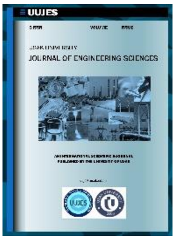

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Research article

EVALUATION OF FATIGUE PARAMETERS ON POLYMER MODIFIED BITUMENS

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Abstract

Since exact behaviour of components within bitumens is not completely determined and the absence of cooperative study related to modification of bitumens, the values found in the study are thought to be useful in determining which type of polymer would be better in terms of fatigue parameter for the needs of petroleum refineries. The scope of this study is to minimize the fatigue cracking within bitumens obtained from different sources. In this paper, virgin bitumen samples were composed by using different types of polymers such as elastomers, plastomers and polyethylene groups. For this purpose; bitumen samples were modified by recommended content of three different polymers as elastomer, plastomer and polyethylene polymer at concentration of 3.2%, 1.4% and 1.5% by weight of the bitumen respectively. Following the determination of the chemical characteristics of bitumen samples by spectroscopy, resistances of fatigue deformation levels of polymer modified bitumen were determined by Dynamic Shear Rheometer.

Keywords: *Modification; polymer; polymer modified bitumen; fatigue parameter; elastomers; plastomers; polyethylene.*

1. Introduction

Petroleum is a mixture of many hydrocarbons, which are considered to be formed as a result of the decomposition of organic substances by bacteria and natural catalysts millions of years ago [1]. The bottom product obtained by atmospheric or vacuum distillation of oil is called as bitumen. Thus, bitumen is a mixture of hydrocarbons of natural origin or a mixture of phylogenic hydrocarbons, which can be in liquid, semi-solid or solid form depending on temperature [2].

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Bitumen is particularly interesting for engineers because of its strong characteristics of binding, adhesive, waterproof and durability. Bitumen is a viscoelastic material which provides a controllable flexibility to the mineral aggregate mixtures. Furthermore, bitumen is highly resistant to the action of many acids, alkalis and salts. Although it is either solid or semi-solid at normal atmospheric temperatures, it can be liquified by dissolution or emulsification in petroleum solvents with heat or variable volatility [3].

Bitumen is a viscoelastic material and a thermoplastic material as well as its consistency changes when heated. This is one of the features that make bitumen use as a binder [4]. Viscoelastic materials show higher elasticity and higher strength at higher loading speeds (fast vehicles). However, they exhibit viscous behavior and low strength at low loading speeds (slow vehicles) [5]. They exhibit common elastic and viscous behavior at moderate speeds. Bitumen also has low mechanical strength at high temperatures due to its thermoplastic properties and high strength at low temperatures [6]. The deformations in the bituminous layers are largely dependent on these properties of the bitumen and the asphalt mixture.

Modification is defined as the mixing of various additives in the bitumen in certain proportions and conditions to increase the performance of the bitumen or mixture used in asphalt pavements [7]. Recent researches have revealed that adding some polymers and additives compatible with bitumen to the bitumen affects the rheological behavior of bitumen, improves its properties and gives superior properties to asphalt mixture. Therefore, the main purpose of the addition of polymer to the bitumen is to change the viscoelastic behavior of the bitumen and to reduce its temperature sensitivity behavior at low temperatures [8].

Styrene-butadiene-styrene (SBS) is the most widely used polymer for bitumen modification and followed by other polymers such as ethylene vinyl acetate (EVA) and polyethylene (PE) [9]. SBS polymers are defined as elastomers and increase the elasticity of bitumen. Elastomers perform their strength and elastic from a physical cross-linking of the molecules into a three-dimensional network [10]. Modified bitumens are produced with SBS show excellent thermal stability and high durability [11]. EVA copolymer is an irregular shaped thermoplastic material produced by copolymerization of ethylene and vinyl acetate. The properties of copolymer vary as the content of vinyl acetate increases [12]. Vinyl acetate provides amorphous and rubbery properties to the bitumen [13]. Polyethylene is produced by high temperature polymerization and wax oxidation. PE is a thermoplastic used in a wide range of products. PE becomes fluid when heated and harden when cooled. This different behavior is caused by secondary physical bonds rather than the primary bond and the chemical bond [14]. The weak Van Der Waals ties between the parallel chains of the polyethylene provide a high elongation during drawing. The increase in the same load with the increase in temperature can also be explained by the weak Van Der Waals bonds between the parallel chains [15]. Many researchers have indicated that the addition of PE into the bitumen increases shear complex modulus of bitumen [16-20]. Moreover its addition into bitumen represents an environment-friendly option for the future of waste PE [21].

