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ABSTRACT

Polymer modified asphalt is increasingly used in road surfacing. Unmodified asphalt is sensitive to changes in temperature, it becomes brittle and cracks in cold weather and soften in high temperature, causing rutting and surface deformation. This research aims to prepare hot mix asphalt (HMA) for paving using polymer prepared from stearyl acrylate and methyl methacrylate and styrene in molar ratios: 0.5:0.5:0.2 and 0.5:0.5:0.5, respectively. The solid materials in the mix include normal and highly porous aggregates. 4,6,8% of two polymers by weight of asphalt were used to prepare special binders. The samples were tested for physical, chemical, ageing, SEM and TGA. The results revealed that the prepared hot mix asphalt (HMA) polymer had high performance as compared to ordinary one and the two polymer prepared could be used in road construction.

Key words: Asphalt, ester, hot mix asphalt, modified asphalt, polymer, Marshall.

INTRODUCTION

The addition of polymeric chains of repeated small molecules, to asphalt has been shown to improve performance. Pavement with polymer modification exhibits greater resistance to rutting and thermal cracking, and decreases fatigue damage, stripping, and temperature susceptibility[1]. Bitumen, residue from crude oil distillation, is a complex mixture of four main families of compounds, referred to as SARAs fractions (saturates, aromatics, resins and **asphaltenes**)[2]-[3]. Polymers that are used for asphalt modification can be grouped into three main categories: thermoplastic elastomers, plastomers and reactive polymers. Thermoplastic elastomers are obviously able to confer good elastic properties on thermo modified binder; while plastomers and reactive polymers are added to improve rigidity, and reduce deformations under load. Belonging to the first category, styrene-butadiene-styrene block (SBS) copolymers are probably the most frequently used asphalt modifiers for paving applications [4]-[7]. Examples of the plastomeric types of polymers were studied since asphalt modifications are polyethylene (PE), and ethylene-butyl acrylate (EBA) random copolymers [8]-[11]. Due to its low compatibility with asphalt, PE is not widely used for paving applications, and thus ethylene copolymers are

preferred. Recently, reactive polymers have been introduced as asphalt modifiers. Their “reactivity” is due to the presence of functional groups supposedly able to bond with asphalt molecules. Polarity of the polymer can enhance its solubility and compatibility with base bitumen. Polar groups present in the polymer molecules can react with the polar constituents of bitumen. Subsequently, phase separation is prevented, which in turn enhances the materials consistency, and decreases oxidative ageing [12]-[15]. Among polar polymers, a very limited number of studies discuss the fundamental properties of modified bitumens with acrylate polymers. Most frequently used acrylates as bitumen modifying agents in road applications are ethylene vinyl acetate. (EVA) glycidyl methacrylate (EA) terpolymer, ethylene butyl acrylate (EBA) copolymer, etc. [16]-[18]. In this work, use prepare the octadecylacrylate, then polymerized it with styrene and methyl methacrylate. This polymer was added to asphalt for improving the performance of bitumen in pavement.

2. EXPERIMENTAL

2.1. Materials Used

Methyl methacrylate monomer and styrene was supplied by Navol, and stearyl alcohol from SASOL,, Acrylic acid from BASF, benzoyl per-

oxide (DBPO) was obtained from Merck, Toluene and methanol were obtained from Carloerba reagents. Local asphalt of penetration grade 60/70, produced by El-Nasr Petroleum Company, Suez-Egypt. The crushed limestone aggregate, limestone mineral filler, and crushed sand were originally obtained from Ataka Suez-Egypt. The physical properties of the asphalt binder and the aggregates are given in Table(s) 1, 2 and 3 respectively.

2.2.1. Preparation of Octadecyl acrylate :

Octadecyl acrylate was prepared by the reaction of acrylic acid and stearyl alcohol in a molar ratios: 1.2:1, using toluene as solvent, p-toluene sulfonic acid (PTSA) as catalyst, hydroquinone as inhibitor, water was separated a zeotropically using Dean–Stark apparatus [19]. The alcohol, toluene and hydroquinone were mixed in a four-necked flask, then heated to 60 °C. After the mixture completely mixed, acrylic acid and PTSA were added, and the mixture is gradually heating to 115–120 °C. The reaction was stopped after a theoretical amount of water is separates. Reaction products were washed several times with an aqueous solution of Na₂CO₃ (5 %) until the lower layer became clear, then washed by distilled water, vacuum distilled using a rotary evaporator and them vacuum dried.

2.2.2 Polymerization of additives

All additive samples were prepared by free radical solution polymerization in xylene using benzoyl peroxide as the initiator[20]. Polymerization was performed in a reaction flask equipped with a condenser, mechanical stirrer, and temperature controller. Polymerization reaction was carried out in nitrogen atmosphere at 90°C for 5 h. During that time, more than 95% of monomer was polymerized. The resulting homogeneous product was then cooled to room temperature and used as additive without any further treatment.

