

INVESTIGATION OF NOVEL METHODS TO IMPROVE THE STORAGE STABILITY AND LOW TEMPERATURE SUSCEPTIVITY OF POLYETHYLENE MODIFIED BITUMENS

S. Hassan Firoozifar^{1*}, Yashar Azimi Alamdary¹, Orang Farzaneh²

¹*R&D Department, Pasargad Oil Company, Tehran, 1879913111, IRAN*

²*Civil Engineering Department, Faculty of Engineering, Tehran University, Tehran, IRAN, *Email: h-firoozifar@pasargadoil.com, hfiroozifar@gmail.com*

Received May 11, 2010, Accepted June 15, 2010

Abstract

In recent decades, high traffic rate and higher number of trucks for freight transportation causes more pavement distresses and weak pavement conditions. Therefore, modification of bitumen or asphalt concrete is the best way to increase the asphalt life cycle.

In polymer modification technique, different types of polymer used such as styrene butadiene styrene block copolymer (SBS), polyethylene, polypropylene and rubbers. As Polyethylene is produced locally in Iran and has many advantages in bitumen modification, the aim of this project is to evaluate the bitumen characteristics using different grades of polyethylenes. Although, the addition of polyethylenes would modify bitumen in a cost effective manner, it could face to some problems, such as low compatibility and poor storage stability. So, this paper focus on various ways to stabilize these modified bitumens. Although, high instability for linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) were found, low density polyethylene (LDPE) can be stabilized in bitumen easily using small amounts of oil. Addition of oil to the samples containing mixture of LDPE and SBS was also investigated and improvement in the stability and low temperature properties were found.

Key Words: Modified bitumen; polyethylene; stability; asphalt; polymer.

1. Introduction

Bitumen is one of the most important materials in road constructions and maintenance. This hydrocarbon based material is responsible for the flexibility, adhesion, and thermal behavior of the asphalt concrete [1]. Therefore, to have asphalt pavements which are suitable in a vast range of temperature or under high traffic loads, first of all the bitumen properties must be modified [2].

In recent years, different types of polymers were used for this modification, such as styrene-butadiene-styrene block copolymer (SBS), polyethylene (PE), polypropylene (PP), and so on [3]. Although each of these polymers has its own advantages and disadvantages, most researchers believe that SBS is the best one [4-6]. It improves both high and low temperature behavior of bitumen, and increases asphalt resistant to rutting and cracking. As SBS is not produced in Iran, its usage looks unreasonable from the economic point of view.

Unfortunately, polyethylene modified bitumen suffer from lack of storage stability [5, 7] and the polymer separated from bitumen gradually. Actually, polymers act as solid or semi-solid particles in modified bitumen [8]. So, like asphalt molecules they need some dispersion agents to reach a complete homogeneity. In pure bitumen, maltene molecules (especially polar aromatics) disperse asphalt particles perfectly. However, in the modified bitumen the amount of maltene are not sufficient for both asphalt and polymer particles [2]. Therefore, polymers would separate from the mixture gradually, and make a polymer rich layer on top of the mixture. This process named instability and must be prevented as much as possible.

Actually, it is not easy to find practical papers about increasing the storage stability of polyethylene modified bitumen using maltene like compounds. On the other hand, polyethylene is a suitable bitumen modifier for many areas in Iran which their temperature never goes below zero, even in winter. Therefore, the aim of this project is to determine the possibility of use of different types of polyethylene as bitumen modifier agents, and improve their storage stability.

2. Experimental

2.1 Materials

Bitumen and vacuum bottom residue (VB) were obtained from Pasargad Oil Co. (Iran), which its specification summarized in table1. Three types of polyethylene from BEP Co. (Iran) were selected. These polyethylenes are low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE). SBS from Dynasol Co. (Spain) was also used. The properties of these polymers are summarized in table 2 and table 3. Oleic acids, aromatic oil, and base oil (B-Oil) were also prepared from different supplier in Iran.

