficial thermal safety , extended life of the asphalt, and its resistance against the rain water .According to the following hydrolysis:



Cross - link in Poly (Dipentene- co Maleic anhydride)



Fig(1) FT-IR spectra of Indine –g- copolymer maleic anhydride(A_1) showed absorption peaks at 3087 cm^{-1} (C-H aromatic), of indine aromatic ring ,and 2891 cm-1 0f (C-H), 1604 cm-1 of (C=C), 1431 cm^{-1}(and 1020 (C-O). [21]. Since the characteristic absorptions of anhydride overlapped with each other at1770-1875cm^{-1} . Fig(2) of A2 which revealed the absorption peaks dominated by anhydride during the formation, a new peak appeared at1780- 1870cm^{-1}due to (C=O),indicated the insertion of maleic anhydride copolymer , the formation of characteristic absorptions of acrylo nitril was appeared at 2340 cm^{-1} due to nitrile group.

Fig(3) FTIR spectra Dipentine –maleic anhydride copolymer (A_3) showed absorption peaks at 2960 cm-1 (C-H) aliphatic , 2870 cm^{-1} was attributed to the (C-H) stretching (C=O) groups in maleic anhydride , (1847-1770) cm^{-1} assigned to C=O of maleic anhydride , 1653 cm-1 to(C=C)aromatic of Dipentine ring. Ammonium per sulphat as an initiator was used for grafted maleic anhydride as unsaturated acid anhydride on more useful method to modify physicochemical properties in order to obtain new properties by grafting anhydride through the backbone polymer which could be opened by water with more interesting features, with a suitable improvement because of its potential loading for both hydrophilic and hydrophobic using as obviously desirable for application .The sample was analyzer by UV- spectroscopies periodically withdrawn for every days ,it was appeared at ƛmax 320 nm .

Fig(4) The^{1}H-NMR spectrum of polymer [A1] was indicated the signal δ 1.3 ppm , (2.4ppm) as signal (C-CH-CH), (7.1ppm) for 4H (CH) aromatic ring of indene., (3.3ppm) as single for 2CH (CH -C=O) of maleic anhydride.

Fig(5) The^{1}H-NMR spectrum of polymer [A2] was indicated the signal (CH2-CH-CN)2H,d.and (2.5ppm) as triplet , (-CH-CN) 1H (3.7 ppm) as triplet 2CH (CH -C=O) at (3.1ppm.

Fig(6) The^{1}H-NMR spectrum of polymer [A3] was indicated the signal (1.8ppm) as single to (CH3) 3H terminal and at 3.4ppm of other CH3 which attached with aromatic ring.COCH-CH.CO) 2H were appeared at3.7-4.4ppm due to maleic anhydride .at 6ppm ofCH2=C as d.2H,and6.5ppm T. of attached with ortho aromatic ring. and at 7-7.9ppm was attributed to4H of aromatic

All asphalts blends which were compared with the asphalt .samples, it appeared high enhancement. softening points and ductility were chanced with high improvements. Table(1) lists the Intrinsic viscosities dL\g for three prepared copolymers.

Table(1)

Copolymers	Intrinsic viscosities dL\g
A1	0.82
A2	0.86
A3	0.89

The results showed high properties of these blends when compared with the original asphalt. The physical properties of a specific polymers are determined by the sequence and chemical structure , When polymers are added to asphalt , the properties of the modified asphalt cement depend on polymer characteristics and, asphalt characteristics, and compatibility of polymer with asphalt.,

All these prepared copolymesrs were blending with asphalt, which gave the Increasing in viscosity of the binder .the thermal susceptibility of the binder, Increasing the cohesion of the bitumen, Increasing the resistance to permanent deformation, Improving the resistance to fatigue at low temperatures and ,Improving binder-aggregate adhesion (higher viscosity of the binder when the cross linking with Sulfur.