3. Experimental Procedure:

3.1. Characterization of raw materials

- Penetration, softening point, specific gravity and Brookfield viscosity were determined for the virgin asphalt samples (AC 60/70). The results are illustrated in Table (1). The polymer

constituent illustrated in Table (2) and molecular weight in Table (15) and FTIR spectra were reported as shown in figure (2).

- TGA analysis was carried out using SDTQ 600 thermo-gravimetric analyzer (TA-USA) to test the thermal stability of the virgin asphalt sample and all polymers in the temperature range of 25° to 500°C and a heating rate of 10°C/min under dynamic nitrogen gas Table (3).

- The temperatures susceptibility of virgin and modified asphalt sample was expressed in term of penetration index (P.I) using the penetration at 25°C (pen25) and softening point (soft. pt) values.

P.I. can be calculated from the following equation[21]:

$$P.I. = \frac{1952 - 500 \times \log(\text{pen } 25) - 20 \times \text{soft. pt}}{50 - \log(\text{pen } 25) - \text{soft. pt} - 120}$$

3.2. Preparation and Characterization of polymer modified asphalt samples (PMAs).

Blends of virgin asphalt and three types of polymer modifiers (4, 6 and 8% w/w of asphalt) were prepared. The blending conditions were conducted at 163°C with stirring for 2 hours with complete addition of polymer into asphalt. The prepared samples were tested for compatibility test using Shell method[22], and then characterized physically and chemically. The characterization of PMAs are illustrated in Tables (7-13).

3.3. Evaluation of Best Polymer Modified Asphalt Samples :

FTIR (figure 2), SEM (figure 3) , TGA (figure 4) and analysis were carried out on virgin asphalt and modified AC with 4,8% of each polymer which gave a suitable physical and chemical characteristics. SEM photographs have been observed using scanning electron microscope (SEM; Philips). Infrared spectra of all samples were recorded via FTIR spectrophotometer (Model 960 Mooog, ATI Mattson Infinity Series, USA).

3.4. Preparation of hot mix asphalt :

Hot mix asphalt samples were prepared using virgin asphalt and modified binders and

Table (1): Characteristics of Virgin Asphalt Samples Using

Determined parameters:	Asphalt Virgin	SP*
Penetration (at 25°C , 100 g, 5 s), 0.1mm	63	60/70
Softening point, °C (ring and ball)	50	45/55
Penetration index ⁽¹²⁾	-0.97	-2: +2
Specific gravity using a pycnometer, (at 25°C)	1.018	NS**
Flash and fire points (Cleveland Open Cup), °C	+250	+250
Ductility (cm) (at 25°C, 5 cm/min),	+150	+150
Kinematic viscosity (cst) (at 135°C),	332	>320
Brookfield viscosity CP (at 60 C°),	120.7	NS**
Thermo Gravimetric Analysis (TGA)		
*** Initial degradation temperature, °C	246.18	NS**
*** Final degradation temperature, °C	520.42	NS**
*** Total weight loss (wt. %)	86.20	NS**
Metal content:		
*** Vanadium (ppm)	141.0	NS**
*** Nickel (ppm)	234.0	NS**

N.B: (*) Standard Specification for "General Authority for Roads, Bridges and Land Transportation in Egypt. Item No 102.1

(**) Not specified.

(***) Shear rate 80 s^{-1} , Spindle No. 40& RPM= 20 using Brook Field viscometer (model DV- 111+ programmable rheometer)

(****) According to literature, maximum difference is [2]

Table (2): ingreading of the polymers

Polymer code Compound (mole)	Octadecylacrylate (mole)	methyl meth acrylate (mole)	Styrene (mole)
A	0.5	0.5	0.2
B	0.5	0.5	0.5

Table (3): Values of TGA for polymer A and B

Polymer:	°C / wt %
Polymer (A)	
- Initial degradation temperature, °C	232
- Final degradation temperature, °C	497.9
- weight % decomposed	97.7
Polymer (B)	
- Initial degradation temperature, °C	234.71
- Final degradation temperature, °C	500.4
- weight % decomposed	98.4

Table (4): Physical Properties of modified asphalt samples

Property	Virgin asphalt (AC)	Modified asphalt using					
		Polymer (A)			Polymer (B)		
		4%	6%	8%	4%	6%	8%
-Penetration (at 25 °C, 100 g, 5s) 1mm	62	48	44	37	57	52	42
- Softening point (ring and ball) °C	51	58	62	65	60	63	67
-Specific gravity (at 25 °C)	1.02	1.07	1.13	1.16	1.05	1.12	1.14
- kinematic viscosity (at 135 °C) cst	385	1880	2170	2330	1950	2200	2350
- penetration index (P.I)	-0.40	0.998	1.616	1.594	1.366	1.708	1.855

Table (5): Calculations of the Job Mix formula of the surface course asphalt mix, 25mm Max.

