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Research Article

Asphalt Additives for Improvement of Rheological properties

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Abstract : asphalt s50 was improved by adding some additives such as poly styrene graft co dipentene or indene a1-a2 then sulfur was used as cross linking agent to protect the fracture of pavement to superior presentation to be expediency cost, beneficial thermal safety, extended life of the asphalt, preparing conditions which gave high thermal resistance with more stabilities, all these prepared polymers have been characterized by FTIR and ¹H-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 softening temperatures with higher stabilities to resist the deformations of roads. The blend of asphalt showed high properties when compare with the origin asphalt. The physical properties of a specific polymers are determined by the succession 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. When polymers are added to asphalt is to produce binders have acceptable rheological for using in different weathering conditions. All these prepared polymers were tested by softening points and penetration for all asphalt blends which were compare with the asphalt sample. all the improvement 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, to avoid permanent warp, and to prevent the fatigue at low temperatures, improved binder adhesion (higher viscosity of the binder). Rheological properties of asphalt were improved.

Keyword: asphalt, polymer additives, rheological properties.

INTRODUCTION

Asphalt is a dark brown to black, cement like semisolid or, viscous) cementations substance, composed principally of high molecular weight hydrocarbons, and soluble in carbon disulfide. Produced by the nondestructive distillation of crude oil during petroleum refining the three major types of asphalt products are paving asphalts, roofing asphalts, and asphalt-based paints also called asphaltum, used as cement for pavements¹⁻². 1.5.2 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 tracks³⁻⁴. Polymers that have been used to modify asphalt include styrene–butadiene–styrene (SBS), styrene–butadiene rubber (SBR), rubber, ethylene vinyl acetate (EVA), polyethylene, and others. Desirable characteristics of polymer modified binders include greater elastic recovery, a higher softening point, greater viscosity, greater cohesive strength and greater ductility⁵⁻⁶.

Polymer modified asphalt improves the fracture resistance of HMA overlay and reduces the deterioration around the cracks and joints. This treatment method does not prevent reflective cracks from occurring but will control or reduce the severity of reflective cracks with time. In other words it keeps the crack severity to a low level⁷⁻¹³. During periods of high temperature and under heavy traffic, a variety of pavement distresses continues to develop affecting the performance and economy of pavement construction. Polymer modified asphalts are commonly used to reduce pavement distress and to extend service life by enhancing the binder's adhesion, cohesion, and elasticity. The addition of polymers alters the rheological properties of asphalt so that it can retain sufficient flexibility at low temperatures while attaining a marked resistance to permanent deformation at high temperatures. It makes the binder more resistant to temperature variations and high traffic loads¹⁴⁻¹⁸. There are three types of polymers which can be used in treating asphaltic materials for different applications of road paving field. These includes {A- elastomers, B- plastomers, and C-thermosetting resins¹⁹⁻²⁰. 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 conditions²¹⁻²².

The polymers are added to asphalt binder in order to:-

- 1- Increase elasticity
- 2-Increase tensile strength.
- 3-Reduce temperature susceptibility.
- 6-Increase water resistance

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 such as shown in Fig.(2), 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 such as shown in Fig.(1). 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 result²³ When the polymer is in amorphous state, it can be brittle and easily penetrated by solvent, so it can be penetrated from the maltene

phase and it can be compatible with asphalt binder components. But, when the polymer is in semi - crystalline state, it cannot easily be penetrated by solvents, so it cannot be penetrated from the maltene phase and it can be incompatible with asphalt binder components²³.

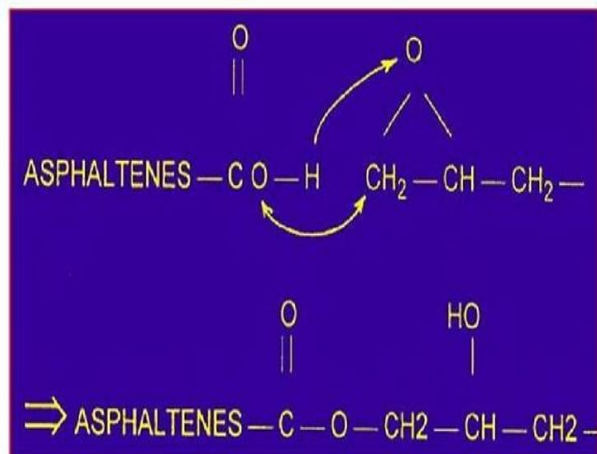


Fig. 1: dispersion of polymers in asphalt involving Chemical interaction between asphaltene and polymer