In this study, bitumen samples were modified by recommended contents of three different polymers as elastomer, plastomer and polyethylene polymer at different concentrations by weight of the bitumen. The chemical characteristics of modified bitumen samples were evaluated by infrared spectroscopy and the resistance of fatigue deformation levels of polymer modified bitumen was determined by Dynamic Shear Rheometer. The values found in the study are thought to be useful in determining which type of polymer would be better in terms of fatigue parameter for the needs of petroleum refineries.

2. Materials and methods

50/70 penetration grades samples are identified as Bit-Batman and Bit-Izmir as well as these bitumen samples have been obtained from TUPRAS® Batman and TUPRAS® Izmir refineries respectively. Bit-Batman with performance grade PG 70 and Bit-Izmir with performance grade PG 64 were manufactured in the east part of Turkey and in Middle Eastern countries respectively. Chemical composition of bitumen samples have not been specified by manufacturers. Experimental design procedure is given in Fig. 1 with the help of a flow chart.

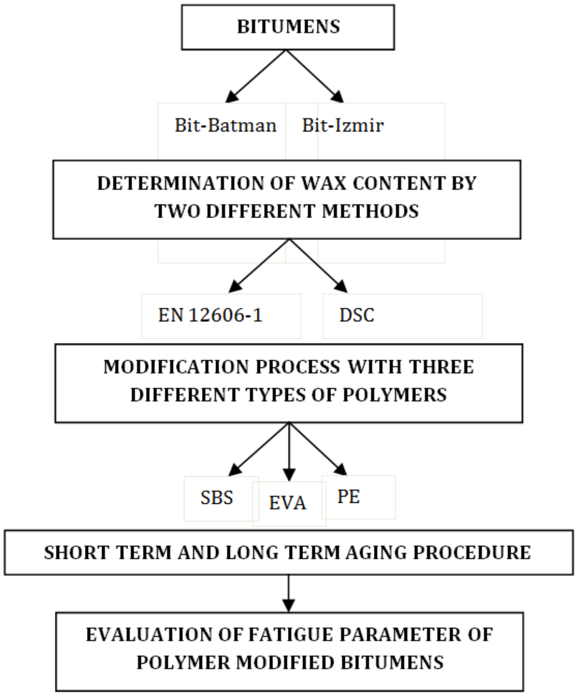

Fig. 1 Experimental design procedure.

Detail information about typical properties of polymers is given in Table 1. By utilization SBS polymer, bitumen and bituminous mixtures are modified so that road pavements are resistant to adverse effects such as wheel tracking, stripping, undulations and low temperature cracking. Within the scope of experimental studies, the SBS contribution examined in the SBS class was considered appropriate in the light of the opinions of the manufacturer and in the light of the detailed literature studies [9, 10]. SBS polymer modified bitumen samples are manufactured at 160°C with 800 rpm for 3 hours with low speed mixer.

The EVA polymer (1.4% by weight of the bitumen) was supplied in pellet form by DuPont, USA. When bitumen is modified with EVA, the polymer amount has to be chosen carefully because an excessive quantity can cause the formation of an insoluble bitumen gel. EVA polymer modified bitumen samples are manufactured at 180°C with 200 rpm for 2 hours with laboratory type mixer.

The used PE was in white pellet form obtained from Honeywell Company, USA. Polyethylene has low molecular weight and semi-crystalline structure. Addition of PE significantly improves the mechanical properties of bitumens, especially at high temperature ranges. The concentration of PE used was 1.5% by weight of the bitumen. PE polymer modified bitumen samples are manufactured at 150°C with 800 rpm for 1 hour with low speed mixer.

Table 1 Information about typical properties of polymers.

Polymer type	Molecular type	Unit weight	Physical state	Volumetric weight (g/cm^3)
SBS	Linear	0.94	Granular	0.502
EVA	Linear	0.96	Transparent Granular	0.557
Polyethylene	Quasicrystal	0.99	Granular	0.625

Spectroscopy is the most commonly used method in determining the molecular structure of materials. Spectroscopy is a science that examines the relationship between electromagnetic radiation and material. Usually, the vibration transitions of the molecules fall to the range of 14000 cm^{-1} to 20 cm^{-1} wave counts. Generally; Infrared Spectroscopy (IR) can examined the application area of 12800 cm^{-1} to 10 cm^{-1} wave length. IR spectrum is divided into three groups in terms of application and device. Vibration spectra are formed by changing the vibrating energy levels. The electrical dipole moment must be changed during the vibration of the molecule in order to observe a vibration band in the infrared region.

