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Modifying Asphalt with Magnesium Alginate Biopolymer to Improve Rheological Performance

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ABSTRACT

Petroleum-based asphalt poses environmental challenges, and renewable biopolymers offer a potential alternative. This study aims to examine the viability of the application of the biopolymers derived from alginate: Alginic acid (ALA) and magnesium alginate (MAL) as a direct sustainable substitute for traditional asphalt. These polymers have been characterized by field emission scanning electron microscopy (FESEM), energy-dispersive X-ray (EDX), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA) methods. They were measured afterward to asphalt concentrations of 0.5-4 wt.% under controlled conditions 180 ℃ 90 min with a fixed quantity of polyphosphoric acid (PPA) added (0.5 wt.%). Best modification parameters were considered: quantity of polymer, reaction temperature, reaction time, and dosage of PPA. Standard performance tests, which include softening point, penetration testing, ductility, and penetration index (PI), were carried out. samples AsQ39 (ALA-modified) and AsQ44 (MAL-modified) were further analysed on FTIR and high-resolution proton nuclear magnetic resonance (H-NMR) techniques in addition to Marshall stability, moisture resistance, and aging resistance analysis. The findings indicated that asphalt modified with alginate has been proven to have good flow characteristics and higher resistance to aging and less loss of weight; hence, it can be used in road paving, levelling the surface, and creating moisture barriers. Such findings demonstrate that ALA and MAL can be used as effective and sustainable substitutes for petroleum-based asphalt.

1. INTRODUCTION

Enhancement and development of the available road networks and infrastructure have gained a pressing need with the growing number of cars all over the world. Statistical reports show that the market size of asphalt across the world will be estimated to have increased by about 28 percent in the coming 2018-2027 to about US2.48 billion $. Demand for asphalt is likely to increase drastically based on this growth. Asphalt is composed of high molecular weight hydrocarbon compounds of crude oil refining and its majority constituent is asphalt [1, 2]. It finds extensive application in infrastructure and road paving projects because it possesses unique rheology and adsorption factors, as well as its relatively low permeability to water; this is a suitable and reliable compound [3, 4]. During its service life, asphalt is subjected to thermal and mechanical loads and weathering, leading to changes in its quality [5]. Consequently, researchers should develop asphalt formulations for roads that are highly resistant to these adverse factors [6]. Work [7] shows that biodegradable materials are widely used in various industries, and humic acids, polylactic acid (PLA), and alginates [8] can be used as raw materials for biodegradable materials. Particularly geopolymers [9] and nanomaterials [10]. Alginates are groups of natural anionic heteropolysaccharides that are a cross-linked, water-swollen polymer network produced by a simple reaction of one or more monomers. They are usually extracted from seaweed (brown algae *Phaeophyceae*) and bacteria. They are made up of alternating copolymeric blocks of β-D-mannuronic acid and α-L-guluronic acid linked through (1 → 4) glycosidic bonds, referred to as M and G units, respectively. The relative proportion and sequential distribution of these units play a crucial role in determining physicochemical properties of alginate hydrogels [11].

Alginate hydrogels are known for their biodegradability and low toxicity, which have led to their extensive use in biomedical applications [12]. Hydrogenated alginate gels are typically prepared via ionic crosslinking, where G blocks react with divalent cations such as Ca^{2+} or Mg^{2+} to form a stable three-dimensional network. These gels are characterized by their hydrolysis flexibility, mechanical strength, biological activity, and biochemical modifiability [13, 14].

Some articles have been done on the possibilities of enhancing the qualities of asphalt with the aid of biopolymers. Aguirre et al. [15] compared the performance of sodium alginate fibers with a regenerating agent to improve the

performance of asphalt binders with recycled materials, and this aspect made the asphalt properties better. The obtained results indicated that the ratio of high to low molecular weights was positive when these fibers were added, which is an indication that the polymer has a positive impact on the molecular structure of the asphalt. Various stress creep recovery tests suggested that asphalt mixtures with modified asphalt with the addition of alginate fibers and recycled materials have lower rutting capacity than asphalt, which proves that these materials are effective in increasing the resistance of asphalt to abrasion and deformation.

Porto et al. [16] stated that alginates extracted from *(Eucheuma spp*.) at a concentration of (4.8%) enhance thermal resistance of bitumen, and specifically rheological properties of bitumen by forming soft bridges between various asphalt groups. Rasheed and Al-Hadidy [17] prepared asphalt concrete mixes with waste sulfur and asphalt binder, PG76-16, as fillers of pavement and compared them to a control mix in terms of the filler, which in this case was calcium carbonate ($CaCO_3$). The proportion of waste sulfur in the SWAC mixes was between 4% and 6% of the overall mass, whereas the proportion of calcium carbonate in the reference mix was held constant at 5% of the overall mass. They were the tests on the mechanical properties of AC and SWAC mixes by Marshall Stability and Marshall Quotient tests, indirect tensile strength at 25 and 60 ℃, and the saturation tensile strength ratio (TSR). The findings revealed that concrete mixes with sulfur residues (SWAC) had a relatively low performance in relation to plain concrete AC in regard to Marshall stability and total TSR. The tensile strength of mixes with 5 percent of sulfur residues was found to be higher than the acceptable TSR necessary at 85 percent, implying that they could be used within reasonable performance ranges. Successfully, Malinowski et al. [18] designed asphalt mixtures containing RAP with a bio-derived modifier and evaluated their performance characteristics. Cross-linked Na-alginate was used to modify the bitumen. Studies were conducted at four different modifier concentrations: 1.0%, 2.5%, 4.0%, and 5.5%, with or without a cross-linking agent. Bonding agent test results showed that the optimal additive content is 2.5%. Analysis of both the basic and modified binders revealed the effect of adding biopolymer. Properties of these mixtures showed that the use of the biopolymer-modified binder resulted in an estimated 9% increase in frost and water resistance.

Hemady and Owaid [19] reported that the properties of refined asphalt at the Al-Durra refinery were improved using cellulose polymerases. Cellulose acetate was added to the asphalt at varying percentages, ranging from 1% to 6% by weight, at 150 ℃ for 60 minutes. Optimal formulations were then characterized using (FTIR, HNMR, TGA, DTA, and DSC), with the glass transition temperature (Tg) being determined. Modified asphalt samples exhibited good rheological properties, making them suitable for a wide range of applications, particularly in the construction of damp-proof barriers and road paving. Jamil et al. [20] studied the possibility of using polyethylene as a partial replacement for environmentally friendly paving materials. Different percentages of polyethylene were used (3, 6, 9, and 12 wt.%). Polyethylene-replaced asphalt binders were subjected to compatibility and rheological property tests. According to standard and durability tests, a 6% polyethylene replacement of the raw binder is recyclable and suitable for use as a sustainable material in paving applications.

Jexembayeva et al. [21] were able to determine the effect of varying PLA content on the chemical and physical properties of biopolymer bitumen during its modification. The quality indicators of biopolymer bitumen were determined upon addition of 4%–10% PLA. All tested biopolymer bitumen samples exhibited increased plasticity at 25 ℃ (> 100 cm). The addition of 8% PLA to bitumen was found to yield optimal quality biopolymer bitumen.