Sieve Size, (mm)	C . Agg 25mm:19mm		C . Agg 19mm:4.75mm		Filler		(Crushed sand)		JMF
	%Passing		%Passing		%Passing		%Passing		
	100	24	100	26	100	5	100	45	
25.4	100	24	100	26	100	5	100	45	100
19	92.9	22.3	100	26	100	5	100	45	98.3
9.5	8.1	1.9	68.9	17.9	100	5	100	45	69.9
4.75	2.0	0.6	11.0	2.9	100	5	100	45	53.5
2.36	0	0	2.1	0.5	100	5	70.1	31.5	37.1
0.6	0	0	0	0	100	5	51.7	23.3	28.3
0.3	0	0	0	0	100	5	30.9	13.9	18.9
0.15	0	0	0	0	95	4.8	8.7	3.9	8.7
0.075	0	0	0	0	80	4.0	5.9	2.7	6.7

* C. Agg: size of aggregates
sand and filler

JMF: Size of coarse and fine aggregates,

** Filler: Calcite (CaCO₃)

% passing: Aggregate passing from sieve

Table (6): Final Grading & Tolerance of the Surface Course Asphalt Mix, 25mm Max. Agg. Size.

Sieve Size, (mm)	Proposed JMF, % Passing	JMF Tolerance	
	JMF	Lower Limit	Upper Limit
1(25.4)	100	100	100
3/4(19)	98.3	80	100
3/8(9.5)	69.9	60	80
NO.8(4.75)	53.5	48	65
NO.8(2.36)	37.1	35	50
NO.30(0.6)	28.3	19	30
NO.50(0.3)	18.9	13	23
NO.100(0.15)	8.7	7	15
NO.200(0.075)	6.7	2	8

JMF:Size of coarse and fine aggregates, sand and filler

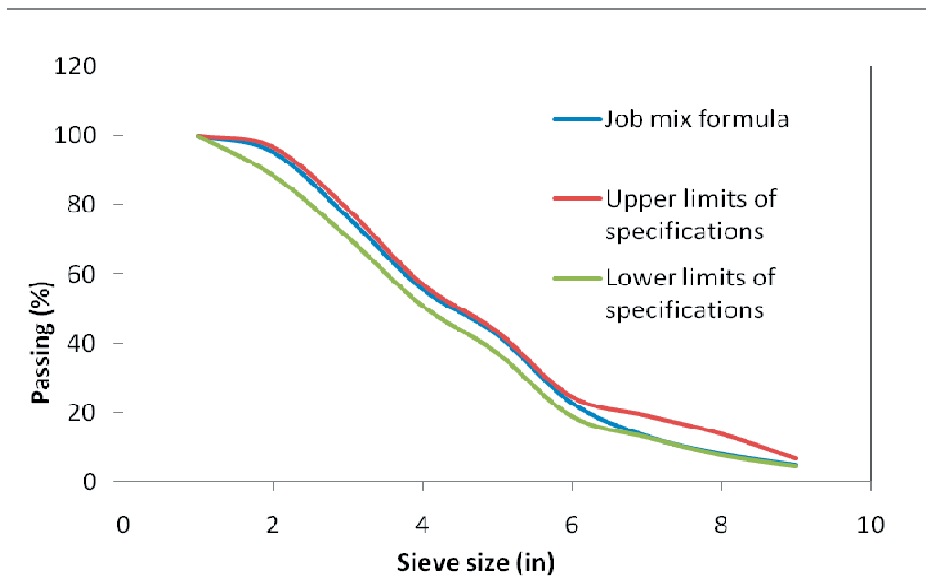


Figure (1): JMF gradation curve

Table (7): Marshall Characteristics of paving mixture No (1) using virgin asphalt.

Marshall Design parameters:						
Asphalt content, (wt%)	Bulk Specific Gravity (g / cm ³)	Stability, (N)	Flow (mm)	Air voids in mix, (%)	Air voids in solid materials, %	Marshall Stiffness, (N/mm)
4	2.288	1870	3.5	7	15.4	534.3
5	2.315	2200	3.8	4.3	15.1	578.95
6	2.338	2440	4.1	2.6	15.5	595.12
7	2.319	2110	4.4	1.7	16.6	479.5

Table (8): Marshall parameters for Mixture No (4) Hot mix asphalt using modified asphalt with 4% of polymer (A).