Table 1 Bitumen properties as discussed by the producer

Test	Test Method	VB	Bitumen
Specific Gravity @ 25°C	ASTM D-70	-	1.01/1.06
Penetration @ 25°C	ASTM D-5	>300	60/70
Softening point (°C)	ASTM D-36	32.5	49/56
Ductility @ 25°C	ASTM D-113	-	100 min
Loss on heating (wt %)	ASTM D-6	1.0 max	0.2 max
Drop in penetration after	ASTM D-6 & D-5	-	20 max
Flash Point (°C)	ASTM D-92	180	250 min
Solubility in CS ₂ (wt %)	ASTM D-4	99.0	99.5 min
Spot Test	AASHTO 102	Negative	Negative

Table 2 Polyethylene properties

	Grade	Melting Point (°C)	Density (gr/cm ³)
LDPE	LH0075	123	0.921
LLDPE	LL0209kj	148	0.921
HDPE	HD6070EA	132	0.960

Table 3 SBS properties

Test method	Quantity	Test
MA 04-3-064	5	Toluene soluble viscosity (Pa.s)
MA 04-3-018	0.1>	Toluene insoluble materials(%)
ASTM D-5669	0.35>	Ash content(%)

2.2. Sample preparation

Bitumen (1000gr) is added to a 2 liter flask equipped with Silverson[®] high shear mixer and a hot plate. The bitumen is stirred under 1200 rpm at 120° C, while kerosene (40 gr, 4%) is being added. Stirring at the mentioned temperature continues for another 10 minutes, then, the mixture is heated up to 180°C and the stirring rate increased to 8000 rpm. Polymer is added to the mixture at this step, in different portions. Also any kinds of additives (if applicable) are added. The process is carried out till a homogenous mixture could be visible under a microscope.

A KarlZeiss[®] (Ste-REO[™] Lumar[™]) fluorescent microscope was used to observe the homogeneity of the samples. Generally, a few drops of the sample were taken from the flask and its image is observed under the microscope. Under the fluorescent microscope the polymer rich areas would be visible in bright color (yellow), which can be distinguished from the bitumen rich areas (black or brown). Sampling is repeated every 30 min, until a homogeneous mixture of polymer in bitumen matrix is observed.

2.3. Sample testing

Different tests were performed to characterize the samples, such as softening point (ASTM D36-76), penetration (ASTM D5-97), ductility at 25°C (ASTM D113-99), ductility

at 5°C (Chinese specification GB/T 4508), thin film oven test (ASTM D1754-78), Vialit-plate adhesion test (BS EN 12272-3), and storage stability (BS EN 13399).

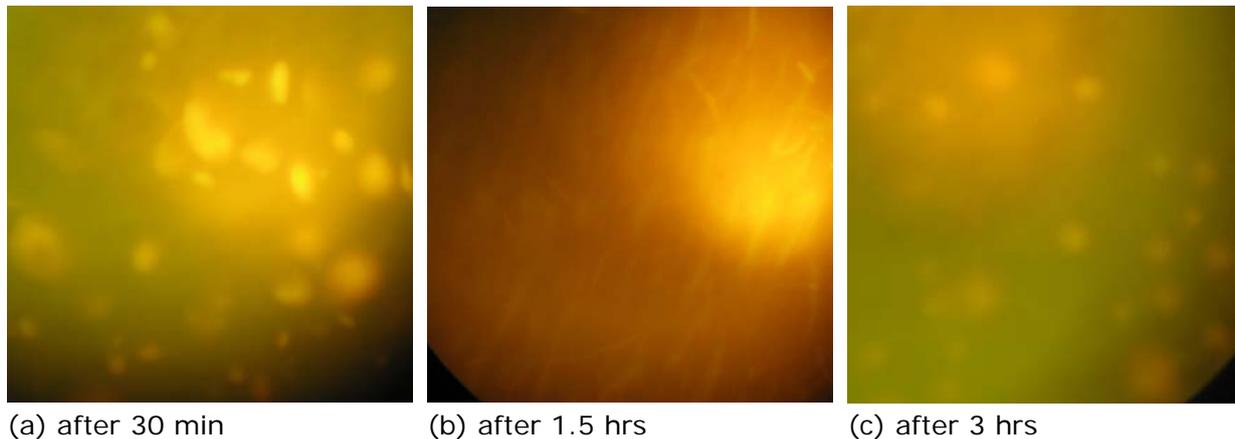
3. Results and discussion

3.1 Morphology

Mixing period must be continued until a homogenous mixture is seen under microscope. In a homogeneous mixture, PE particles become uniform spheres with equal diameters [9]. This diameter is a function of PE's molecular weight, its chain configuration, shear rate, and obviously the bitumen type [7].