Table (3)Weight loss in different temperature stages

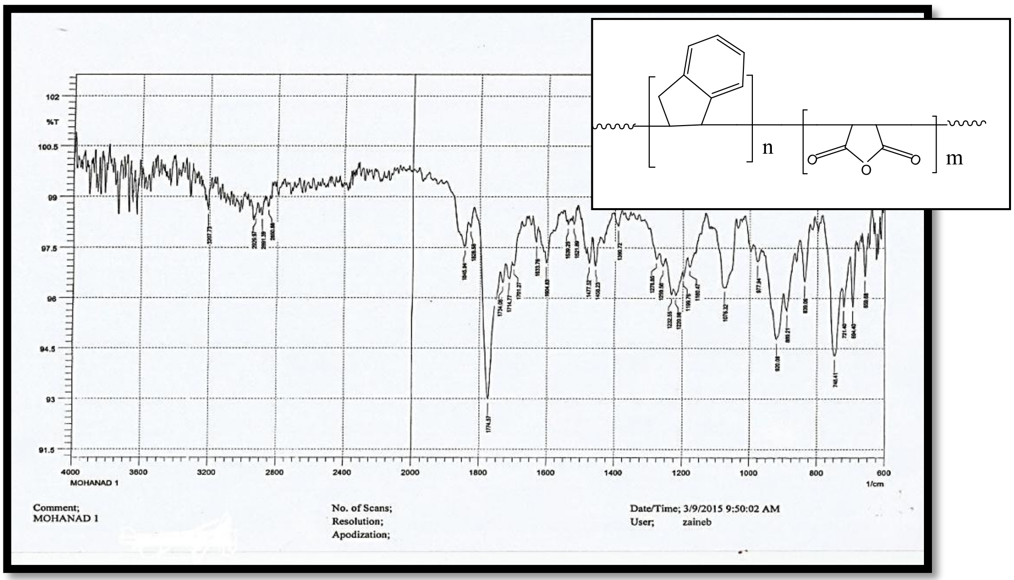
sample	First stage		Second stage		Final stage	
	Temp.C^0	Weight loss%	Temp.C^0	Weight loss%	Temp.C^0	Weight loss%
A_1	78.4	5	150	20	300 375 556	50 70 90
A_2	60	0	220	45	250 410	50 90
A3	50	0	180	25	500	68
A3d	150	0	367	40	650	70

The final step of thermal degradation with high thermal properties leads to wide application uses.

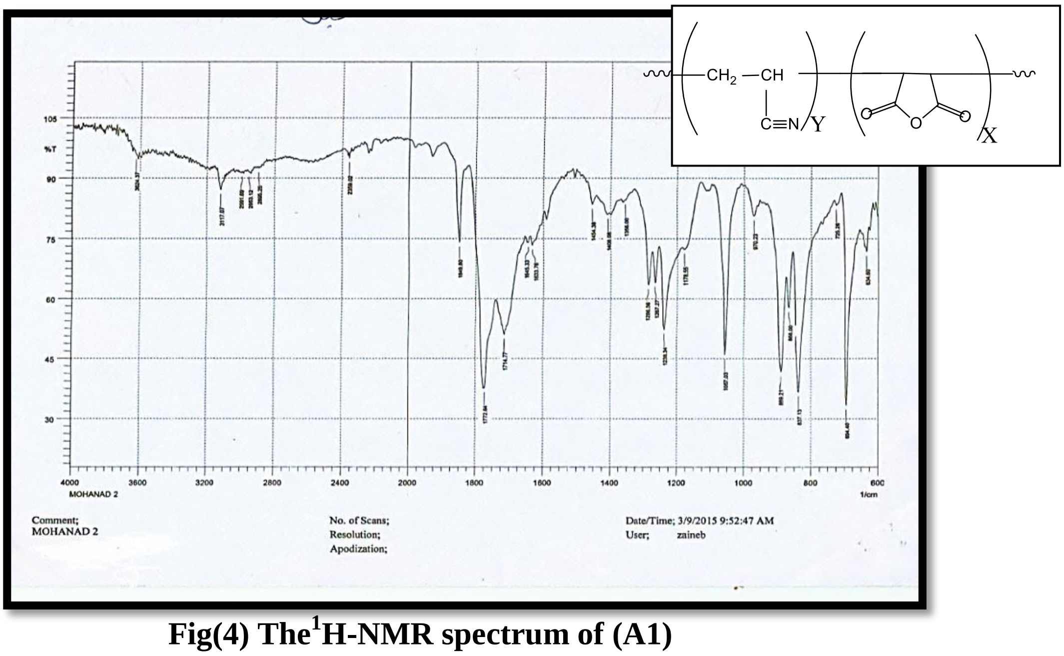
The graft copolymer (A_2) was measured in different stages, Fig (7) indicated the rate of thermal degraded through backbone of grafted copolymer above500. Where as A3d was higher degraded at 600 due to cross linked through un saturated bond with sulpher . with asphalt blend.

