1026-1265/2002

Rubber-modified Bitumens

Ali Akbar Yousefi*
Department of Plastics, Iran Polymer and Petrochemical Institute,
P.O. Box: 14965/115, Tehran, I.R. Iran

Received 3 July 2001; accepted 3 July 2002

ABSTRACT

Bitumen in pure form is not suitable for modern roads and present traffic. This has forced engineers to modify bitumen to improve its performance during service life. Two routes are known for bitumen modification, namely: chemical and physical modifications. Therefore, there are chemical and physical modifiers. Among physical modifiers polymers (thermoplastics, rubbers and thermosets) are the most interesting ones. Rubbers are very good bitumen modifiers. In this work, non-vulcanized rubbers were incorporated into bitumen. The resulting range of blends showed higher and intermediate performance compared to the base bitumen. The improved properties are lower penetration degree and higher softening point. The low temperature property such as Frass breaking point was not improved. New formulae for estimating bitumen's performance using the results of conventional Frass and ring & ball tests were introduced. The morphology of the blends depending on the rheological properties and compatibility of the rubber with bitumen was different. Polybutadiene formed a continuous phase mixture in bitumen. This was observed due to the compatibility of this rubber with bitumen. Due to lesser compatibility between polymer and bitumen, SBRs and natural rubber formed polymeric inclusion dispersed in bitumen.

Iranian Polymer Journal, 11 (5), 2002, 303-309

Key Words:
bitumen,
rubber,
polymer-modified bitumen,
asphalt,
performance.

INTRODUCTION

Bitumen in pure form is not suitable for modern pavements and undergoes too many types of failure during service time. This is the reason for interests in bitumen modification field. After being clarified by many laboratory and field tests many types of materials were used to modify bitumen properties and performance [1-4]. Two types of modifications were developed such as: chemical and physical types. In chemical modification chemicals like acids and metallic oxides were

(*) E-mail: a.yousefi@ipi.ac.ir

Table 1. Rubbers' available properties [13].

Rubber	Green rubber Mooney viscosity* at 100°C (ML 1+4)	Oil content (%)	Bond styrene (%)	Ultimate elongation (35 min cure)
PBR1220	41-49	0	0	----
SBR1502	46.0-58.8	0	22.2-24.5	<350
SBR1712	42-52	0	22.5-24.5	<530
SMR 20	~90*	5	0	--

(*) Experimentally determined using Mooney rheometer.

used to modify bitumen [1]. Due to very complex structure of bitumen, chemical modifications of bitumen have not been commercialized. In physical modification the added material does not enter in any type of chemical interaction with bitumen. Therefore, in physical modification the chemical structure of bitumen is not supposed to be changed.

On the addition of polymers to bitumen, chemical composition and performance of bitumen change accordingly. The ability of polymer to absorb and/or adsorb some bitumen constituents, which are compatible with the polymer is responsible for this observation [5-7].

Among many different polymers used in bitumen modification such as thermoplastics, thermosets, thermoplastic elastomers and rubbers, the latter seems to be more attractive. Although thermoplastic elastomers such as styrene-butadiene-styrene triblock copolymer (SBS) or its hydrogenated forms and plastomers such as ethylene-vinylacetate copolymer (EVA) are good bitumen modifiers [3], rubbers are preferred due to their lower prices. In fact, bitumen is supposed to keep its physical and rheological properties constant at different service temperatures and loading conditions and transforms itself to a low viscosity Newtonian fluid at mixing temperature (165°C). This type of bitumen is called "ideal bitumen". Constant rheological properties in a wide range of temperatures correspond to rubbery behaviour [8]. It is concluded that the rubbers should be able to modify bitumen properties very well.

Therefore, many types of rubbers were introduced in bitumen (PBR, SBR and its latex, groundtire rubber etc.) [1-3, 9-11].

In the present communication we are reporting on the effect of three domestic synthetic rubbers and one grade of natural rubber on properties and performance of a locally refined bitumen.