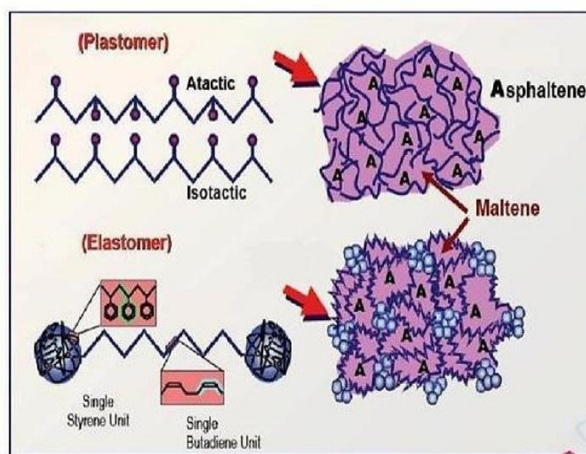


Fig.2: dispersion of polymers in asphalt

EXPERIMENTAL

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

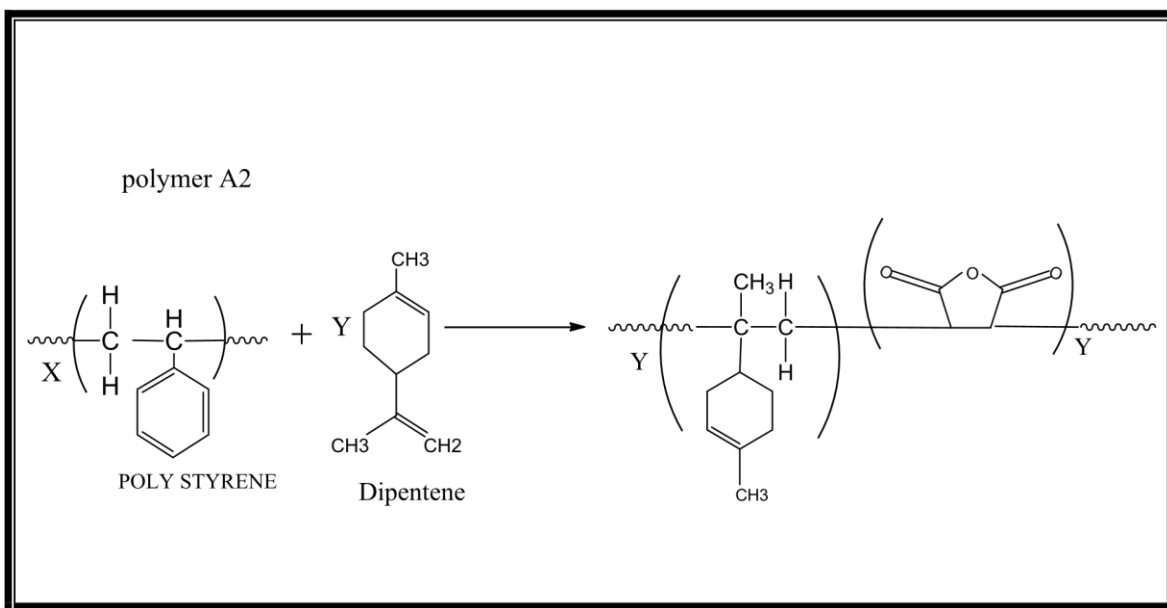
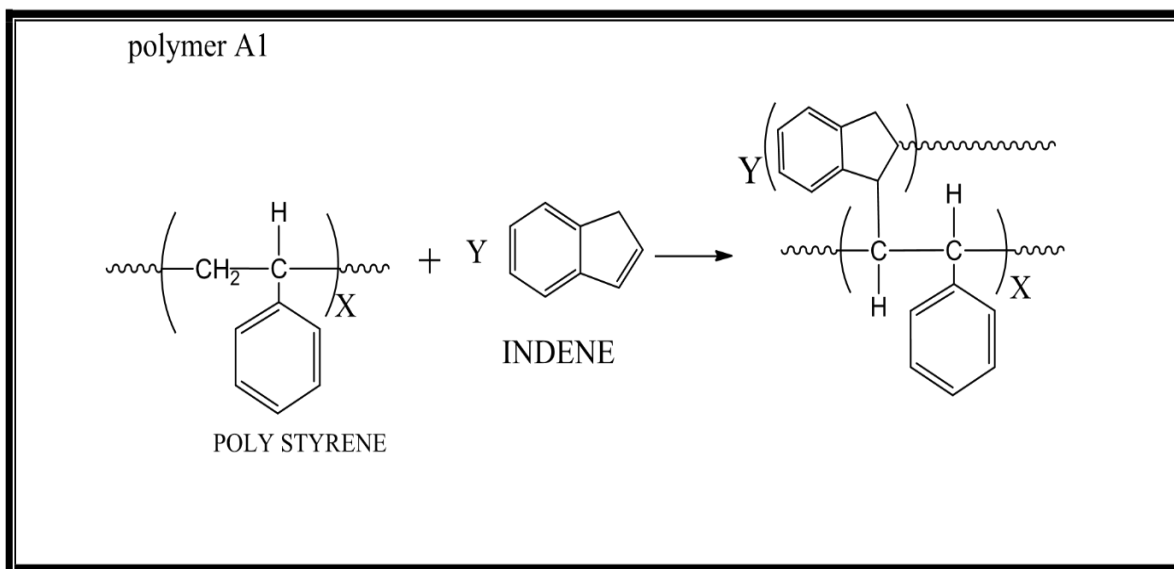
Polystyrene- Indene Graft Copolymerization (A1): In a screw capped polymerization bottle (20gm.0.2 mole) of polystyrene dissolved in (12 ml) of toluene and (17gm, 0.2mole) of Indene (0.05gm) of dibenzoylperoxide were introduced in the bottle. It was flushed with nitrogen for few minutes inside a glove and firmly stopped. The solution was maintained at 90, using water bath for 2 hr. The solvent was evaporated under vacuum; the product was obtained, washed three times with ethanol. Dried in a vacuum oven at 50, produced 95% of polymer with $\mu_{in} = 0.97$ dL /g.