Norambuena-Contreras et al. [22] have managed to fabricate already enhanced multinucleate alginate-based capsules with vibratory jetting (5 wt.%) calcium chloride and 1:7 biopolymer-to-oil mass ratio. These enhanced capsules were introduced in asphalt mixtures with concentrations of (0.125, 0.25, 0.5 wt.%). The spatial density of capsules in asphalt mixes was determined using tomography. Asphalt samples to which (0.125 wt.%) of capsules were added exhibited excellent mechanical performance, although the percentage did not result in a considerable increase in self-healing properties. Adding (0.25 wt.%) or higher quantities of capsule increased the self-healing ability of mixes significantly.

Frey et al. [23] indicated that bonding materials were tested in terms of durability, microstructure, and rheological behavior using red algae (agar) based biopolymer. The findings showed that these materials had similar properties to the conventional engineering materials. The information showed that agar-based products are of good preservation potential and good biodegradability.

Abdul Wahhab et al. [24] have managed to alter the asphalt bonding materials with the recycled plastic waste mixed with commercial polymers. Experiments conducted on asphalt that had been modified with low-density polyethylene, as well as polypropylene and high-density polyethylene in different proportions of styrene-butadiene-styrene (SBS) rubber and polyethylene terephthalate, revealed that recycled plastic led to a significant increase in abrasion resistance and a substantial increase in the sensitivity range of the bonding material.

While the studies above show the potential of various biopolymers, the use of the base alginic acid form and its cross-linked metal derivatives (like magnesium alginate) for asphalt modification remains unexplored. We hypothesize that the ionic cross-links in MAL could provide.

This research aims to study the effect of adding novel natural biopolymers, namely ALA and its derivative MAL, on modifying the chemical and physical characteristics of asphalt. The use of this natural polymer is characterized by its low cost and ease of availability, in addition to being derived from marine animal waste, making it an economical and sustainable option that contributes to resource recycling and reduces environmental impact. To achieve this objective, the following steps were followed:

(1) Determining asphalt quality indicators for research purposes, in addition to developing a technology for adding ALA and MAL to asphalt at different weight percentages (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4 wt.%).

(2) Determining the effect of adding ALA and MAL on asphalt quality indicators, for example: ductility, penetration point, softening point, and penetration index (PI), according to developed methods.

(3) Determining the optimal amount of ALA and MAL added to asphalt in terms of the best ratio for their specific properties, the optimal reaction temperature and time, and the optimal PPA weight ratio.

2. EXPERIMENTS

2.1 Materials used

Qayyarah asphalt was obtained from the Qayyarah refinery, which has the specifications shown in Table 1.

Table 1. The rheological specifications of the Qayyarah asphalt used

Property	Value
Softening point, ℃	50
Penetration (25 ℃, 5 sec, 100 gm)	42
Ductility (25 ℃, cm)	+100
Separated asphaltene (SA), %	18.5
Penetration index (PI)	-1.573

n-Hexane, Ethanol (95%) (Obtained from Fluka company), Magnesium hydroxide 98% from B.D.H, Polyphosphoric acid (Physical properties of PPA: Physical form viscous liquid, Melting point (16 ℃), Boiling point (300 ℃), Density 1.9 g/ml at 25 ℃) from BDH, Na_2CO_3 99% from BDH.

2.2 Instruments

The following instruments and equipment were used in this study: Field emission scanning electron microscopy (FESEM)- Thermo Fisher FEI Quattro (India); TGA- SDT Q600 V20.9 Build 20 (TA Instruments, USA); FTIR- Alpha II FTIR Spectrometer (Bruker, Germany, 2024); Proton Nuclear Magnetic Resonance (H-NMR) (India); Ductility tester- YUFENG (China); Penetrometer- YUFENG (China); Ring and ball apparatus- measuring softening point, and treatment apparatus asphalt by polymer; Electrical shaker- Hamber Ggo Shaker (Germany); Marshall device- Wykeham Farrance (UK); Thin Film Oven Test (TFOT) aging oven- Model 71081 (Japan).

2.3 Procedure

2.3.1 Alginic acid from brown algae $(C_6H_8O_6)_n$

Alginic acid is a natural polysaccharide extracted from brown algae (*Phaeophyceae*). Figure 1 shows the molecular structure of alginic acid.

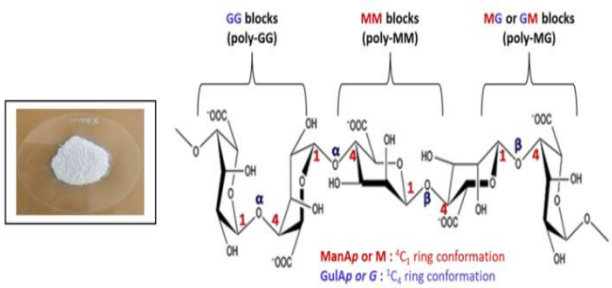


Figure 1. Chemical structure of alginic acid

2.3.2 Preparation of cross-linked polymers, magnesium alginate

MAL was synthesized by the reaction of alginic acid (ALA) with (2%) magnesium hydroxide for (3 hrs.) at 100 ℃. Soluble fractions were collected by centrifugation, and polysaccharides were precipitated with (95%) ethanol. The magnesium alginate was washed with 100 ml of acetone and dried at 65 ℃. The magnesium alginate powder was then dissolved in 100 ml of distilled water, precipitated again with ethanol, and dried to form a white powder, as shown in Figure 2.

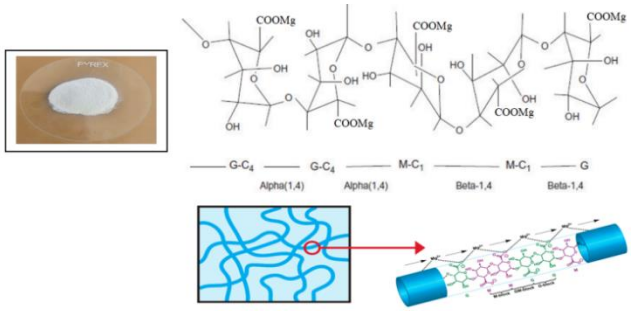


Figure 2. Magnesium alginate and schematic overview of Mg^{2+} hopping between carboxylates

2.3.3 Characterization of polymers

The prepared polymers were characterized using FESEM, EDX, FTIR, and TGA techniques.

2.3.4 Rheological modification of asphalt

The asphalt (100 g) was treated with both ALA and MAL at a weight ratio of 0.5-4% in the presence of 0.5% by weight of PPA for 90 min at 180 ℃ using an asphalt treatment Apparatus with additives (The device consists of: Three-neck flask a 200 ml, thermometer mounted on one of the side openings, mental electrolyte, mechanical stirrer mounted on the middle opening of the flask, and an iron stand to hold the flask). Measurement of rheological properties. The rheological properties of both the original asphalt and the samples resulting from step (2.3.2) were measured, including penetration [25], ductility [26], and softening point [27], as well as the PI [28].