EXPERIMENTAL

Materials

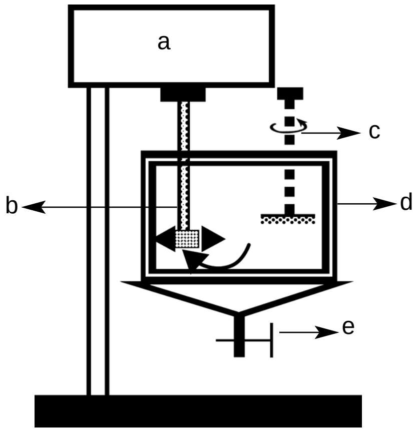
Four types of rubbers were used: The first one was polybutadiene (PBR 1220, Arak Petrochemical Co. Arak, Iran), two others were styrene-butadiene random block copolymers (SBR 1502 and SBR 1712 both from Bandar Imam Petrochemical Co.) and the fourth type was natural rubber (SMR 20). Different available properties of rubbers are listed in Table 1. A 40- and a 60/70-penetration grade bitumens from Tehran refinery were used as base bitumens and all necessary modifications were carried out as presented in Table 2.

Procedures

Rubbers were cut into small pieces prior to mixing with bitumen. The mixer assembly is shown in Figure 1. To mix bitumen and rubbers the mixer was heated up to 170°C and premelted bitumen was transferred into it. A moderate speed of high-shear mixer was adjusted (7000 rpm) at the beginning of mixing and during the first 5 min the rubber pieces were added. Thereafter, the mixing was continued for the next 20 min at a higher speed (12000 rpm). At the end of mixing process, while

Table 2. Tehran's refinery 60/70-penetration grade bitumen composition [14].

Saturates (%)	Naphthene aromatics (%)	Polar aromatics (%)	Asphaltene (%)
38.1	39.38	35.43	10.26



(a) Primary high-speed motor; (b) Disintegrator head; (c) Propeller mixer; (d) Mixing vessel; (e) Drain valve

Figure 1. The schematic representation of a mixer set.

mixers were operating at low speed, samples for penetration and ring & ball tests were taken from the mixer drain valve. The rest of samples was cooled in metallic cans and optical microscopy and Frass test samples were taken from this part of the blend. Conventional bitumen tests were carried out according to Iranian National Standards (2950, 2951 and 3867). The morphology of the samples was viewed on a Zeiss optical microscope (Jenapol model) and optical micrographs were taken using the same microscope.

Penetration index for bitumens is calculated using the following equation:

$$PI = \frac{20 - 500A}{1 + 50A}$$

where, $$A = \frac{\log 800 - \log(\text{Pen at } 25^{\circ}C)}{T_{R\&B} - 25}$$

At this stage we have access only to conventional test equipment and have no means to determine bitumen performance. In the past, an empirical correlation was found between Strategic Highway Research Programmme (SHRP) high temperature criterion obtained from dynamic shear rheometer (DSR) and softening point of bitumen [1,5]. This is expressed as the first part of the following equations:

$$T_{DSR} \cong T_{R\&B} + 20$$
$$T_{BBR} \cong 2(T_{Frass})$$

Therefore, $$PG = T_{DSR} + T_{BBR}$$

Another idea has merged for the possibility to be able to find any type of correlation between the low temperature criterion of SHRP system and Frass breaking point. Some experimental data were already available [1, 5-7]. Accordingly, the second part of the above equations was proposed [12]. Consequently, the last part of these equations was completed using the conventional bitumen testing equipment. It should be noted, however, that the outcomes of these equations are not fully compatible with SHRP equipment data. Therefore, an evaluation of their correctness should also be accomplished using SHRP equipment.

RESULTS AND DISCUSSION

Conventional Tests

The results of the conventional bitumen tests for the 40-penetration grade bitumen and its blends are summarized in Table 3. The properties and performance of the blank bitumen are also reported in the table. This facilitates the subtraction of aging effect on bitumen properties during mixing. Using the equations introduced in experimental section, we are able to estimate the performance grade of the bitumen using conventional tests. This is reported for the first time here. This is not a precise method. It can only help to roughly estimate a bitumen performance in the absence of SHRP equipment. However, for the first time the performance grade of 40-penetration grade bitumen of Tehran's refinery was estimated to be PG=70-16. Upon undergoing the mixing conditions, the blank bitumen shows lower penetration and higher softening point. This leads to a more negative penetration index (PI) compared to the base bitumen, which is not favourable. However, due to rising Frass temperature the PG of this bitumen has changed to PG=76-10, which means the bitumen performance grade is improved at high temperature and it is deteriorated at low temperature.

As it is seen in Table 3, addition of PBR1220 to the base bitumen increases the softening point and Frass breaking point and decreases penetration compared to those of original bitumen. However, the properties of this composition are better than those of the control bitumen. For example, higher penetration and softening point and lower Frass point which result to a positive PI and PG=82-10. These observations translate to lower temperature susceptibility and one performance grade

Table 3. Bitumens properties.