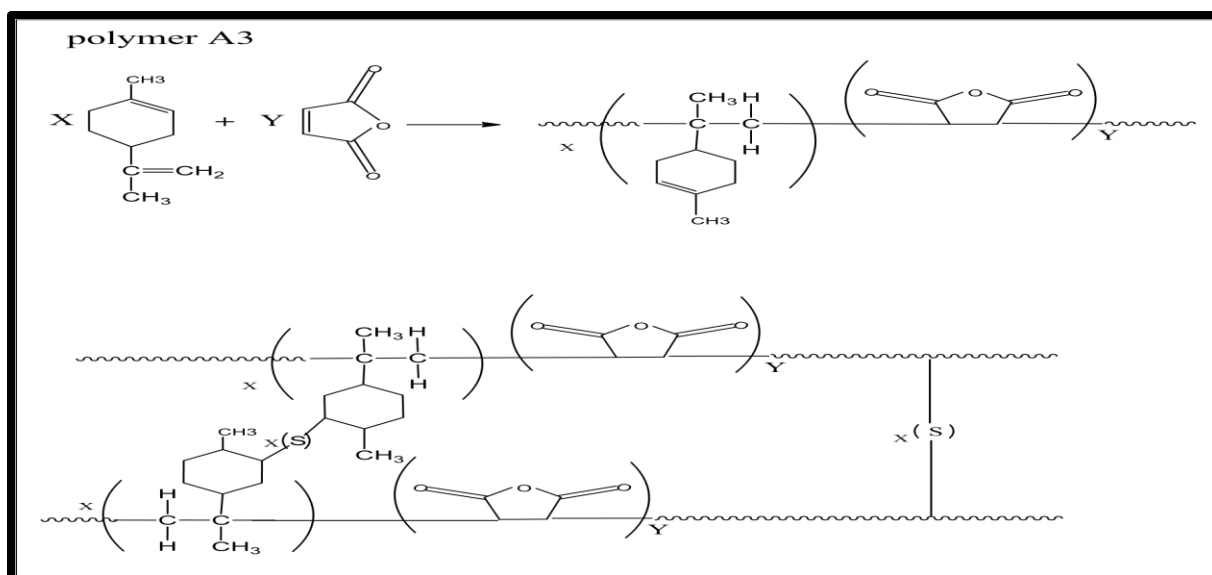
Polystyrene-Dipentene Graft Copolymerization (A2): (2.2gm.0.02 mole) of Polystyrene dissolved in (7 ml) of toluene and (2gm, 0.02mole) of Dipentene and 0.15gm of dibenzoylperoxide was added, the mixture was introduced in polymerization bottle, the bottle was flushed with nitrogen for few minutes inside a glove and firmly equipped and stopped. The solution was maintained at 90, using water bath for 3 hr. The solvent was evaporated under vacuum; the product was obtained, washed three times with ether. Dried in a vacuum oven at 50, produced 85% of polymer with $\mu_{in} = 0.96$ dL /g. Blends of asphalt-polymerA1 and A2 with different ratio.