2.3.5 Study of optimal conditions

1. Effect of temperature on the reaction.
2. Effect of reaction time on the rheological properties of modified asphalt.
3. Effect of adding different weight percentages of PPA on the rheological properties of polymer-modified asphalt.

After determining the optimum conditions, the Marshall test [29], Chemical immersion [30], and aging [31] were performed for the best samples obtained.

3. RESULTS AND DISCUSSION

Among the most renewable materials found in nature are natural polymers, which is why this paper aims at studying the application of these materials to enhance the rheology of asphalt, and thus make it applicable in a wide variety of applications, specifically in road paving. In this study, asphalt modifiers were alginic acid and its derivative in the form of magnesium alginate.

3.1 Field emission scanning electron microscopy and energy-dispersive X-ray analysis

FESEM and EDX spectroscopy are two basic instruments in materials science. FESEM offers high-resolution images both of the surface and structure of a sample, and it becomes

easier to study the shape of particles, distribution, size, and surface properties. Information on the elemental composition of materials is received through EDX, which discloses the elements in the materials, ratios of the elements in the materials, and possible contaminants.

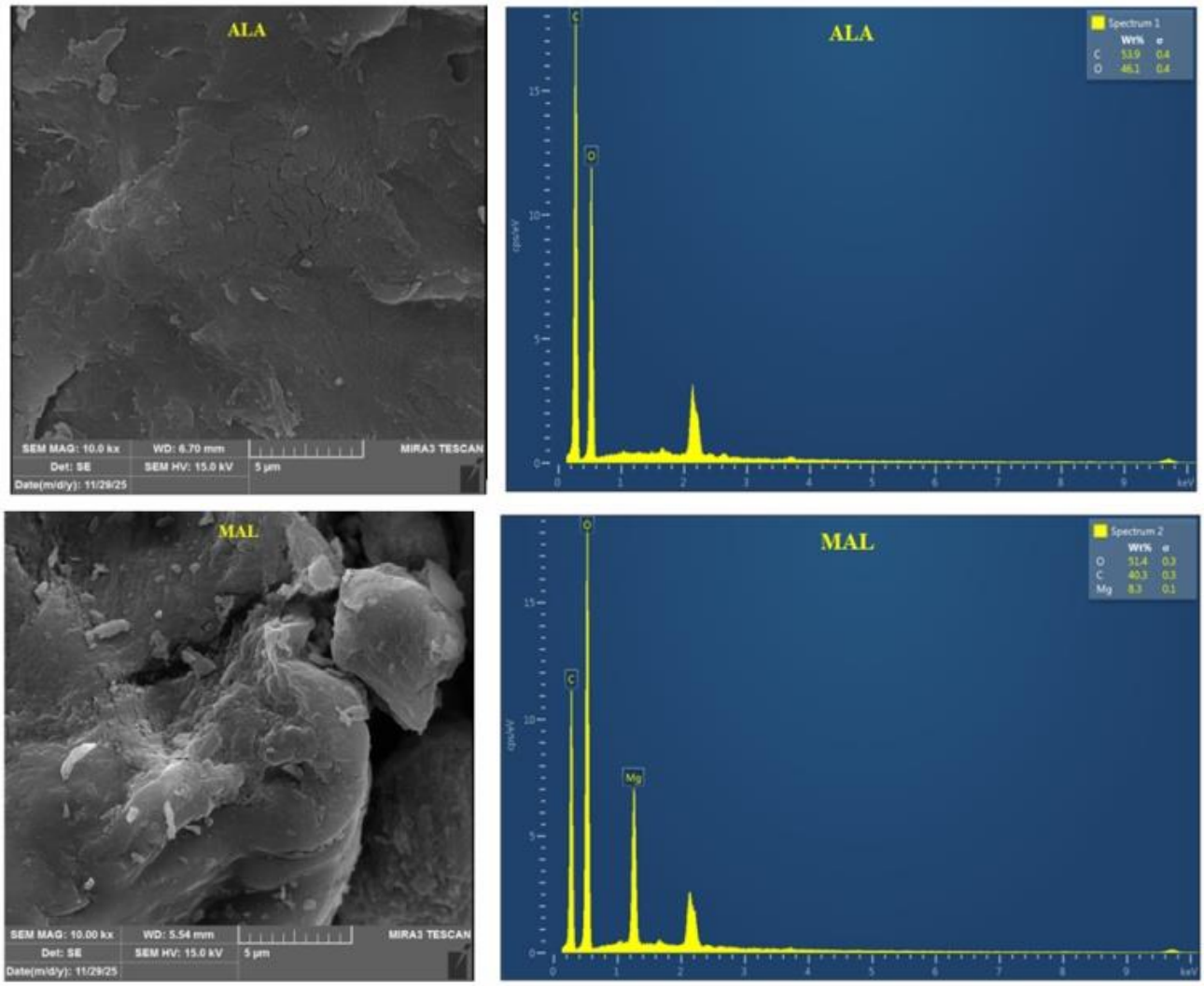


Figure 3. FESEM analysis of ALA and MAL
Note: FESEM = Field emission scanning electron microscopy, ALA = alginic acid, MAL = magnesium alginate

Figure 3 with FESEM analysis demonstrates the different morphological differences between the synthesized biopolymers ALA and MAL, which is connected to the effect that variations in composition and the different methods of preparation have on the morphological structure of the surface of the polymers. ALA analysis indicates that there is a comparatively well-packed and homogeneous surface in which the molecules are slightly agglomerated in a lamellar structure. Some cracks were also found scattered, which might be a result of drying or internal stress. This structural arrangement is a pointer to good intermolecular bonding and low surface porosity, thus low specific surface area.

MAL analysis showed that the surface was rough and irregular with a large number of aggregates of particles and porous, which suggests lower structural homogeneity and increased effective surface area. This has been credited to the fact that these aggregates are formed through intermolecular interaction or partial dispersion during preparation. By contrast, ALA polymer is smooth and cohesive on its surface, which suggests an increase in mechanical and structural integrity. The porosity and roughness of the MAL surface can, however, prove to be beneficial in adsorption-based or surface-active procedures. The fact that the ALA and MAL have huge surface morphology variations is one of the factors that define the functional properties. Analysis of ALA polymer showed that carbon and oxygen were the main peaks in the EDS analysis because of the organic composition of ALA polymer, which comprises carboxyl groups and atomic ratios of carbon. MAL polymer, however, exhibited a significant peak of carbon, oxygen, and magnesium, which demonstrated that the material was organic and that magnesium was present, and no other elements were detected, hence demonstrating the purity of the material. The EDS findings are generally similar to the theoretical frameworks of both ALA and MAL, which proves the validity of this method to reveal the most important factors. This porous morphology might allow for better physical interlocking with the asphalt matrix, potentially contributing to the improved stiffness observed in rheological tests.

3.2 Fourier transform infrared spectroscopy analysis

FTIR can be used to identify the chemical composition and functional groups of substances determined by measuring their

absorbance of infrared light. This method is based on the absorption spectrum that is recorded after the vibration of chemical bonds at certain wavelengths. The chemical bonds possess a characteristic pattern of absorption that is applied in the identification process and the resulting signal is then translated into a clear and precise spectrum. The analysis has a wide application in chemistry, environmental science, and materials science in characterizing compounds, comparing samples, and testing their purity.