Conclusion

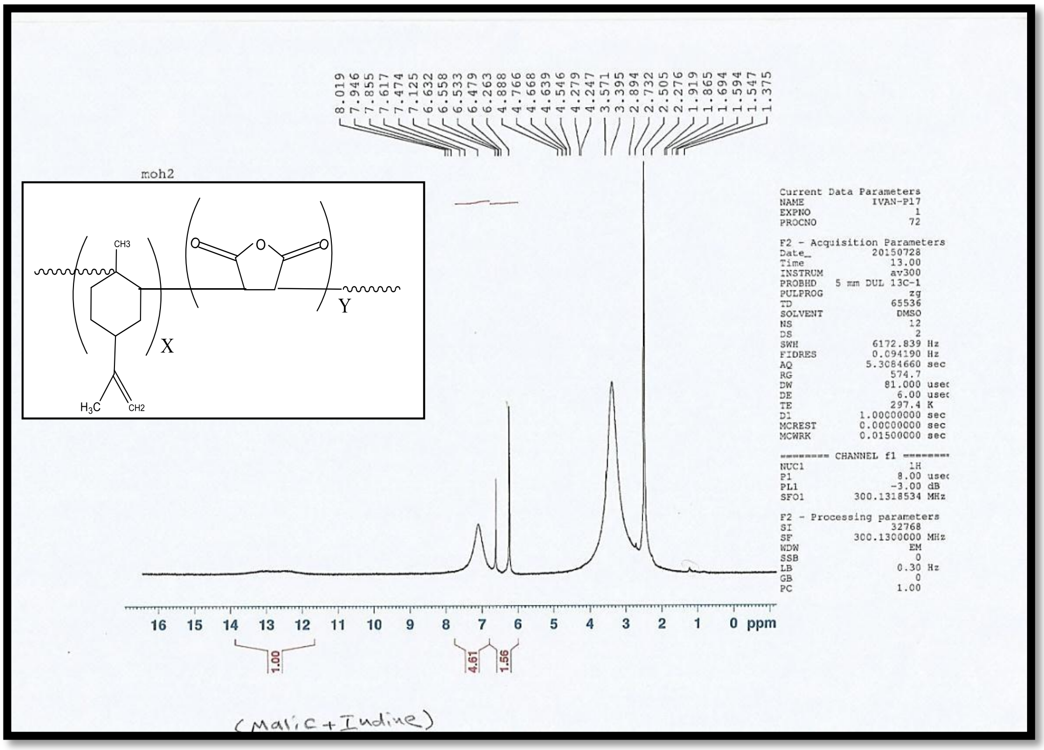
All these prepared copolymesrs were tested by softening points and penetration for all asphalt blends which were compared with the asphalt sample. All the Improvements made by adding polymers to asphalt included the Increasing the viscosity of the binder service, the thermal susceptibility of the binder, Increasing the cohesion of the bitumen, Increasing the resistance to permanent deformation, Improving the resistance to fatigue at low temperatures, Improving binder-aggregate adhesion (higher viscosity of the binder three types of copolymers were prepared a- Indine –Maleic anhydride copolymer A1 b- Acrylonitrile – Maleic anhydride copolymer A2. C-Maleic anhydride. Dipentine copolymer A3 contained through backbone of polymers chains to be high potentially to react with water to protect the crack of pavement .and moisture with inhibit bonding of crack of pavement. the cross linking ofA3 to A3d. by using sulfur. The cross linking ofA3 to A3d. by using sulfur cross linkening gave higher temperatures, improving binder- adhesion (higher viscosity)



Fig(2) FT-IR spectrum of (A1)



Fig(4) The^{1}H-NMR spectrum of (A1)