Marshall Design parameters:						
Asphalt content, (wt%)	Bulk Specific Gravity (g / cm ³)	Stability, (N)	Flow (mm)	Air voids in mix, (%)	Air voids in solid materials, (%)	Marshall Stiffness, (N/mm)
4	2.313	2750	3.35	5.9	14.4	820.9
5	2.340	2910	3.62	3.6	14.2	803.9
6	2.359	2860	3.8	1.6	14.3	752.6
7	2.345	2740	4.1	1.2	15.6	668.3

Table (9): Marshall Parameter's of Mixture No (3) 6% Polymer (A)

Marshall Design parameters:						
Asphalt content, (wt%)	Bulk Specific Gravity (g / cm ³)	Stability, (N)	Flow (mm)	Air voids in mix, (%)	Air voids in solid materials, (%)	Marshall Stiffness, (N/mm)
4	2.320	3200	2.7	6.1	14.1	1185.2
5	2.345	3620	3.3	4.1	14.	1097
6	2.360	3470	3.8	2.3	14.3	913.2
7	2.350	3220	4.5	1.6	15.5	715.6

Table (10): Marshall Parameter's of Mixture No (3) 8% Polymer (A)

Marshall Design parameters:						
Asphalt content, (wt%)	Bulk Specific Gravity (g / cm ³)	Stability, (N)	Flow (mm)	Air voids in mix, (%)	Air voids in solid materials (%)	Marshall Stiffness, (N/mm)
4	2.324	2800	3.50	6.1	14	800
5	2.347	3140	3.74	4.2	13.9	839.60
6	2.365	3370	4.00	2.4	14.13	842.5
7	2.351	3100	4.30	1.7	14.6	720.9

Table (11): Marshall Parameter's of Mixture No (5) 4% Polymer (B)

Marshall Design parameters:						
Asphalt content, (wt%)	Bulk Specific Gravity (g / cm^3)	Stability, (N)	Flow (mm)	Air voids in mix, (%)	Air voids in solid materials (%)	Marshall Stiffness, (N/mm)
4	2.318	2800	3.3	6.6	14.2	848.5
5	2.343	3000	3.5	4.6	14.1	857.14
6	2.358	3100	3.8	3	14.4	815.7
7	2.348	2920	4.2	2.1	15.5	695.2

Table (12): Marshall Parameter's of Mixture No (6) 6% Polymer (B)

Marshall Design parameters:						
Asphalt content, (wt%)	Bulk Specific Gravity (g / cm^3)	Stability, (N)	Flow (mm)	Air voids in mix, (%)	Air voids in solid materials, (%)	Marshall Stiffness, (N/mm)
4	2.316	2700	3.2	6.8	14.6	844
5	2.341	3050	3.6	4.9	14.2	847.2
6	2.35	2950	3.9	3.3	14.5	756.41
7	2.344	2900	4.3	2.4	15.2	674.42

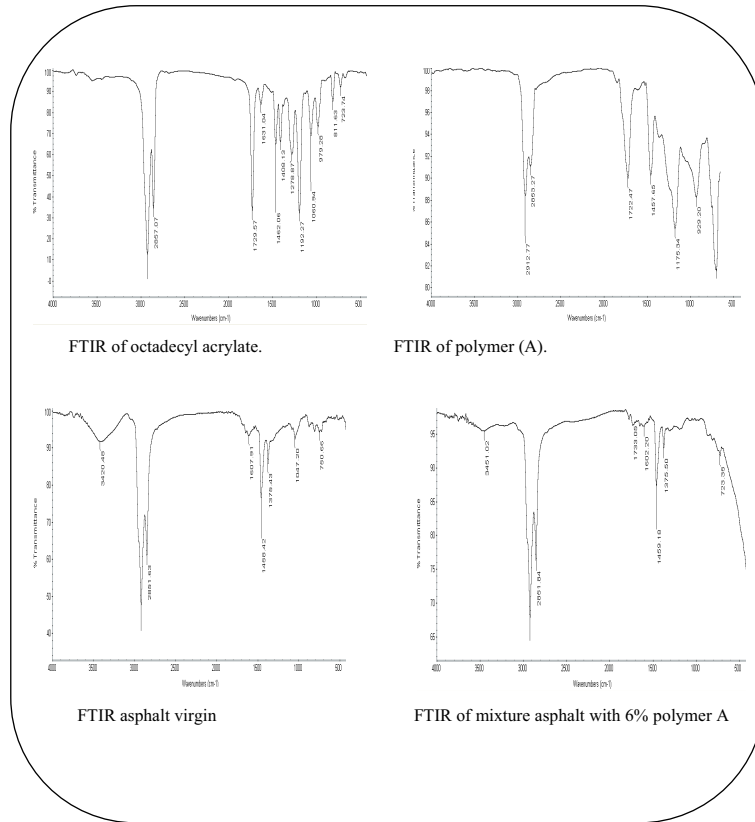
Table (13): Marshall Parameter's of Mixture No (7) 8% Polymer (B)