RESULTS AND DISCUSSION

To modify asphalt that the main reasons to modify asphalt materials with different types of prepared graft copolymers additives to obtain different blends with improvement rheological properties of asphalt S50 and to 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 graft copolymers.





These copolymers were designed by inserting C=C contained through backbone of polymers chains to be high potentially to react with sulfur to protect the crack of pavement as crosslink gent which improved the penetration and softening points 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 crosslinking.

Fig(1) FT-IR spectra of Indine-g-copolymer (A1) showed absorption peaks at 3087 cm^{-1} (C-H aromatic), of indine aromatic ring, and 2891 cm^{-1} of (C-H), 1604 cm^{-1} of (C=C), 1431 cm^{-1} (and 1020 cm^{-1} (C-O)²³. Since the characteristic absorptions of all asphalts blends which were compared with the asphalt samples, it appeared high enhancement softening points and penetration were changed with high improvements as shown in Table(1).

Table-1: Rheological properties

Asphalt	polymerA1	PolymerA2	Sulfur	Penetration	Softening point
95	4		1	41	55
95		4	1	40	59
90	8		2	38	60
90		8	2	35	66

Fig(2) FT-IR spectra of A2 which revealed the absorption peaks dominated by anhydride during the formation, a peak appeared at C=C of dipentineand at 1600 cm^{-1} and at 3080 cm^{-1} due to (C-H aromatic),indicated the insertion of styrene copolymer , the formation of characteristic absorptions of Dipentine showed absorption peaks at 2960 cm^{-1} (C-H) aliphatic , 2870 cm^{-1} was attributed to the (C-H) stretching to (C=C) aromatic of dipentene ring more useful method to modify physicochemical properties

in order to obtain new properties by grafting un saturated C=C through the backbone polymer which could be crosslinks with sulfur which is more interesting features, with a suitable improvement because of its potential loading for both hydrophilic and hydrophobic using as obviously desirable for application.