In the study, FSM 1202 device was used to obtain IR spectroscopy results of bitumen samples. The IR spectrum results were analyzed by a special computer program which is called ESPEC. In order to determine the molecular bond characterization of bitumen samples, IR spectroscopy was performed on original, short-term and long-term aged samples. IR spectroscopy revealed the presence of CH_3, CH_2, aromatic groups (C=C), carbonyl groups (C=O) and saturated resins (CH_2 / CH_3).

Superpave binder specification requires testing the long-term aged bitumen samples before intermediate temperature behaviour is determined by the dynamic shear rheometer (DSR) device. In the Superpave specification, resistance to fatigue cracking is indicated by $G^*.\sin\delta$ * data obtained from DSR device. In this factor, G^* is the complex shear modulus, and δ is the phase angle. In order to minimize the occurrence of fatigue cracking, $G^*.\sin \delta$ value should be at most 5000 kPa for long-term aged bitumen. In the experiment, the rotational frequency is about 1.59 rpm (10 rad/s). The experiment is started at 40°C to reflect the ambient conditions in the experiment and then the test must be repeated by reducing the test temperature to 3°C. Sample sizes are 8 mm in diameter and 2000 microns in height to determine fatigue crack strength.

3. Results and discussion

In this study, Infrared Spectroscopy analysis (IR) was performed to determine the chemical components of virgin bitumen samples. “Infrared Fourier Spectroscopy FSM 1202” analyzer was used in advanced analysis laboratory.

Bitumen samples were dissolved in 50% of tetrachloride before irradiation with IR spectroscopy. The prepared solution was applied on a glass produced from potassium bromide and it was allowed to dry for 30 min. at 25°C. The IR spectroscopy test was started when the solvent in the sample was completely removed. Fig. 2 shows the functional groups seen in the IR spectroscopy bands of the original bitumen samples.

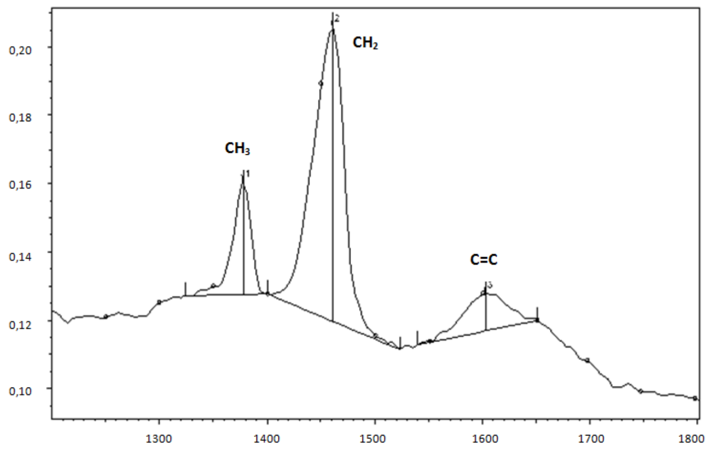

Fig. 2 IR spectroscopy of original bitumen sample.

As seen in Fig. 2, it was observed that strong absorption peaks in the range of 1358-1400 cm^{-1} define CH_3 (methyl) groups, the absorption peaks in the range of 1400-1530 cm^{-1} designate CH_2 (methylene) groups, the presence of peaks around 1530-1648 cm^{-1} also represent C=C (aromatic) groups. Since the sample tested belongs to original bitumen sample, there are no peaks indicating the presence of carbonyl groups (C=O). In the results of IR spectroscopy of the bitumen samples exposed to short-term and long-term aging process, it was concluded that the absorption peaks around 1648-1740 cm^{-1} represent the carbonyl groups (C=O) chains. IR results of the original, RTFOT and PAV-aged bitumen samples are given in Table 2.

Table 2 IR results of the original, RTFOT and PAV-aged bitumen samples.