Marshall Design parameters:						
Asphalt content, (wt %)	Bulk Specific Gravity (g / cm ³)	Stability, (N)	Flow (mm)	Air voids in mix, (%)	Air voids in solid materials (%)	Marshall Stiffness, (N/mm)
4	2.319	3300	3.67	6.4	14.1	899.2
5	2.347	3850	3.83	4.5	13.75	1005.22
6	2.351	3590	4.	3.4	14.5	897.5
7	2.337	3350	4.2	1.5	15.9	797.619

Table (14): Marshall Characteristics of the prepared paving mixes

Characteristics	Virgin asphalt	Modified asphalt with:						ESS*
		A			B			
		4%	6%	8%	4%	6%	8%	
-Optimum asphalt content%	5.73	5.16	5.33	5.72	5.75	5.47	5.5	
Stability of the mix asphalt (N)	2390	2910	3600	3310	3080	3800	3730	>1200
Bulk Specific Gravity (g / cm ³)	2.36	2.345	2.35	2.36	2.36	2.354	2.35	
-Flow of the mix (mm)	4	3.65	3.44	3.85	3.72	3.91	3.9	2-4(mm)
-Air voids in the mix (%)	3.15	3.25	3.45	3.0	3.35	3.9	4.0	3-5
-Air voids in solid materials,%	15.3	14.2	14.05	14.	14.3	14	13.98	>13.5
Marshall stiffness, (N/mm)	746.9	793.2	1027.1	851.3	850	974.3	798.3	

* ESS: Egyptian standerd spesification



Fig(2): FTIR of octadecyl acrylate, polymer A, asphalt virgin &mix asphalt with 6% polymer A.

Table(15): Avrage molecular weight of the prepared polymers:

code polymer	Retention time	\overline{M}_n	\overline{M}_w	Mp	Mz (daltons)	Mz^{+1} (daltons)	Poly-dispersity
A	24.244	7789	24845	24102	51962	78468	3.19
B	24.251	10756	27411	24008	51188	75434	2.525

\overline{M}_n : average number molecular wight;
 \overline{M}_w : average weight molecular wight;
 Mp:molecular wight of the highest peak ;
 Mz: size average molecular weight ;
 Mz^{+1} : Higher size average molecular weight ;