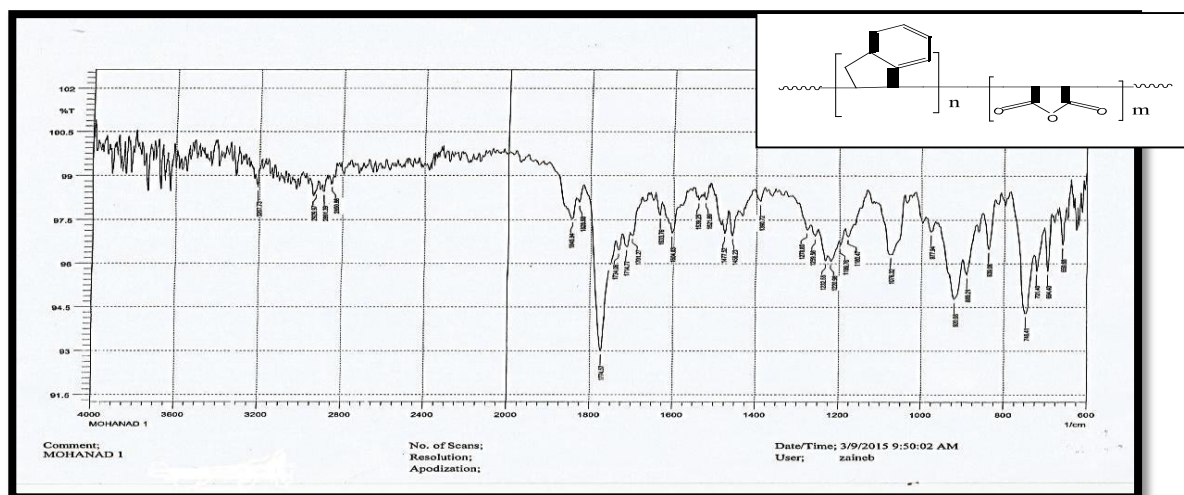


Fig.1: FT-IR spectra of (A-1)