Bitumen samples		**CH_3**	**CH_2**	**C=C**	**C=O**	**Saturated resins CH_2/ CH_3**
Bit-Batman	Original	12.4	75.1	12.6	-	6.1
	RTFOT	12.2	73.9	14	-	6.0
	PAV	11.1	70.3	13.9	4.6	6.3
Bit-Izmir	Original	11.7	75.2	13.1	-	6.4
	RTFOT	11.4	73.9	13.5	0.7	6.5
	PAV	11.08	72.3	13.3	3.4	6.3

Regarding to all bitumen samples, the proportion of CH_3 and CH_2 groups decreased as a result of aging processes. This decline has been more pronounced in the long-term aging process. The higher pressure factor (PAV) is more effective than the short term oxygen oxidation (RTFOT) in the change of the CH_3 and CH_2 group ratios. In the case of the original and short-term aged of the Bit-Batman sample, the carbonyl groups were not present, whereas in the long term aged of the Bit-Izmir sample, carbonyl groups were formed. This shows that Bit-Batman bitumen can only react with oxygen under high pressure. Besides, Bit-Batman is not affected by short-term aging process and it is highly resistant to oxygen.

According to the result of IR spectroscopy, the CH_2/CH_3 ratio is referred to as the amount of saturated resin. Saturated resins are the groups that ensure the distribution of asphaltenes in the bitumen. Thus, saturated resins give flexibility to bitumen. Bit-Izmir example shows that they are more flexible compared to the Bit-Batman example.

Considering the saturated resin ratios of the bitumen samples subjected to long-term aging, the results of the original and short-term aged samples were very different. This can be considered as evidence that RTFOT and PAV tests have very different effects on the chemical structure of bitumen.

Fatigue cracking test has been performed on polymer modified bitumens to determine intermediate temperature performance. In order to minimize the occurrence of fatigue cracking, G*.sin δ value should be at most 5000 kPa for long-term aged bitumen. In the experiment, the rotational frequency is about 1.59 rpm (10 rad / s). The experiment is started at 40°C to reflect the ambient conditions in the experiment and then the test must be repeated by reducing the test temperature to 3°C. Sample sizes are 8 mm in diameter and 2000 microns in height to determine fatigue crack strength in dynamic shear rheometer. Fatigue parameters for SBS, EVA and PE modified bitumen samples have been illustrated in Fig. 3, Fig. 4 and Fig. 5 respectively. On the other hand, Table 3 can be present the following conclusions based on fatigue cracking requirements.

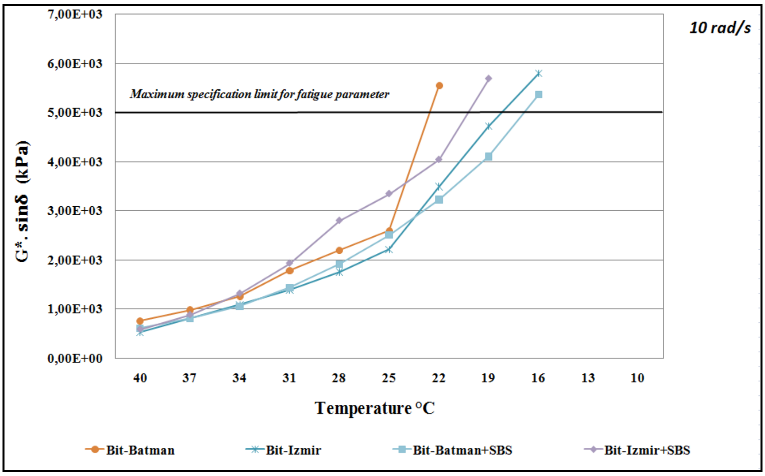

Fig. 3 Fatigue parameters for SBS modified samples.

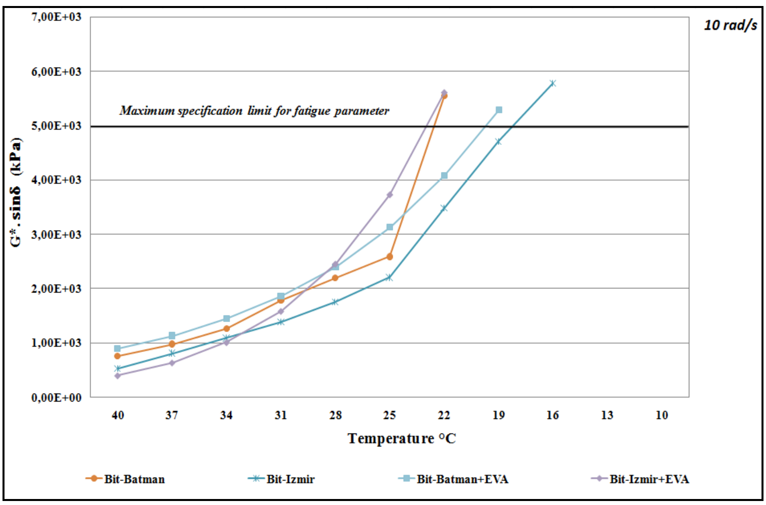

Fig. 4 Fatigue parameters for EVA modified samples.