As shown in Figure 4, several peaks were shifted or changed in intensity compared to ALA, in particular, C-O (1000 cm^{-1}) and -COO- (1400-1600 cm^{-1}) bands. MAL exhibits a peak at (1440.05 cm^{-1}) that is absent in ALA, likely representing -COO- stretching due to the presence of Mg^{2+}. ALA and MAL show a peak that corresponds to free acid -C=O stretch (1700 cm^{-1}). MAL was prepared such that the amount of Mg was just enough to bind to the carboxylate group of G-residue. MAL had additional Mg to bind to the carboxylate group of both the G- and M-residues, which would explain why it has the free acid -C=O peak.

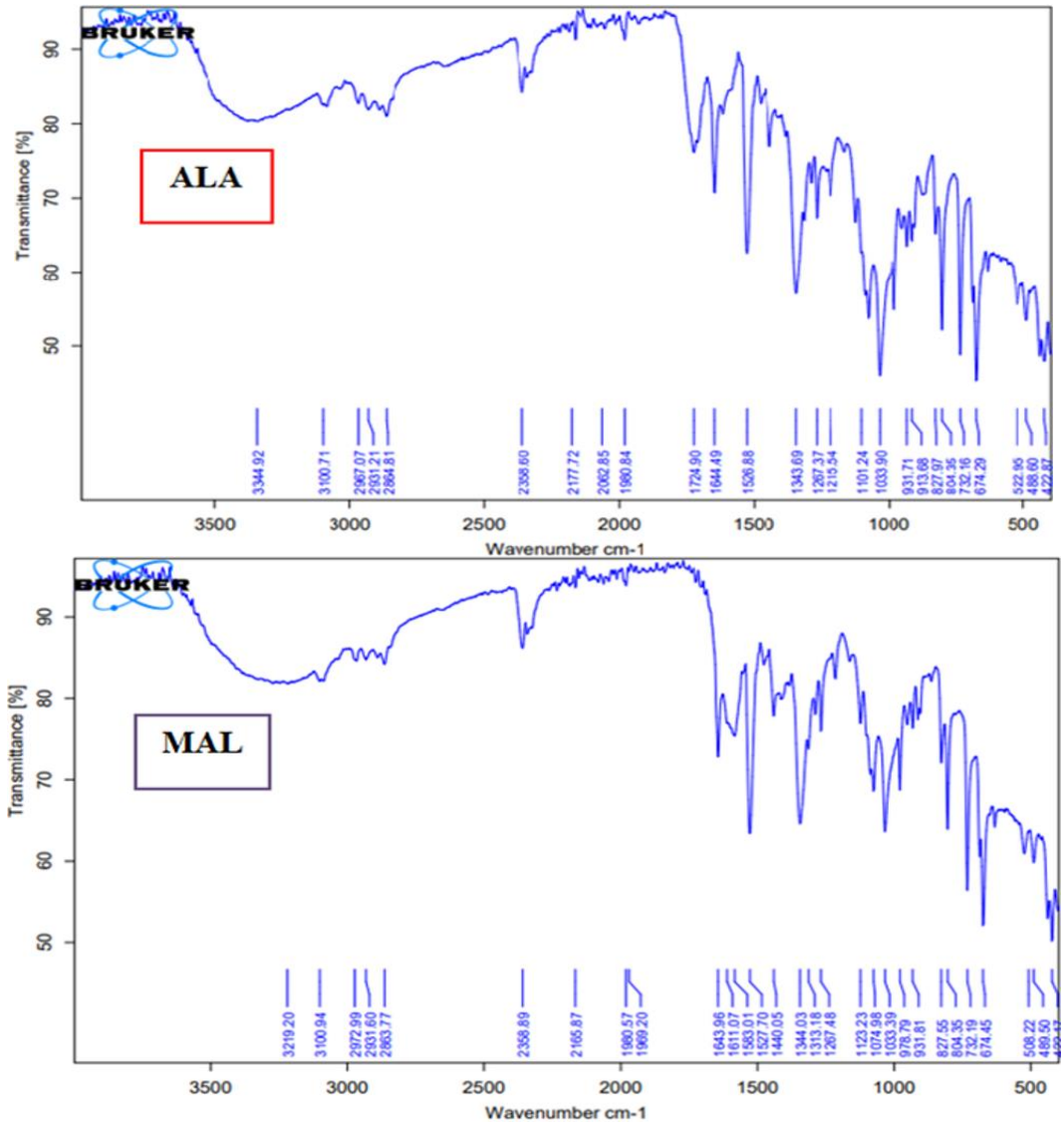


Figure 4. FTIR analysis of ALA and MAL
Note: FTIR = Fourier transform infrared spectroscopy, ALA = alginic acid, MAL = magnesium alginate

3.3 Thermogravimetric analysis

TGA is a thermal analysis method that is applied to examine the behavior of materials in controlled temperature increments. The test will give data on the alteration of sample mass with time or temperature to determine the stability of the samples at a certain temperature, the content of moisture, the stages of decomposition, the solvents, and inorganic and organic constituents. The analysis finds extensive application in materials science and polymers because it gives true information on the chemical and thermal characteristics of materials in the presence of heat.

Figure 5 shows various steps of weight loss in two polymers. In the case of ALA, there was a minor loss in mass at about 31.67 °C, which was probably related to the loss of moisture or volatile substances on the surface. The primary degradation phase commenced at about 130.4 °C, which is the decomposition of organic elements. The total mass loss was 13.748 mg (72.896%), and a thermally stable fraction of 5.328 mg (28.252%) was left, which could be carbonized or inorganic residues. It was identified that the thermal inflection point (Tinf) was 221.26 °C (which is the temperature at which the highest rate of degradation was attained). In the case of MAL, a gradual weight loss was noticed, whereby the first loss was at a temperature of around 37.10 °C as a result of weakly bound volatile substances or moisture. The first degradation

took place at (159.6 ℃), meaning that biodegradable components of the sample were being decomposed. The overall weight loss was 5.245 mg of the original mass, or 41.53% of this mass, which represents a moderate content of organic or thermally unstable material. On the other hand, the mass left after analysis was 7.592 mg or 60.11%, indicating that there is a considerable amount of material that is highly thermally stable. Tinf was also established at 111.42 ℃, the maximum rate of mass loss, and thus the major extent of decomposition is 111.42 ℃, which is the lowest temperature at which the sample starts to lose its thermal stability relative to more stable materials.