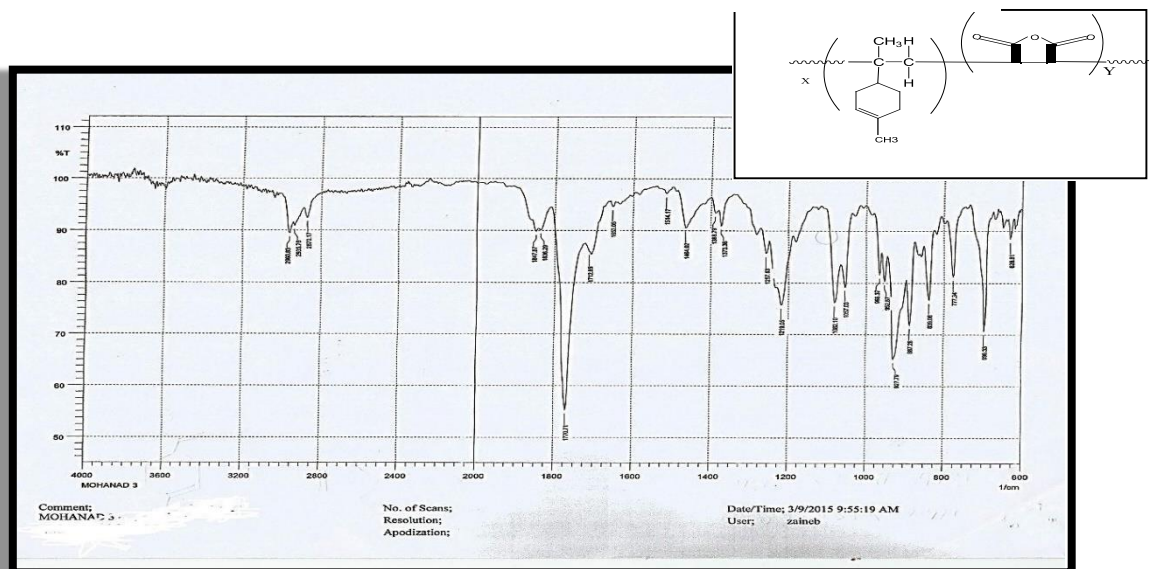
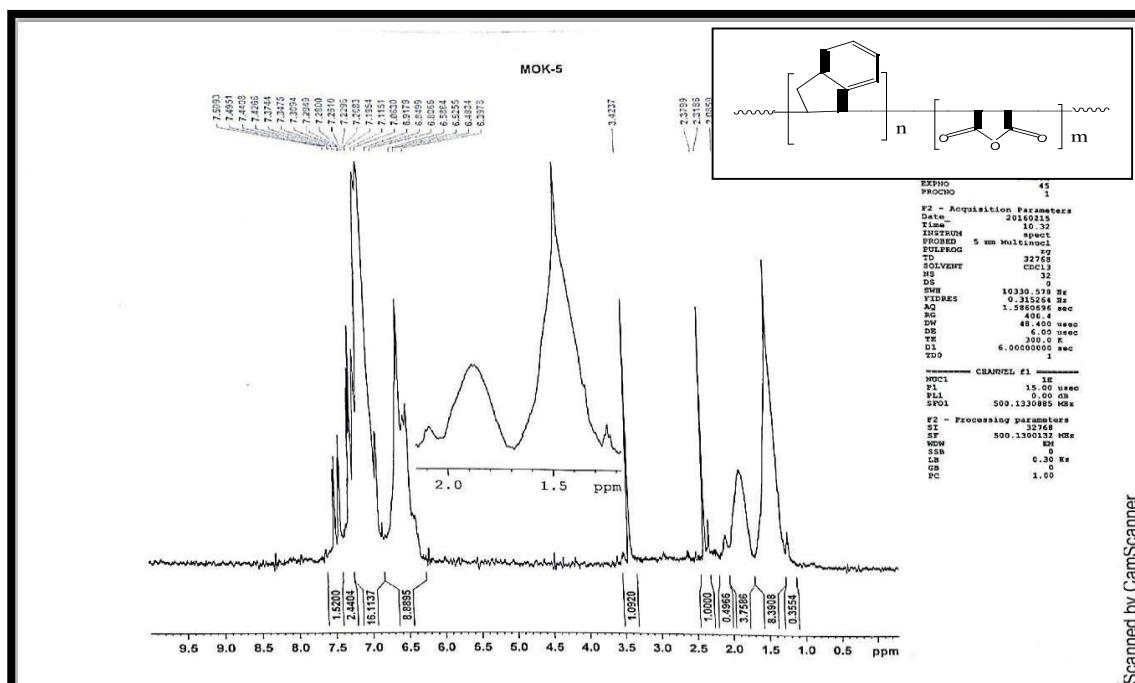
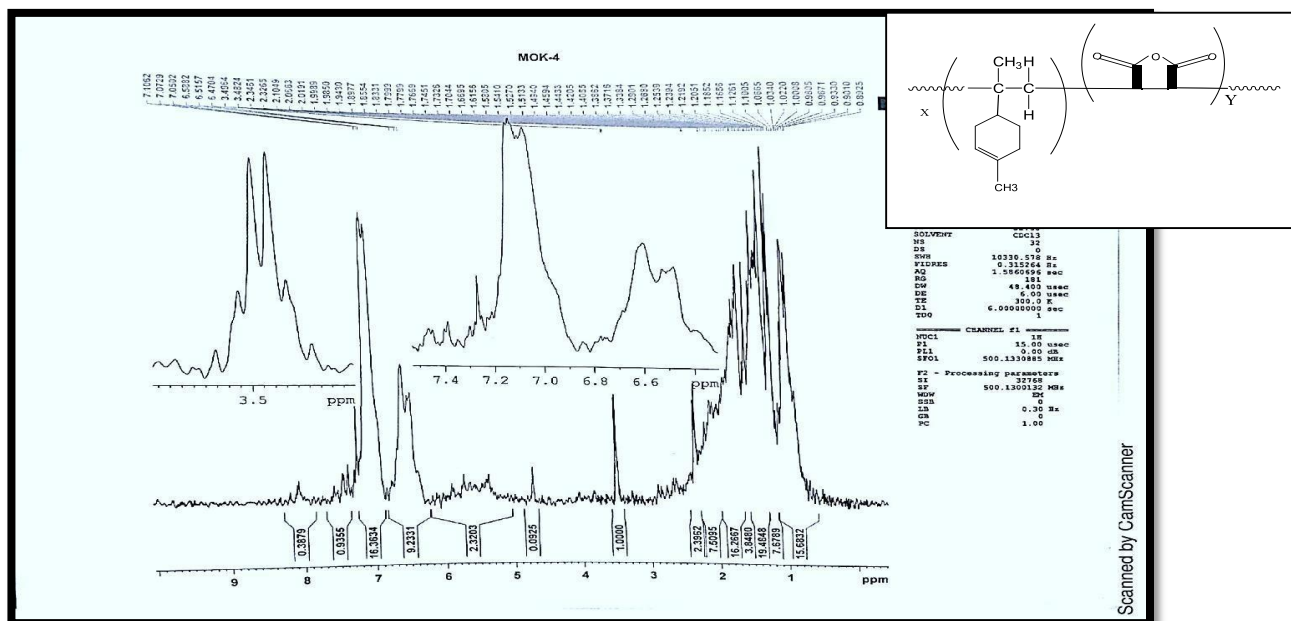


Fig.2: FT-IR spectra of A

Fig(3) The ^1H -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) of styrene.