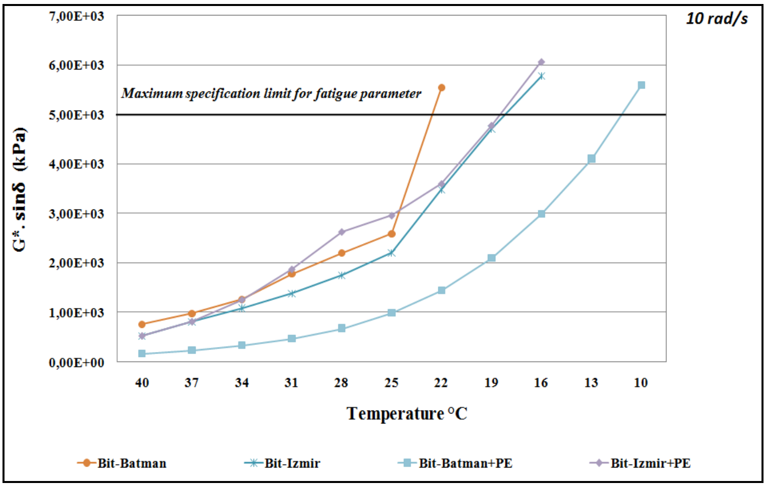

Fig. 5 Fatigue parameters for PE modified samples.

Bit-Batman samples exhibit the highest G*.sinδ value at all intermediate temperatures. High G*.sinδ values are not preferred because high G*.sinδ values indicate that asphalt pavements are more sensitive to fatigue crackings.

The addition of each type of polymers into Bit-Batman containing the lowest wax content increases fatigue resistance of asphalt. The utilization of styrene-butadiene-styrene and ethylene vinyl acetate within Bit-Izmir containing the highest wax content of wax does not cause any significant positive effect on the fatigue cracking properties on the samples. However, the limitation of 5000 kPa value is reached at Bit-Batman+PE which occurs at the test temperature 13°C as well as Bit-Izmir+PE meets with specification limit at the temperature 19°C. Consequently, utilization of PE into bitumen samples develops resistant of fatigue cracking deformation compared to SBS and EVA modification.

Table 3 Temperature at fatigue cracking values reaches 5000 kPa.

Bitumen sample	Temperature (°C)
Bit-Batman	25
Bit-Izmir	19
Bit- Batman +SBS	19
Bit- Izmir +SBS	22
Bit- Batman +EVA	22
Bit- Izmir +EVA	25
Bit- Batman +PE	13
Bit- Izmir +PE	19

4. Conclusions

In spite of the fact that the many significant researches which have been performed related to the polymer modified bitumen in road applications, more studies should be undertaken on the compatibility and in the interaction between polymers.

When the results of infrared spectroscopy of original, short-term and long-term aged bitumen samples were evaluated together, long-term aging effects were found to be more effective on methyl (CH_3) and methylene (CH_2) group ratios compared to short-term aging. Saturated resins are groups that allow homogeneous distribution of asphaltenes in bitumen and give flexibility to bitumen.

Oscillation test was performed on PAV aged bitumen samples using DSR so as to determine the Superpave fatigue cracking parameter (G*.sinδ). Lower values of G*.sinδ are desired properties from the stand point of resistance to fatigue cracking.

When the results of G*.sinδ, which shows the fatigue cracking parameter at moderate temperatures by using of DSR device, it was revealed that the Bit-Batman sample had the highest G*.sinδ values and the Bit-Izmir sample had the lowest G*.sinδ values. The best resistance to the formation of fatigue cracks in middle temperatures (with the lowest G*.sinδ values), Bit-Izmir samples were exhibited.

Regarding to polymer additives are evaluated together; it has been determined that polyethylene additive is the most effective polymer which provides resistance of the bitumen to fatigue cracks at medium temperature.

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