Figure 1 shows the images of a sample containing 6% LDPE, after 30 minutes, 1.5 and 3 hours of mixing. Figure 1-a shows that after 30 minutes, LDPE turned to irregular shaped islands with different particle sizes. These islands show that LDPE granules swell in bitumen and start to shred under high shear mixer. After 1.5 hours of high shear mixing, LDPE particles formed needle shaped particles which floating in the bitumen matrix (figure 1-b). Finally, as it can be seen in figure 1-c, equal diameter LDPE particles will form after 3 hours. In this condition, polyethylene particles form equal diameter islands between the maltene phase of bitumen. Thus, the optimum mixing time to reach a homogeneous mixture is 3 hours.

The same processes are used for the mixtures of other polymers like LLDPE and HDPE. The main difference is that the diameter of the homogenized polyethylene particles is not the same. As can be seen from figure 2, HDPE particles have the smallest diameter and LLDPE have the biggest one.

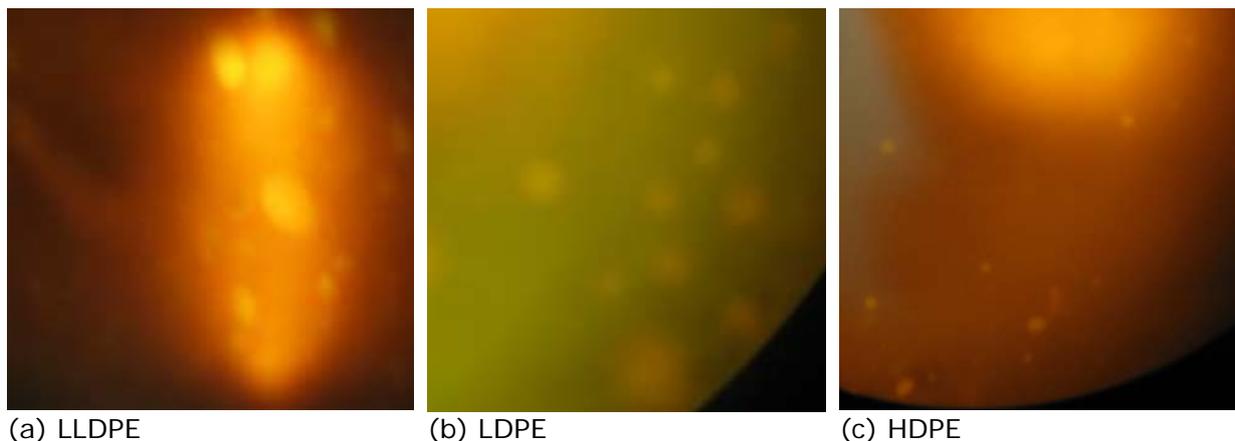


(a) after 30 min

(b) after 1.5 hrs

(c) after 3 hrs

Figure 1 Images of the sample contains 6% LDPE, scale 1:10 000



(a) LLDPE

(b) LDPE

(c) HDPE

Figure 2 Images at the end of mixing period for (a) LLDPE, (b) LDPE, and (c) HDPE, scale 1:10 000

3.2 Sample preparation and selection

Different samples with different formulation were prepared according to table 4. In the first six ones, only different grades of polyethylenes have been used. As it can be seen in table 5, addition of 2% LLDPE or HDPE causes 25°C or 20°C increase in softening points,

respectively. However, these two polymers are highly unstable in bitumen, especially at higher concentration. Therefore, the samples contain high amounts of HDPE or LLDPE ignored from the aim of this project. On the other hand, as LDPE is more stable in bitumen than others, it was considered as the main modifier agent in this work.

Table 4 Sample compositions

Code	Composition	Code	Composition
1	2% LDPE + 4% Kerosene	12	6%LDPE + 4%Kerosene + 4% B-oil
2	4% LDPE + 4% Kerosene	13	6%LDPE + 4%Kerosene + 6% B-oil
3	6% LDPE + 4% Kerosene	14	6%LDPE + 4%Kerosene + 8% B-oil
4	2% HDPE + 4% Kerosene	15	2% SBS + 4% Kerosene
5	4% HDPE + 4% Kerosene	16	5% SBS + 4% Kerosene
6	2% LLDPE + 4% Kerosene	17	4%LDPE + 4% Kerosene+2%SBS
7	6% LDPE+4% Kerosene+4% Oleic Acid	18	3%LDPE+3% Kerosene+3%SBS+4% B- Oil
8	6% LDPE+4% Kerosene+8% Oleic Acid	19	2%LDPE+2% Kerosene+2%SBS+4% B- Oil
9	6%LDPE+4%Kerosene+4% Aromatic oil	20	4%LDPE+2% Kerosene+2%SBS+4% B- Oil
10	6%LDPE+4%Kerosene +8% Aromatic oil	21	6%LDPE+2% Kerosene+2%SBS+4% B- Oil
11	6%LDPE+4%Kerosene+20% VB	22	8%LDPE+2% Kerosene+2%SBS+4% B- Oil