Fig(4) The ^1H -NMR spectrum of polymer [A2] was indicated the signal (CH₂-CH-ph) 2H, d. and (2.5ppm) as triplet, (-CH-ph) 1H (3.7 ppm) as triplet 2CH (CH-) at (3.1ppm).

Fig.3: The ^1H -NMR spectrum of polymer [A1]Fig.4: The ^1H -NMR spectrum of polymer [A2]

The results showed high properties of these blends when compared with the S50asphalt. 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 copolymer's 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. The final step of thermal degradation with high thermal properties leads to wide application uses. The graft copolymer (A2) was measured in different stages, fig (1) indicated the rate of thermal degraded through backbone of grafted copolymer above500. Whereas A2 was higher degraded at 550 due to cross linked through un saturated bond with sulphur with asphalt blend.

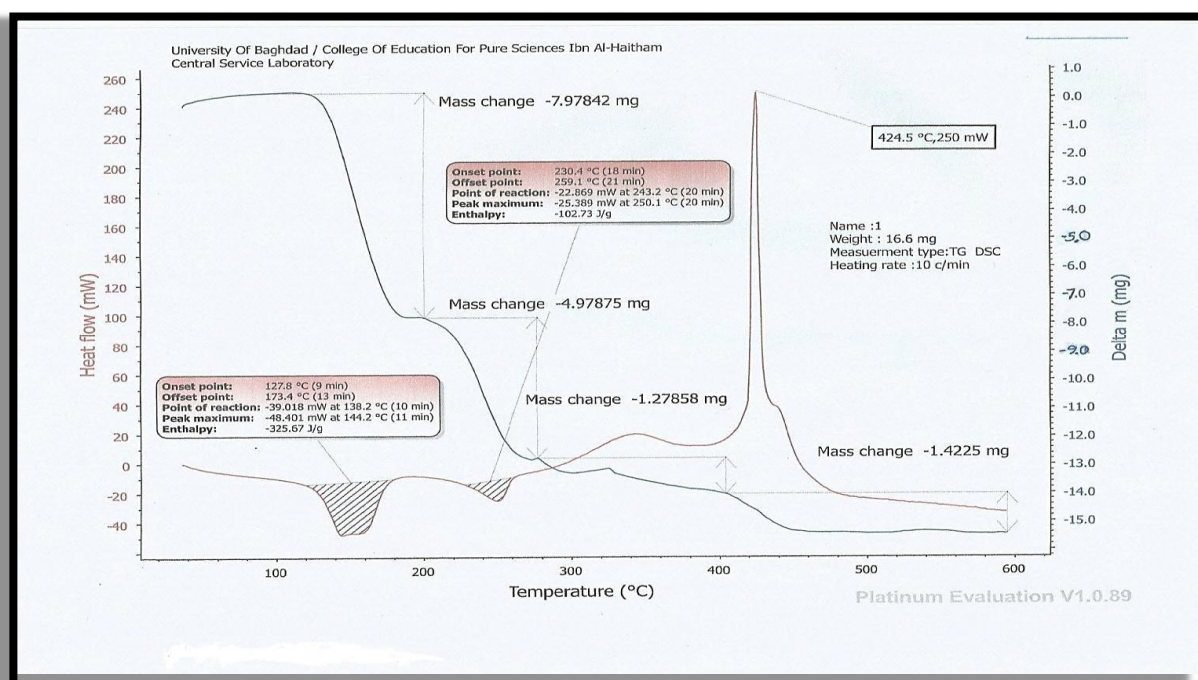


Fig.5: DSC & TGA of polymer (A2)

Table-2: 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%
A1		5		20		50 70 90
A ₂		0	220	45	250 410	50 90

CONCLUSION

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, 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 types of copolymers were prepared contained through backbone of polymers chains to be high potentially to react with sulfur to protect the crack of pavement . the cross linking by using sulfur gave higher temperatures, improving binder- adhesion (higher viscosity and thermal stability and rheological properties of asphalt depend on the physical arrangement of the constituent molecules and this change rapidly with temperature.

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