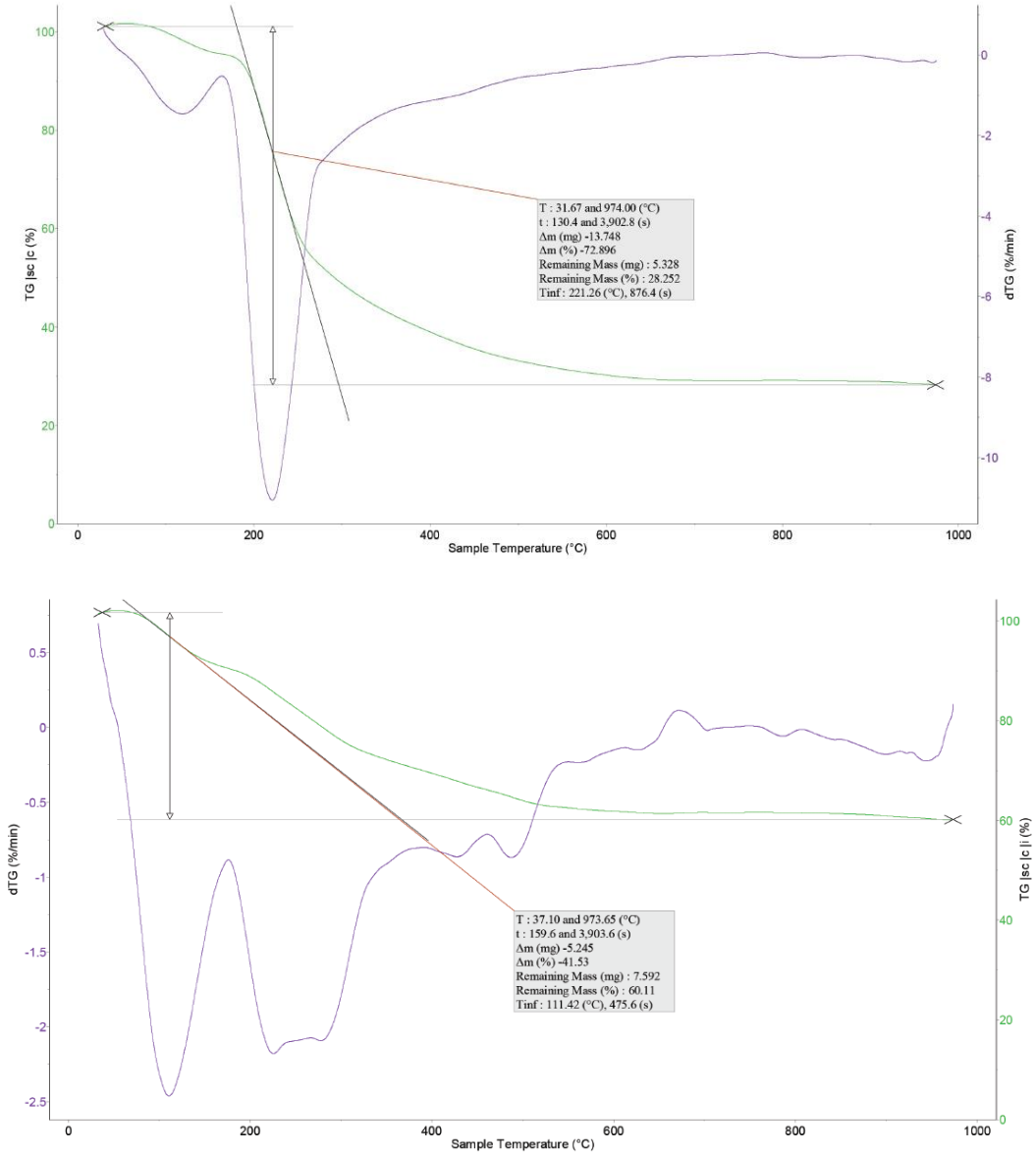


Figure 5. Thermogravimetric analysis (TGA) of alginic acid (ALA) and magnesium alginate (MAL)

3.4 Rheological modification of asphalt

Tables 2 and 3 and Figures 6 and 7 illustrate the rheological characteristics of asphalt using different ratios of ALA and MAL.

Tables 2 and 3 indicate that using a temperature of 180 ℃, a duration of 90 min, and a constant addition rate of 0.5 wt.% with different weights of ALA and MAL gave the best asphalt characteristics at PPA (1.5 wt.%) for both polymers to induce the desired reaction and improve the rheological properties.

3.5 Study of optimal conditions

3.5.1 Effect of temperature on the reaction

Table 4 shows that the best conditions for obtaining the best rheological properties were for the AsQ19 and AsQ24 models, which are a reaction time of 90 min and a temperature of 160 ℃ for both ALA and MAL.

3.5.2 Effect of reaction time on the rheological properties of modified asphalt

After fixing the weight percentage of asphalt-modifying additives and the reaction temperature, the effect of reaction time on improving the rheological properties of the modified asphalt was studied with ALA and MAL.

Table 5 shows that the reaction time (90 min) fixed at the beginning of the improvement process was optimal in improving the properties of the modified asphalt.

3.5.3 The effect of adding different weight percentages of (PPA) on the rheological properties of polymer-modified asphalt

While the initial PPA catalyst loading was 0.5 wt.%, the results in Table 6 indicate that 1 wt.% is the optimal concentration for both additives. Accordingly, the modified asphalt samples AsQ44 and AsQ39 were selected as the best performers.

Table 2. Asphalt specifications using different ratios of ALA in the presence of a fixed ratio of 0.5% PPA at a temperature of 180 °C and a reaction time of 90 min

Sample	ALA wt.%	Penetration Point (25 °C, 5 sec, 100 gm)	Ductility (25 °C, cm)	Softening Point (°C)	Penetration Index (PI)
AsQ0	0.0	42	+100	50	-1.573
AsQ1	0.5	41	+100	55.5	-0.372
AsQ2	1.0	40	+100	58.0	0.101
AsQ3	1.5	39	+100	60.5	0.537
AsQ4	2.0	37	+100	62.0	0.699
AsQ5	2.5	36	+100	64.5	1.090
AsQ6	3	34	97	67	1.393
AsQ7	3.5	33	85	69	1.659
AsQ8	4	32	79	71	1.909

Note: ALA = alginic acid, PPA = polyphosphoric acid

Table 3. Asphalt specifications using different ratios of MAL in the presence of a fixed ratio of 0.5% PPA at a temperature of 180 °C and a reaction time of 90 min

Sample	MAL wt.%	Penetration Point (25 °C, 5 sec, 100 gm)	Ductility (25 °C, cm)	Softening Point (°C)	Penetration Index (PI)
AsQ0	0.0	42	+100	50	-1.573
AsQ9	0.5	41.5	+100	56	-0.234
AsQ10	1.0	40	+100	59	0.298
AsQ11	1.5	37.5	+100	62	0.733
AsQ12	2.0	36.8	+100	64	1.049
AsQ13	2.5	35.2	98	68	1.641
AsQ14	3	32.5	93	70.5	1.862
AsQ15	3.5	31	84	72	1.990
AsQ16	4	29	76	73	1.995