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DS                       2
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DE                    6.00 usec
TE                   297.4 K
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PL1                  -3.00 dB
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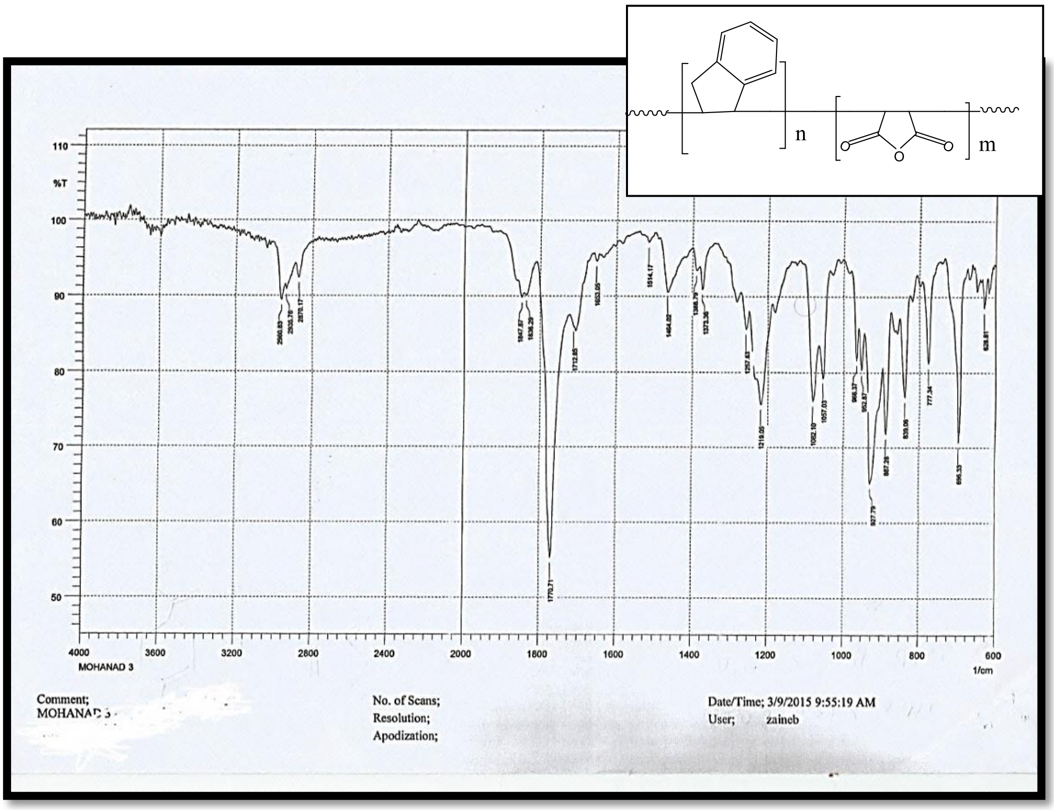
(Malic + Indine)

Fig(5) FTIR spectrum of (A3)



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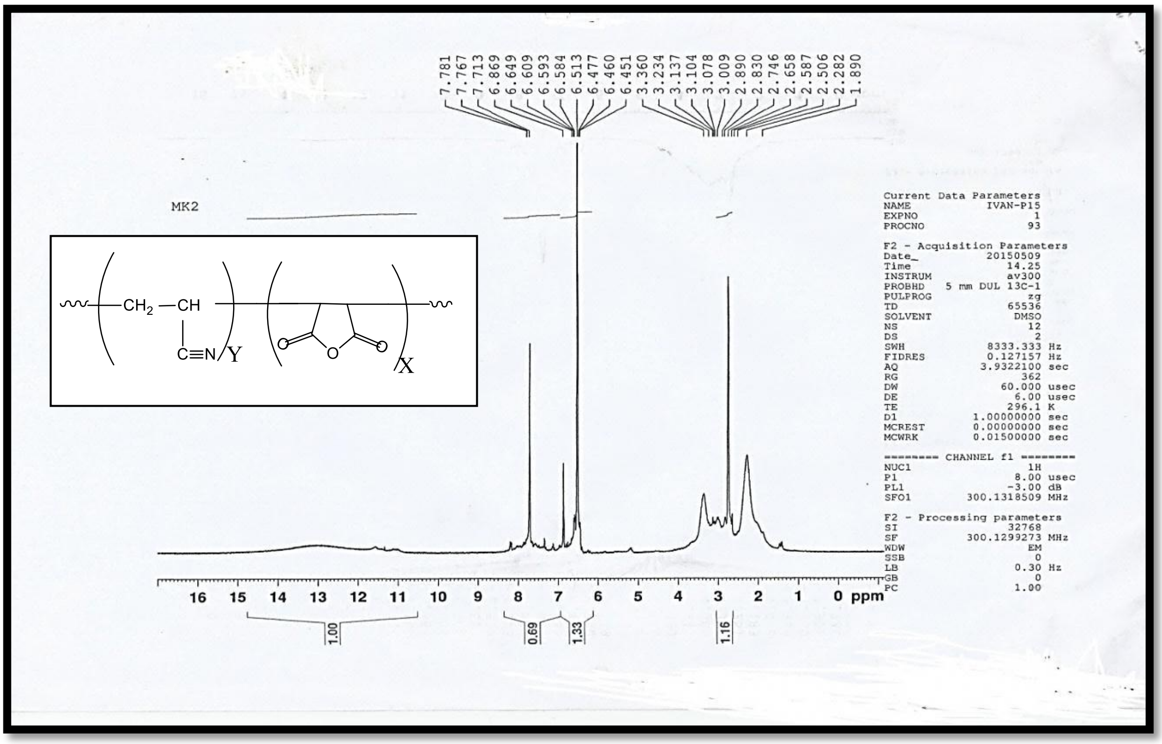