Table 5 Results of the samples containing polyethylenes

Sample	SP (°C)	Pen (dmm)	Ductility @ 25°C (cm)	Ductility @ 5°C (cm)	TFOT Loss (%)	Vialit	Stability
Neat bitumen	50	63	60	8	-1.86	10	Unstable
1	50	61	27.5	7	-1.73	10	Unstable
2	58.5	52.5	9.5	3.5	-0.6	35	Unstable
3	66	51	4.7	2	-0.3	40	Unstable
4	65	34	10	3.6	-1.66	15	Unstable
5	70	21	4	1.5	-0.78	30	Unstable
6	75	14	2.5	0.5	-1.77	10	Unstable
7	63	58	12	4.5	-0.33	35	Unstable
8	61	61	25	8.5	-0.38	40	Unstable
9	63	54	8.5	2.0	-0.45	35	Unstable
10	58	54	11	2.5	-0.37	30	Unstable
11	63	48	7.5	1.5	-0.43	30	Unstable
12	64	54	8.5	3	-0.52	30	Stable
13	63	56	3.5	1.2	-0.56	30	Stable
14	60	55	13.5	3.5	-0.74	30	Stable

The aging resistances of these modified bitumens are also tested. For this purpose, thin film oven test (TFOT) was accomplished at 163 °C, using the standard procedure. According to figure 3, aging resistance was also improved by addition of different kinds of polyethylenes, especially LDPE. For example, addition of 6% LDPE decreases the percentage of weight loss from 1.86 to 0.3. This sample not only shows the minimum amount of weight loss, but also it has the reasonable ranges of softening point and penetration for asphalt manufacturing purpose. Therefore, it was selected as a base material in the rest of this project.

3.3. Improvement of storage stability

One of the main methods to improve storage stability is to add some amounts of maltene-like molecules to the mixture. Therefore, we add different oil based materials such as oleic acid, aromatic oil, base oil (B-Oil) and vacuum bottom (VB) to the mixture. Kerosene which is added to all of the mixtures can not act as a dispersing agent not only

because of its non- aromatic structure but also, as most of it was vaporized during mixing period. Actually, it only adjusts the viscosity of the bituminous phase.

As illustrated in table 5, better stability can be seen in the samples containing base oil. In another word, we can produce a homogenous mixture of LDPE in bitumen, by adding sufficient amounts of base oil as a dispersion agent.

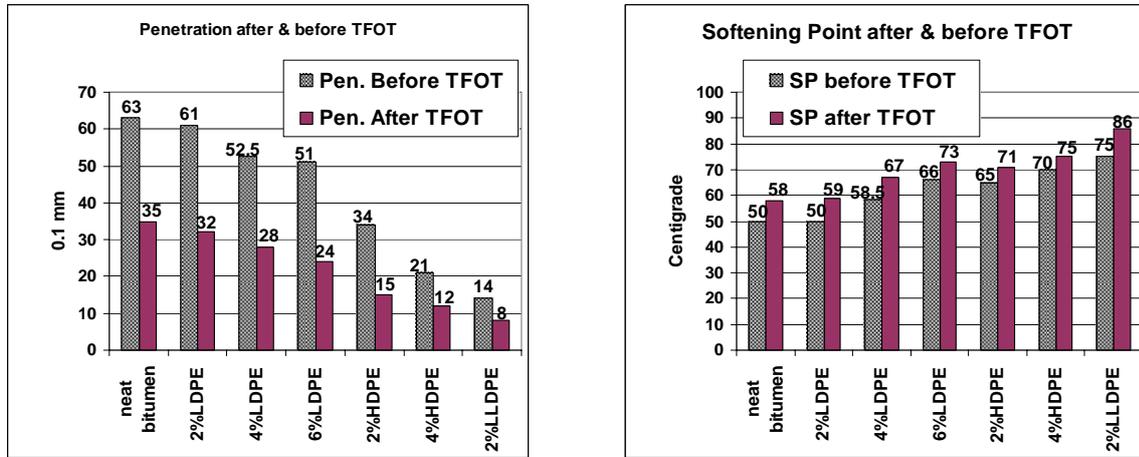


Figure 3- Results of the PE-Bitumen mixture: (a) penetration (b) softening point

3.4. Improvement of low temperature properties

Although, LDPE modified bitumen has good high-temperature properties, its low-temperature properties are still not so good. As, SBS was previously reported as a low temperature modifier [2-4], the effect of small amounts of SBS on the PE modified bitumen was examined too.