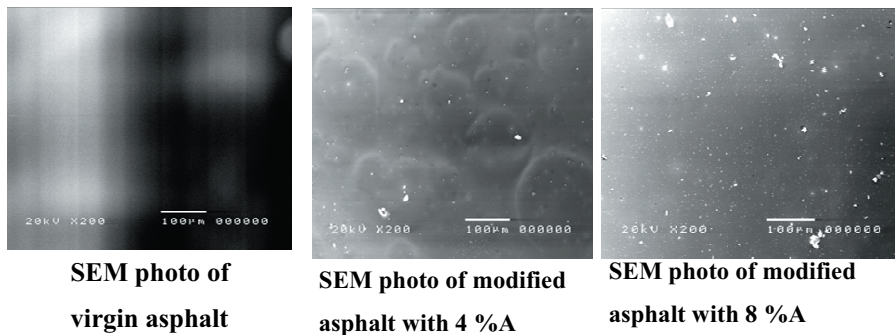


Fig. (3) : SEM photo of virgin asphalt & modified with (4, 8)% polymerA

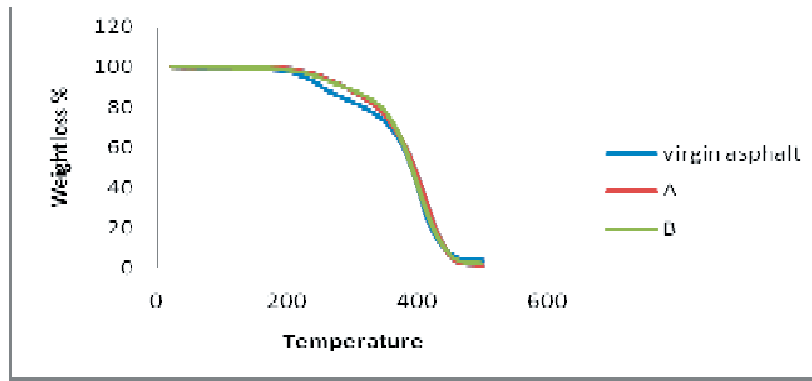


Fig.(4): TGA curves of modified asphalt sample containing 8 wt % polymers A,B

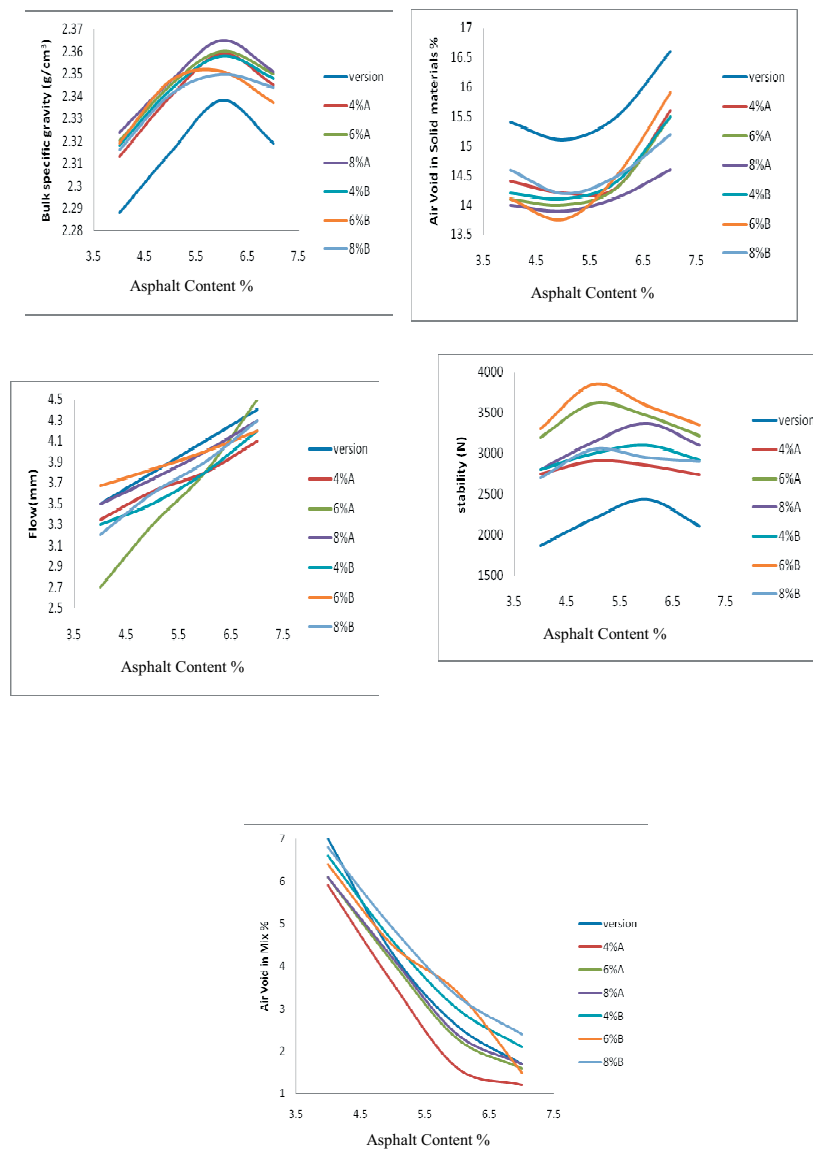
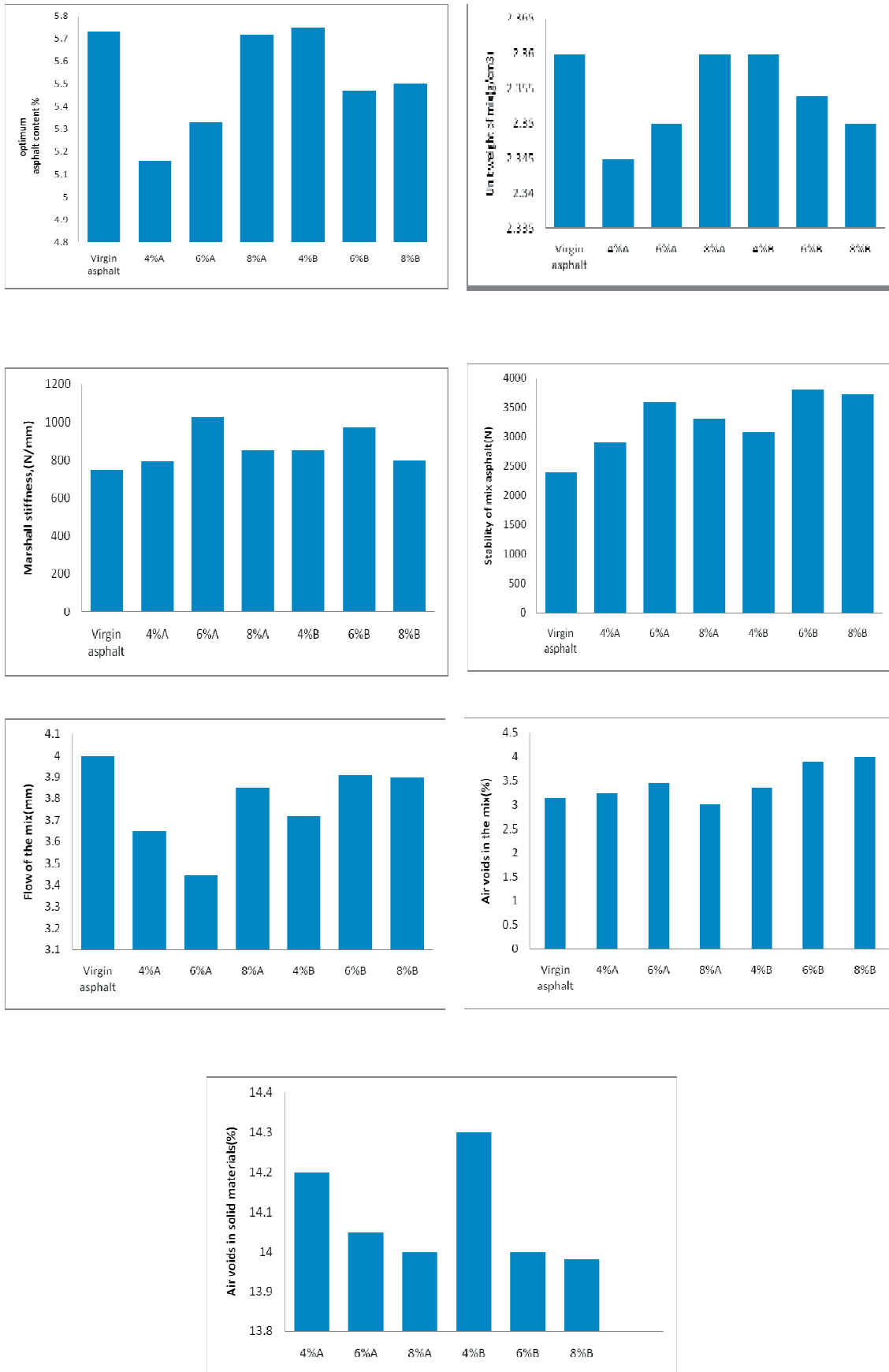