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DS                       2
SWH               8333.333 Hz
FIDRES            0.127157 Hz
AQ               3.9322100 sec
RG                     362
DW                  60.000 usec
DE                    6.00 usec
TE                   296.1 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
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P1                    8.00 usec
PL1                  -3.00 dB
SFO1           300.1318509 MHz

F2 - Processing parameters
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SSB                      0
LB                    0.30 Hz
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PC                    1.00
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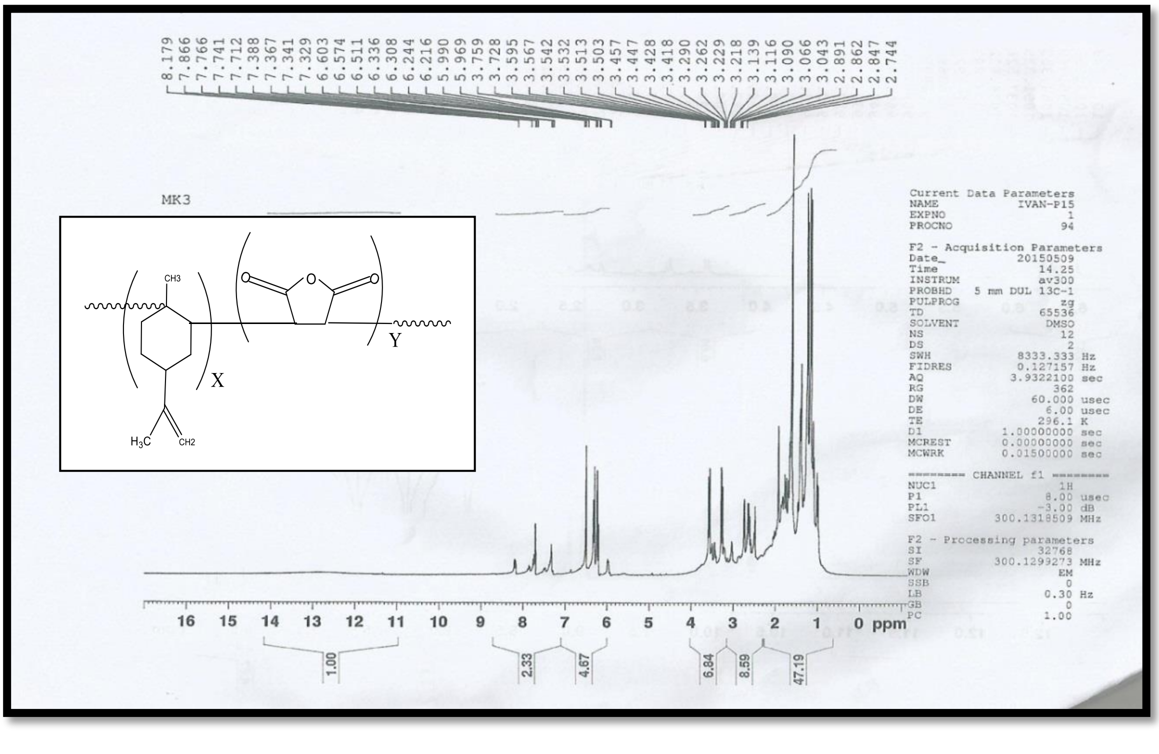
Fig (6) The ^{1}H-NMR spectrum of (A1)



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PROCNO                  94

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PULPROG                 zg
TD                   65536
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NS                      12
DS                       2
SWH               8333.333 Hz
FIDRES            0.127157 Hz
AQ               3.9322100 sec
RG                     362
DW                  60.000 usec
DE                    6.00 usec
TE                   296.1 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.00 usec
PL1                  -3.00 dB
SFO1           300.1318509 MHz