Note: MAL = magnesium alginate, PPA = polyphosphoric acid

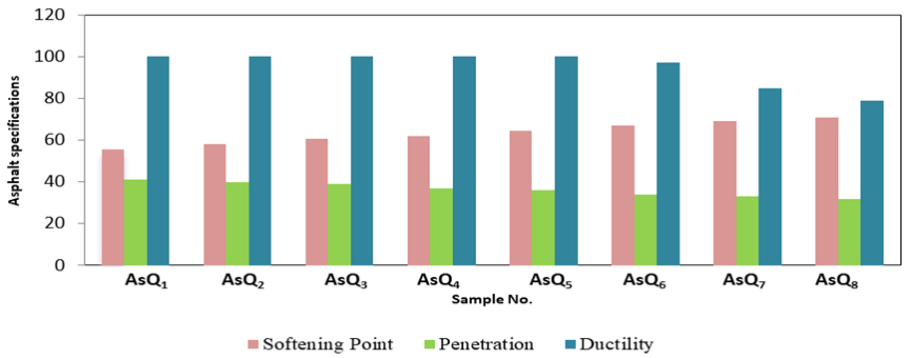


Figure 6. Rheological properties of asphalt treated with ALA at 180 °C in the presence of PPA 0.5 wt.% at 90 min

Note: ALA = alginic acid, PPA = polyphosphoric acid

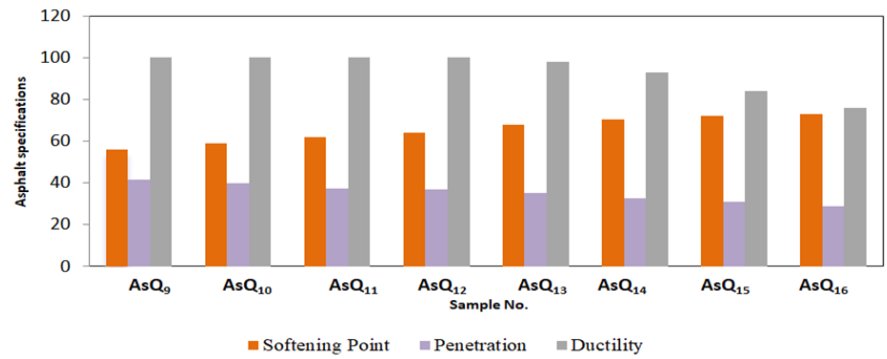


Figure 7. Rheological properties of asphalt treated with MAL at 180 °C in the presence of PPA 0.5 wt.% at 90 min

Note: MAL = magnesium alginate, PPA = polyphosphoric acid

Table 4. Rheological properties of asphalt modified by 1.5 wt.% ALA and 1.5 wt.% MAL in the presence of 0.5% PPA and reaction time (90 min) at different temperatures

Polymer	Sample	Temp. (°C)	Penetration Point (25 °C, 5 sec, 100 gm)	Ductility (25 °C, cm)	Softening Point (°C)	Penetration Index (PI)
	AsQ17	120	38.6	+100	59	0.217
	AsQ18	140	36.4	+100	56	-0.518
ALA	AsQ19	160	36.8	+100	57	-0.291
	AsQ20	180	39	+100	60.5	0.537
	AsQ21	200	38.7	96	61.8	0.760
	AsQ22	120	38.1	+100	61	0.574
	AsQ23	140	34.5	+100	58	-0.224
MAL	AsQ24	160	37.1	+100	60	0.327
	AsQ25	180	37.5	+100	62	0.733
	AsQ26	200	40.8	93	64	1.290

Note: ALA = alginic acid, MAL = magnesium alginate, PPA = polyphosphoric acid

Table 5. Effect of reaction time on the rheological properties of polymers modified asphalt, ALA and MAL

Polymer	Sample	Time (min)	Penetration Point (25 °C, 5 sec, 100 gm)	Ductility (25 °C, cm)	Softening Point (°C)	Penetration Index (PI)
	AsQ27	30	34.9	+100	55	-0.820
	AsQ28	60	35.2	+100	56	-0.589
ALA	AsQ29	90	36.8	+100	57	-0.291
	AsQ30	120	40.5	95	59	0.327
	AsQ31	150	43.7	91	60	0.699
	AsQ32	30	35.8	+100	56	-0.557
	AsQ33	60	34.9	+100	58	-0.202
MAL	AsQ34	90	37.1	+100	60	0.327
	AsQ35	120	39.7	93	62	0.857
	AsQ36	150	44.9	88	64	1.525

Note: ALA = alginic acid, MAL = magnesium alginate

Table 6. Rheological properties of polymer-modified asphalt using different wt.% PPA

Polymer	Sample	PPA (wt.%)	Penetration Point (25 °C, 5 sec, 100 gm)	Ductility (25 °C, cm)	Softening Point (°C)	Penetration Index (PI)
	AsQ37	0.25	35.5	+100	53	-1.217
	AsQ38	0.5	36.8	+100	57	-0.291
ALA	AsQ39	1.0	35.1	+100	60	0.204
	AsQ40	1.5	40.0	92	64	1.248
	AsQ41	2.0	45.5	86	66	1.914
	AsQ42	0.25	36.2	+100	58	-0.121
	AsQ43	0.5	37.1	+100	60	0.327
MAL	AsQ44	1.0	36.2	+100	63	0.834
	AsQ45	1.5	42.0	90	65	1.538
	AsQ46	2.0	46	82	66.5	2.024

Note: ALA = alginic acid, MAL = magnesium alginate, PPA = polyphosphoric acid

3.6 Description of selected modified asphalt models

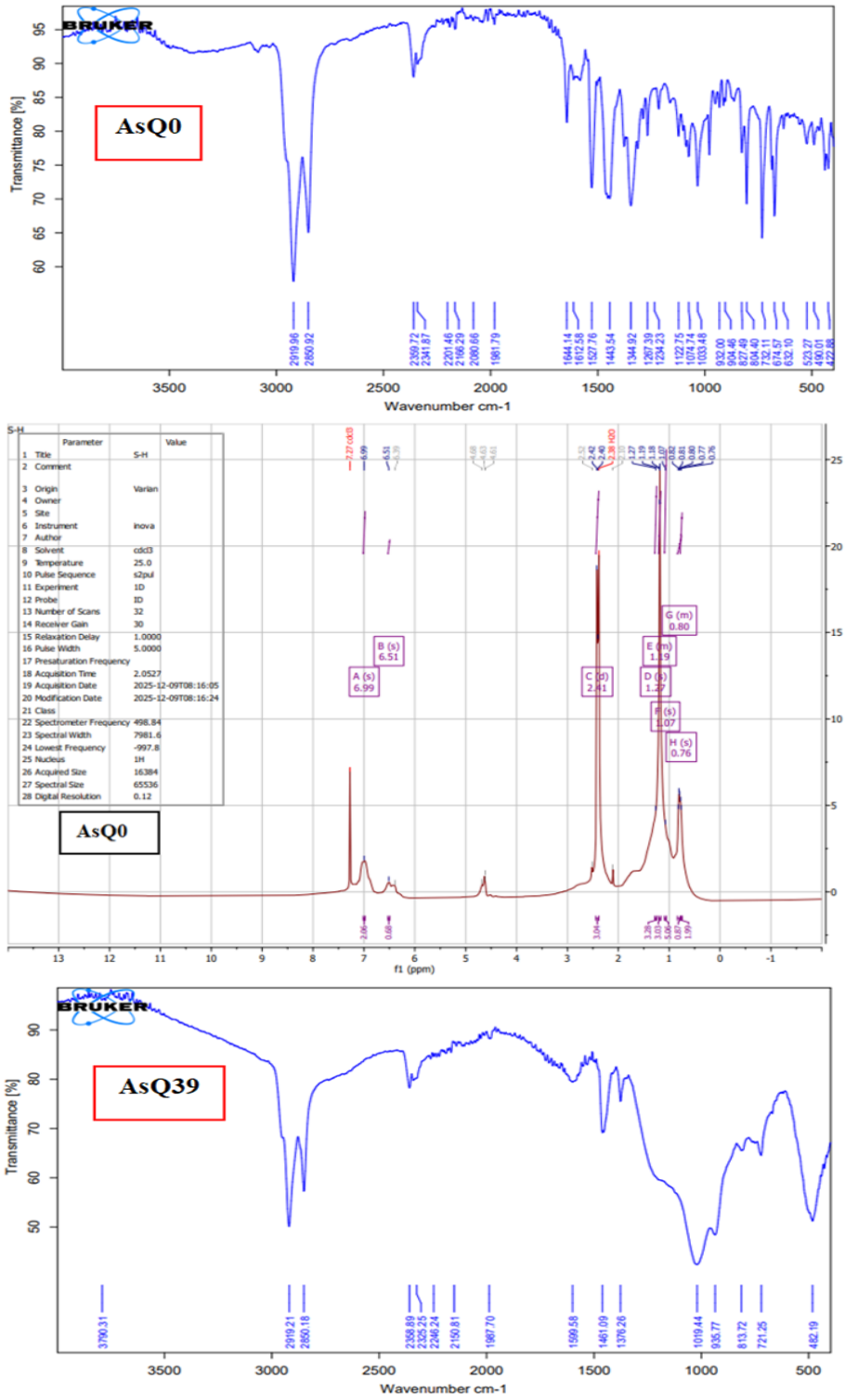
The modified asphalt samples AsQ39, AsQ44 were diagnosed using (FTIR, H-NMR) techniques.