Fig (5): Marshall curves of HMA using virgin and modified asphalt with polymer A,B.



Fig(6): Marshall Characteristics of all prepared paving mixes

evaluated using Marshall Test method (ASTM D-6927). The mixes were designed according to the standard limits of surface (wearing) course 4c. The job mix was formulated (JMF) (%wt) using coarse and fine aggregates, sand and filler as 33, 30, 32, 5 wt %, respectively.

Tables (5-6) and figer (1) illustrates the technical propertes of solid materials according to ASTM standard test methods.

- The mixtures were tested for maximum load and flow. Density and air voids in mix and solid materials were determined:

HMA Table(7) mixture of aggregate type and virgin asphalt samples .

HMA tabels (8,9,10) are mixture of aggregate type and modified asphalt using 4,6,8% of polymer A.

HMA Tables (11,12,13) are mixture of aggregate type and modified asphalt using 4,6,8% of polymer B.

4. RESULTS AND DISCUSSION

4.1- Characteristics of Virgin and Modified Asphalt Samples:

4.1.1. Physical characteristics and Molecular type composition of asphalt samples

Generally, data in Tables (8-13) indicated that the modified samples are more hard than the virgin one. There was an increase in softening point, specific gravity and dynamic viscosities and decrease in penetration value using an increasing values of the polymer content from 4,6,8 wt %. This is attributed to either and the chemical molecular composition of the polymer used. Asphalt modification, modify both cohesion and elasticity. At higher temperatures, the stiffness modulus of polymer phase is higher than that of the matrix. These reinforcing properties of the polymer phase contribute to the increase in viscosity. At low temperatures, the stiffness modulus of the dispersed phase is low compered with that of the matrix, which reduces its brittleness. Consequently, the dispersed polymer phase enhances the engineering properties of asphalt in terms of viscosity, softening point and toughness[23].

4.1.2. Infrared spectroscopy analysis

The FTIR spectrum of octadecylacrylate disappearance of the characteristic absorption band (OH) of the carboxylic acids at about 3200 cm^{-1} , appearance of the carbonyl group of ester band around (1729.57) cm^{-1} , two bands for (C-O-C) appear at 1192.21 cm^{-1} and 1278.8 cm^{-1} and the band for C=C which appear at 1631 cm^{-1} . The FTIR spectrum of the base AC asphalt illustrated that, the strong peaks within 2850–2960 cm^{-1} regions were typical C-H stretching vibrations in aliphatic chains. The peak at 1607.91 cm^{-1} was attributed to C=C stretching vibrations in aromatics. The asymmetric deforming in $-\text{CH}_2$ and CH_3 , and the C-H symmetric deforming in CH_3 vibrations were observed at 1458.2 cm^{-1} and 1375.2 cm^{-1} respectively. The peak at 1047.2 cm^{-1} was ascribed to S=O stretching vibrations. The small peaks within 740–910 cm^{-1} regions were typical C-H vibrations in benzene structure.