F2 - Processing parameters
SI                   32768
SF             300.1299273 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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Fig(7) The ^{1}H-NMR spectrum of (A3)

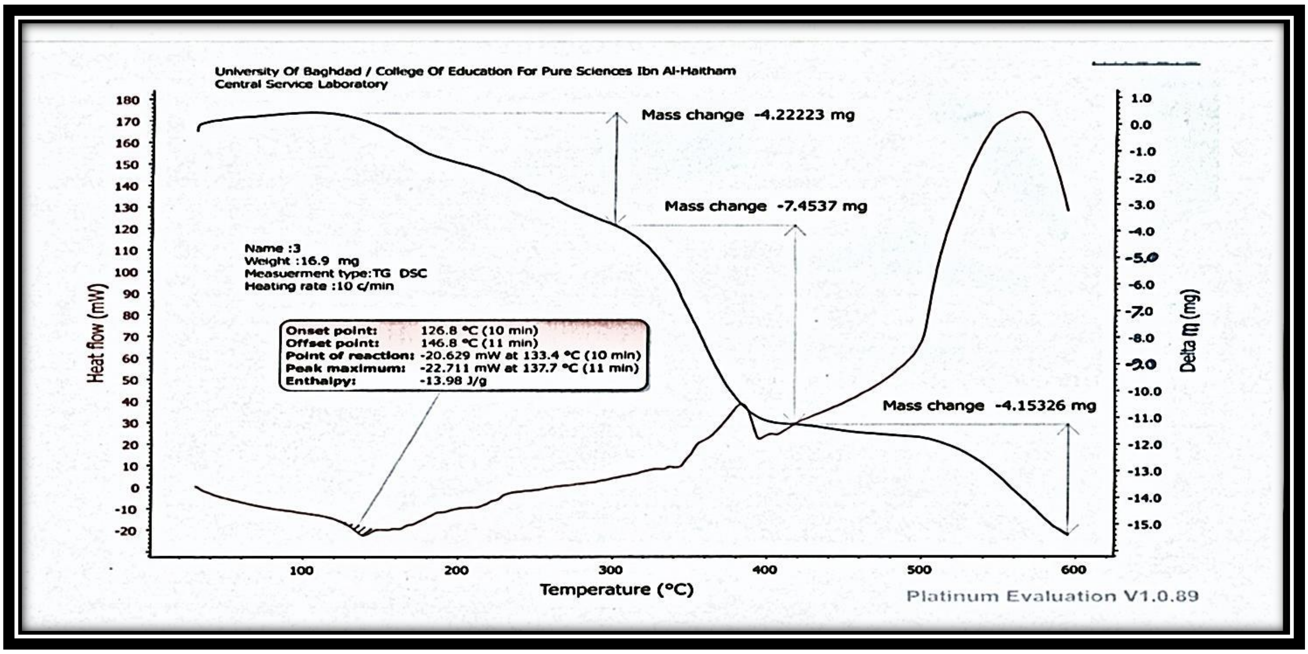

Fig (8) TGA&DSC Thermo gram (A1)