Figure 8 represents the infrared spectrum of the original asphalt and the asphalt treated with ALA and MAL. FTIR analysis of the AsQ39 and AsQ44 samples shows a high degree of similarity in overall shape and absorption bands, indicating a clear convergence in the chemical structure of both materials. Distinct absorption peaks are observed in the 3000-2850 cm^{-1} region, attributed to stretching vibrations of aliphatic (C-H) groups (CH_2 and CH_3), suggesting the presence of organic hydrocarbon chains. FTIR analysis showed that there was a characteristic absorption band in the (1650-1750 cm^{-1}) area. The vibrations at the carbonyl (C=O) groups are attributed to the presence of ester, carboxyl, or ketone groups. Other peaks were observed in the (1500-1600 cm^{-1}) spectrum, which can be explained by (C=C) bond stretching or (C-H) bond bending. Vibrations of strong absorptions at 1000-1250 cm^{-1} represent C-O and C-O-C bond vibration, which is typical of polymeric or oxidized organic compounds. A spectral signature range (500-1000 cm^{-1}) contained numerous and complicated peaks, which proved the organic nature of the two samples. Notably, the intensity of some peaks, particularly those associated with carbonyl groups, appears relatively higher in AsQ44, which may reflect a higher degree of oxidation or functional content compared to AsQ39.

Figure 8 shows the H-NMR spectrum of the original asphalt and the asphalt treated with ALA and MAL. When observing the proton NMR spectrum, a change in signal intensity is noted upon the addition of each of (ALA, MAL). In the aliphatic region, the probability of converting aliphatic compounds to aromatic compounds is low, as evidenced by the fact that the alkyl moiety signal at 2.5 ppm shows no significant change. Therefore, we believe that PPA did not contribute to the alkylation process. This is supported by the lack of effect at 2.5 ppm, suggesting that the PPA role is to contribute to the

remodeling and formation of the aromatic moiety, as evidenced by the strong signal at approximately 6.3 ppm ALA and 6.5 ppm. chemical and structural changes to the improvements in the macroscopic performance of the asphalt binder. The addition of PPA plays a key role in modifying the internal structure of asphalt. PPA interacts with polar components in the binder, particularly the resins and asphaltenes, promoting the conversion of resins into larger and more structured asphaltene-like molecules. This process leads to the restructuring and aggregation of asphaltene domains, resulting in a more interconnected and stable colloidal network. As a consequence, the binder exhibits increased stiffness and improved resistance to deformation at elevated temperatures, which is reflected in a higher softening point and a higher PI.

Furthermore, Mg^{2+} ions introduce an additional modification mechanism through ionic crosslinking. They interact with oxygen-containing functional groups within the asphalt matrix, forming coordination bonds that act as physical crosslinks between molecular structures. This crosslinking effect reinforces the network formed by the restructured asphaltenes induced by PPA. The synergistic interaction between PPA-driven asphaltene restructuring and Mg^{2+}-mediated crosslinking leads to a denser and more cohesive microstructure. As a result, the binder demonstrates enhanced thermal stability, reduced temperature susceptibility, and improved mechanical performance, which are evidenced by the increased softening point and the improved PI values.