Comparing the spectrum of asphalt modified with (6% polymer A) with that of the base AC asphalt, a new peak appeared at 723 cm^{-1} illustrating the bending vibration of C-H in the double bonds $-\text{CH}=\text{CH}-$ in aromatics. the FTIR spectrum fig(2) showed the same characteristic peaks of asphalt spectrum except the appearance of C=O group at 1733 cm^{-1} and this was due to the presing of polymer which have ester group (octadecylacrylate).

4.1.3. Determination of molecular weight of the prepared polymer:

The molecular weights of the prepared polymer were determind by using vapoar pressure osmometr. The molecular weight (Mn) of the prepared polymers were determined by Gel permeation Chromatography (GPC), model 510 using polystyrene standerd. Ultra-Styrigel column, and tetrahydrofuran as solvent Table 15.

4.1.4. TGA Analysis

From Fig. (4) it was found that, addition of polymers to asphalt produces PMA samples haveing lower decomposition ability percentages compared to polymers themselves. This maybe attributed to the increase of asphaltene content for PMA as compared to virgin one. Either virgin and PMA samples have nearly the same thermal

stability. This may be attributed to the nature of each addition as well as to the partial compatibility between virgin asphalt and polymers as illustrated in SEM photos fig.(3)

4.1.5. SEM of PMAs

SEM is used to predict the shape of bitumen, surface texture even polymer distribution in modified bitumen. The typical morphology of base bitumen with SEM is shown in Figure (3) In SEM photos of the virgin and polymers modified blends the light phase in the picture represents the swollen polymer while the dark phase is the asphalt. Small polymer spheres swollen by asphalt compatible fractions (*e.g.*, aromatic oils) spread (dispersed phase) homogeneously in a continuous asphalt phase.

Polymer particles extensively spreading on PMA's surface lead to a decrease in technical properties such as toughness and tenacity. This may be attributed to differences in molecular weight, polarity and structure of the used polymers. A chemical dissimilarity asphalt and polymer showed. The morphology of PMA samples is the result of the mutual interaction polymer and asphalt, and, consequently, is influenced by both asphalt composition, polymer content and structure. There is a good compatibility between asphalt and polymers.

4.2- Characteristics of the Prepared asphalt Paving Mixes:

All mixtures prepared (tables 7 and 13) comply with the standard specification of HMA for surface course in roads having high traffic volume.

Comparing to mixture (1), it was noticed that for all prepared mixtures there was a decrease in asphalt content, accompanied by increasing stability and higher Marshall stiffness. The asphalt for virgin 5.75 decreased to 5.16, 5.33, 5.72 for asphalt modified by polymer A additive (4,6,8%) respectively in percentages of 10.26, 7.3& 0.52 from Tables (8, 9,10) respectively while the stability increased from 2390 (N) to 2390 (N) to 3600 (N) and 3310(N). asphalt content for additive polymer B for 4% increase to 0.35% and 6,8% decrease to 4.5%, 4% respectively and the stability increase to 3080(N), 3800(N)

and 3730(N), This may be attributed to different molar ratios of polymer, and high absorptive aggregate. asphalt absorbed by inter and intra aggregate particles. So, there was an increase in stability, flow at and Marshall Stiffness. Increase in air voids and solid aggregates caused by increasing viscosity of PMA samples. On the other hand, the unit weight decreased.

4.2.1 Effect of using modified asphalt in HMA containing HA aggregate (mixes 2(a,b), 3(a,b) and 4(a,b)):

The use of modified asphalt in mixes preparations lowered the asphalt content as compared to HMA (mix(1)). This is attributed to the increase in asphalt viscosity resulting in a decrease in the absorbed partiton by the aggregate.

HMA was found to have the most hardened pration of modified mixtures, as it had highest stability and air voids in mix and solid aggregates as well as lowest flow value. This may be attributed to the observed toughness in polymer.

The Marshall stiffness increased for virgin asphalt 597.5(N/mm) to HMA polymer A (4,6,8%) to HMA polymer B(4,6,8%) in percentages of 33.4, 75.14& 43.9% and of 38.6, 62.65& 60.06%.

CONCLUSION

The aim of this work is to prepare and characterica a special type of HMA consisting of spicial materials having the property of decreasing the cost of paving and maintenance, keeping the premium aggregates for a long period . To achieve this, 4,6,8% of polymer prepared from synthesis of octadecylacrylate from stearyl alcohol and acrylic acid in presence of P- toluene sulphonic acid as a catalyst and then polymerizing with styrene and methyl methacrylate in different molar ratios . The polymer was used in modification asphalt. High absorptive aggregate and marble fillers were used in mixtures preparations. The obtained results showed that:

A mixtures of polymers and solid materials are suitable in road paving.

The mixtures comply with the standards and have reduced temperature susceptibility.

The best modifier was either 6% polymer A and B

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