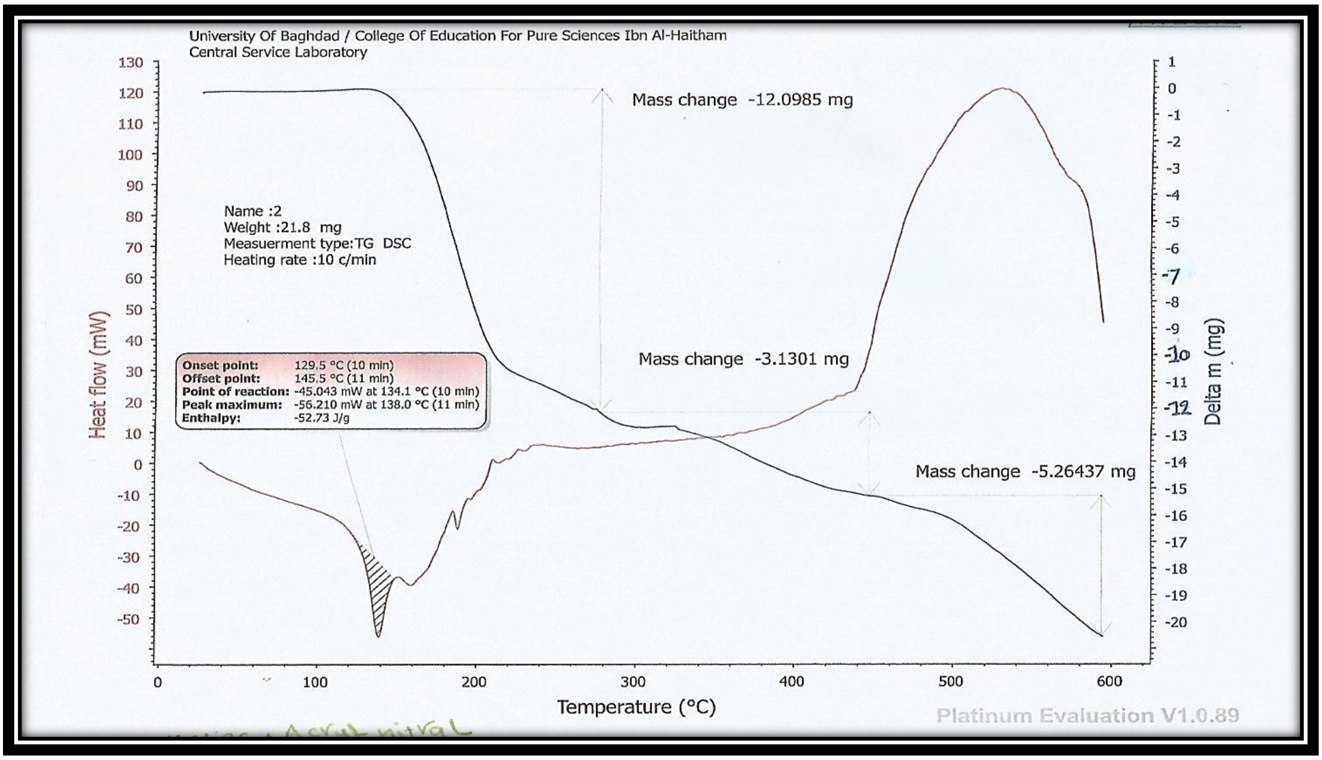

Fig (9) TGA&DSC Thermo gram (A2)

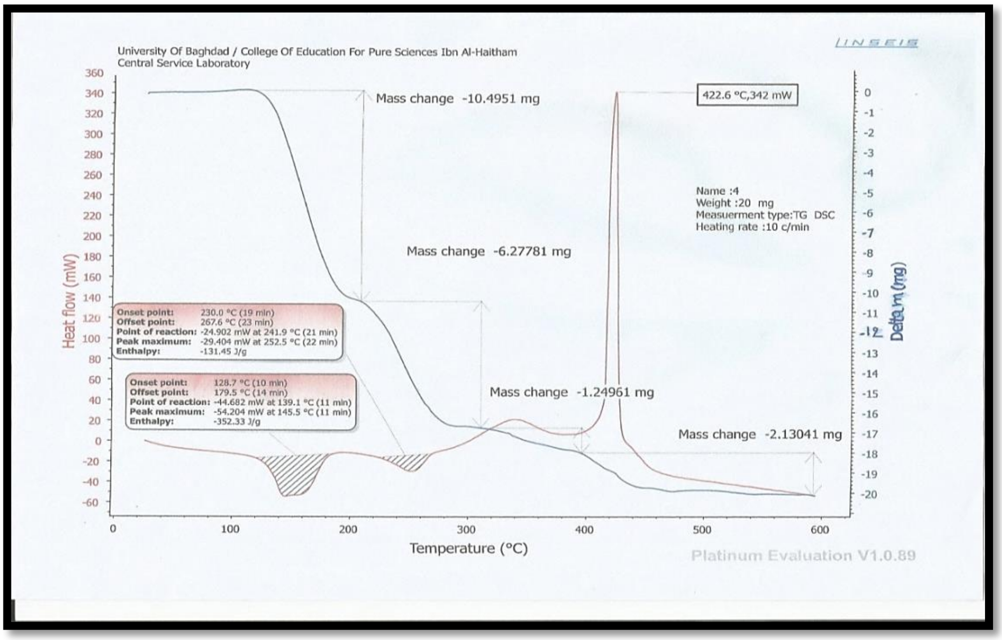

Fig (9) TGA&DSC Thermo gram (A3)

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