Sample	Penetration at 25°C (0.1 mm)	Softening point (°C)	Frass breaking point (°C)	Penetration index	Performance grade
Base 40 bitumen	39	54	-8	-0.625	70-16
Control bitumen	20	60	-5	-0.769	76-10
5%PBR1220	32	65.2	-5.5	0.969	82-10
5%SBR1502	38	67.4	-7.6	1.733	82-10
5%SBR1712	24	62.1	-3.7	0.157	82-4
5%SMR 20	26	64	-5	0.435	82-10

improvement at high temperature compared to that of the control bitumen.

Surprising aspect is that the poor properties are observed for SBR1712 blend in bitumen. As a matter of fact, this copolymer is not a pure copolymer and contains a quantity of oil (say 5%). The reason for extending rubber is that the processing of this rubber is easier in the presence of oil. However, in bitumen medium this additive does not play a positive role and makes bitumen very brittle at low temperatures and results in PG=82-4. Morphological observation should help to explain this point, as it is explained in morphology section.

Incorporation of SBR1502 in bitumen results in recovery of the base bitumen properties with an improvement in high temperature consistency, which in turn induces an improvement in performance grade (PG=82-10) (Table 3). The PI of this blend is located around +1, which is more or less favourable for paving purposes. The highest penetration and softening point along with the lowest Frass point among the series is observed for this blend. This could be resulted from purity of the composition as indicated in morphology section.

Natural rubber is a very high molecular weight polymer and contains some impurities. Due to these facts dispersing these giant rubber molecules in bitumen is not an easy task. However, our laboratory high-shear mixer was able to disperse SMR 20 in bitumen. The resulting blend is very stiff and brittle. This should be originally related to the absorption of bitumen constituents by SMR 20. Absence of any oil readily makes bitumen brittle [5, 6, 9]. This results in a positive PI (+0.435) and a performance grade of PG=82-10.

As it is clear, oil absorption by rubber makes the modified bitumens more brittle at low temperatures. This shortcoming could be overcome using some petroleum fraction oils like heavy vacuum slops and vacuum bottom to compensate for the bitumen oil lost [9].

The results of conventional tests and estimated PG for 60/70-penetration grade base, control and rubber-modified bitumens are listed in Table 4. As it is noticed

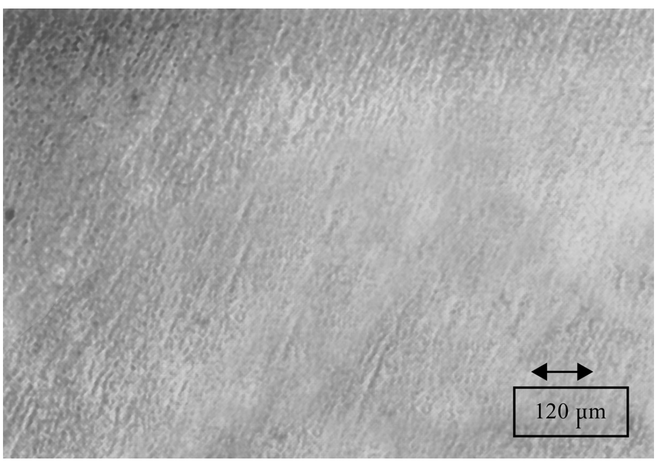


Figure 2. The state of dispersion of 5% PBR1220 in base bitumen.

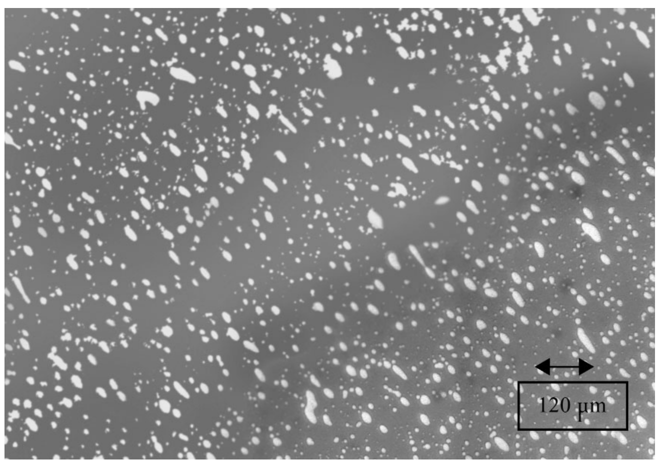


Figure 3. The state of dispersion of 5% SBR1712 in base bitumen.