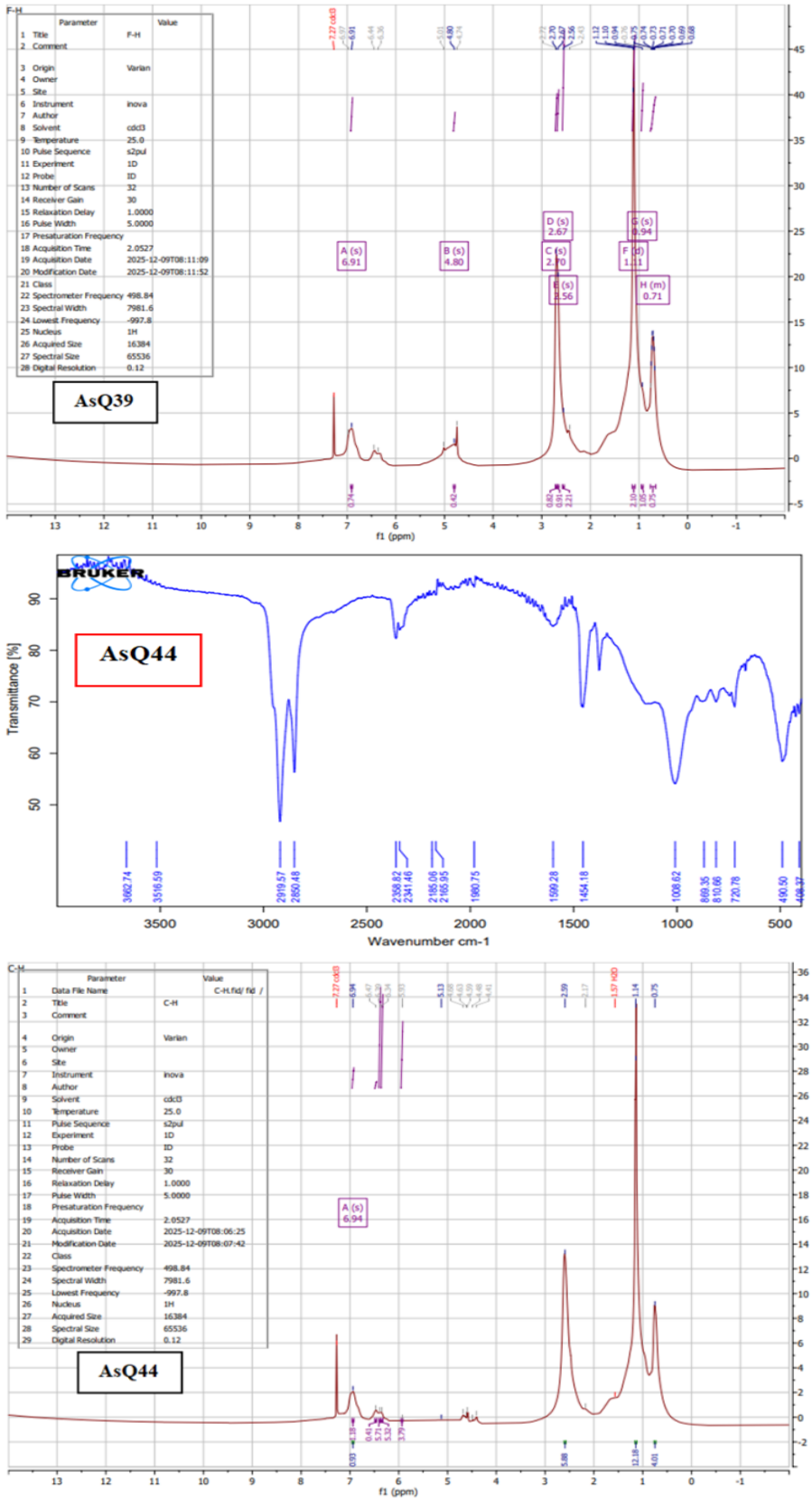


Figure 8. FTIR and H-NMR results of ALA and MAL

Table 7. Stability and creep values for AsQ0, AsQ39 and AsQ44

Sample	Asphalt Added to Cumulus, %	Creep (MM)	Stability (KN)	MQ
AsQ0		11.50	3.20	3.07
AsQ39	4.75	16.47	3.29	6.34
AsQ44		18.05	3.46	7.05
As (Iraqi Roads and Bridges Authority Specifications)	---	7.0	2.4	3.5

3.7 Marshall test

The Marshall test is the comprehensive procedure of assessing the fundamental mechanical attributes of the asphalt mixtures that identifies the ideal proportion of asphalt in the blend through a systematic procedure that ensures the highest stability and strength of the blend under different loading situations [29]. As can be seen in Table 7, the values of the values demonstrate that the modified asphalt was significantly more stable than the original asphalt. In addition, its flow properties are within acceptable requirements as per the SORP/R0 standard. This increases enhancements that involve resistance of roads to deformation by repeated loads to mitigate the effects of stress through proper enhancement of overall performance and durability of roads, besides greatly prolonging the service life of roads.

3.8 Chemical immersion

In order to determine the cohesion of asphalt to gravel when subjected to sodium carbonate (Na_2CO_3), this experiment was carried out. It tried to test the high temperature and acid rain resistance of the asphalt and is denoted by the Riddle and Weber (R&W) value [32]. The R/W value is the value at which the asphalt starts to detach from the gravel surface; this is referred to as (flaking).

The methods of the immersion process were conducted in the way that they were outlined in the references [30]. These results are indicated in Table 8, which reveals that the original asphalt had an R&W value of 4 when 0.082 g of sodium carbonate (Na_2CO_3) was added to it and the modified asphalt had R and W values that varied between 6 and 8. This shows that modified asphalt (AsQ39, AsQ44) is more resistant to acid rain and high temperatures than AsQ0.

Table 8. Separation values of AsQ0 and AsQ39 and AsQ44

Sample	% Na_2CO_3 (g)	R&W No.	R&W Original Asphalt	R&W Modified Asphalt As39	R&W Modified Asphalt As44
---	0.025	1	---	---	---
---	0.041	2	---	---	---
AsQ0	0.082	3	4	---	---
---	0.164	4	---	---	---
AsQ39	0.328	5	---	6	---
---	0.656	6	---	---	---
AsQ44	1.312	7	---	---	8
--	2.624	8	---	---	---

Note: R&W = Riddle and Weber

Table 9. Rheological properties of the AsQ0, AsQ39 and AsQ44 before and after exposure to the Thin Film Oven Test (TFOT) test

Sample	Rheological Properties	Before Test	After Test	Difference
AsQ0	Softening point (°C)	50	53	3.0
	Ductility (25 °C, cm)	+100	+100	
	Penetration, mm (25 °C, 5 sec, 100 gm)	42	40.1	1.9
	Weight of loss %	---	0.13	
	PI	-1.573		
AsQ39	Softening point (°C)	60	62	2.0
	Ductility (25 °C, cm)	+100	+100	
	Penetration, mm (25 °C, 5 sec, 100 gm)	35.1	34.8	0.3
	Weight of loss %	---	0.206	
	PI	0.204		
AsQ44	Softening point (°C)	63	65	2.0
	Ductility (25 °C, cm)	+100	+100	
	Penetration, mm (25 °C, 5 sec, 100 gm)	33.2	32.7	0.5
	Weight of loss %	---	0.623	
	PI	0.834		

3.9 Thin Film Oven Test

This test was carried out to determine the combined actions of air and heat on a thin coating of asphalt or asphalt binder. It tries to imitate the application of hardening of the binders, which are involved in mixing, compaction, and transportation. This test is good for knowing the life of the road surfaces [33].

Table 9 indicates the results of the test, indicating that the starting asphalt (As0) failed to comply with the standard requirements in the government of Iraq regarding roads and bridges [34]. Contrarily, the modified asphalt samples (AsQ39) and (AsQ44) showed a high level of performance, which registered appropriate values of penetration, ductility, and the softening point tests [35]. This helps to increase the life span of the pavements because it is very resistant to hardening processes caused by transportation and compaction [36].

4. CONCLUSIONS

Modification of asphalt with the biopolymers ALA and

MAL, especially when phosphoric acid (PPA) was added, gave a major impact on the rheology and mechanical characteristics of asphalt. The modified asphalt had significant changes in penetration, ductility, softening point, and Marshall stability when compared to the original asphalt. Moreover, FTIR and H-NMR tests have verified that there are effective interactions between components of asphalt and polymers and this is the reason why the structural and functional performances of the material have improved tremendously. The modified samples of asphalt (AsQ39 and AsQ44) proved better in most of the tests and they showed significant improvement in the aging resistance when they were exposed to TFOT and higher peel resistance when undergoing chemical immersion tests. These findings suggest the modified asphalts resist high temperatures and regular traffic loads more efficiently, and oxidative aging, and therefore, making the material less vulnerable to cracking and hardening and aiding the fulfilment of the requirements and standards of approved roads in Iraq. This study suggests that, in the future, adding other elements to the alginic acid polymer and changing the additive ratios to facilitate production of more robust and durable pavements and field tests that will last longer.

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