First of all, samples containing SBS as the only modifier (samples 15 and 16) were prepared. The test results are illustrated in table 6. As it can be seen from tables 5 and 6, ductility at 5°C for SBS modified bitumen are better than PE modified ones. These results show that (as expected); SBS can improve the low- temperature properties of bitumen. Finally, a mixture of SBS and LDPE was selected. According to these results, sample no 21 has desirable properties at high temperatures and acceptable ones at low temperature. Storage stability test were also done on these samples and it was seen that mixtures contain SBS, Polyethylene and B-oil shown closer top and bottom softening point therefore better stability condition.

Table 6 Results for the samples containing PE and SBS

Sample	SP (°C)	Pen (dmm)	Ductility @ 25°C (cm)	Ductility @ 5°C (cm)	Stability
Neat Bitumen	50	63	60	8	-
15	52	57	63.5	10.8	Partially Stable
16	64	33	80	15.5	Partially Stable
17	56	31.7	62.5	11.3	Unstable
18	56	35	59.8	10.9	Stable
19	55	49	54	8	Stable
20	57	41	48.5	9	Stable
21	71	40	48	8	Stable
22	> 95	33	5	1.5	Unstable
23	85.5	29	13	2	Unstable
24	84	18	18	3.5	Unstable

4. Conclusion

Although, polyethylenes do not have good stability in bitumen, it can be improved to a desirable degree by the addition of maltene-like materials into the bitumen modified mixture. Therefore, the LDPE modified bitumen can be produced for asphalt applications with reasonable stability, softening point and penetration by addition of suitable amounts of oil. Production and compaction of these modified asphalts can be done in usual

manner and it is not necessary to modify or change these processes. These asphalts are suitable for hot climate areas such as warm regions of Iran.

On the other hand, to overcome the problem of these bitumens at low temperature, it is possible to add a few percentages of SBS to the mixture. These SBS- LDPE modified bitumens would be suitable for all climate regions, except the frigid areas. Finally, as polyethylenes are locally produced and have more reasonable prices than SBS, it is possible to modify the bitumen and asphalt easily and economically.

References

- [1] Bahia H, Anderson D, "Binder Rheological Parameters: Background and Comparison with Conventional properties", *SHRP*, TRR 1488, 1994.
- [2] Massenza D, "Polymer modified bitumens, technical aspects, production & logistic", Bologna, 2nd ed. Massenza, Italy, 2002.
- [3] Bahia H, Hanson D, Zeng M, Zhai H, Khatri M, Anderson R, "Characterization of Modified Asphalt Binders in Superpave Mix Design", *NCHRP, Report 459, TRB, National Research Council, National Academy Press, Washington DC*, 2001.
- [4] Lu X, Isacsson U, Ekblad J, "Influence of polymer modification on low temperature behaviour of bituminous binders and mixtures", *Materials and Structures*, 36, 652-656, 2003.
- [5] Perez-Lepe A, Martinez-Boza F, Gallegos C, "High Temperature Stability of Different Polymer-Modified Bitumens: A Rheological Evaluation", *J. Appl. Polymer Sci.*, 103, 1166–1174, 2007.
- [6] Sirin O, Kim H, Tia M, Choubane B, "Comparison of rutting resistance of unmodified and SBS-modified Superpave mixtures by accelerated pavement testing", *Const. & Build. Mat.*, 18, 1016-1026, 2006.
- [7] Hinslioglu S, Agar E, "Use of waste high density polyethylene as bitumen modifier in asphalt concrete mix", *Materials letters*, 58, 267-271, 2004.
- [8] Polacco G, Berlincioni S, Biondi D, Stastna J, Zanzotto L, "Asphalt modification with different polyethylene-based polymers", *European Polymer J.*, 41, 2831–2844, 2005.
- [9] Wegan V, Brûlé B, "The Structure of Polymer Modified Binders and Corresponding Asphalt Mixtures", *Road Directorate, Danish Road Institute*, 87, 1999.