Table 4. Different properties of 60/70-bitumen and its modified forms.

Sample	Penetration at 25°C (0.1mm)	Softening point (°C)	Frass breaking point (°C)	Penetration index	Performance grade
Base 60/70 bitumen	64	49.5	-12	-0.754	64-22
Control bitumen	37	63	-9	0.909	85-16
5%PBR1220	50	69.5	-8	2.765	88-16
5%SBR1502	30	63	-12	0.526	82-22
5%SBR1712	34	65	-7	1.111	82-10
5%SMR 20	33	68	*	1.538	88-?

(*) The test was impossible to do.

in the table the 60/70 base bitumen is of better properties at low temperature compared to 40-penetration grade. However, the PI of this bitumen is negative and its PG does not exceed 90. Upon mixing in the absence of any polymeric modifier, the control bitumen properties are very different from those of the base bitumen.

Compared to 40-penetration grade bitumen almost the same trend in properties and performance grade is observed for these bitumens. Addition of PBR1220 results in one performance grade (PG) improvement at high temperature and at low temperature it remains insensitive to rubber presence compared to the control bitumen. This could be related to the strong affinity of PBR towards bitumen constituents (Table 5). This in turn results in a higher Frass temperature or more brittle bitumen at low temperatures. SBR1502, which contains some aromatic segments, absorbs different bitumen constituents makes the resulting bitumen more resistant to thermal cracking at low temperatures.

However, this random copolymer is not able to improve the high temperature properties of bitumen with respect to the control bitumen. If this blend is compared with the base bitumen, the PG is improved by three levels of grades at high temperature, whereas, no change at low temperatures is attained. This is an advantage and it singles out this blend as the best formulation. As an unexpected result, SBR1712 deteriorates low temperature performance of bitumen. In the case of SMR 20 very good improvement in performance is noticed at high temperatures. Comparing the results reported in Tables 3 and 4, it is observed that the blends of softer 60/70 bitumen are of higher softening points. Even the control bitumen in Table 4 is of a higher softening point. This clearly shows the differences between the composition of the employed base bitumens.

Table 5. Solubility parmeters of rubbers and bitumen[1].

Polymer or bitumen	Solubility parameter
Polybutadiene	8.4
Polystyrene	9.1
Natural rubber (NR)	8.1
SBR	8.4-9.1*
Bitumen	8.4-9.3

(*) The actual value depends on bond styrene percent.

Morphology

The state of dispersion of the tested rubbers in bitumen medium is shown in Figures 2-5. As it is observed, PBR1220 forms a continuous phase, whereas, others disperse in bitumen (Figure 2). This difference is essentially related to the higher solubility of PBR in bitumen. Due to their solubility parameters (Table 5), other rubbers form polymer inclusions (Figures 3-5). There is a notable difference between two SBRs. The SBR1502 forms much finer particles in bitumen than SBR1712. This could mainly be due to Mooney viscosity of the SBRs (Table 1). Due to higher rheological properties of SMR 20 compared to other rubbers the particle size of its particles in bitumen is much larger. This could account for the lower penetration of the resulted polymer-modified bitumens and brittleness of the blends of this rubber at low temperatures.

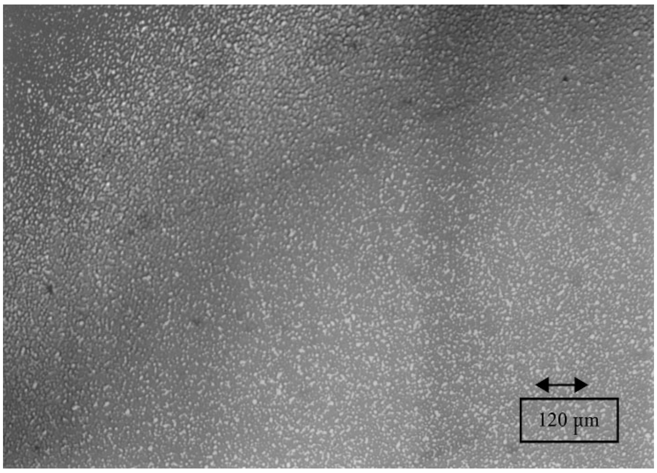


Figure 4. The state of dispersion of 5% SBR1502 in base bitumen.

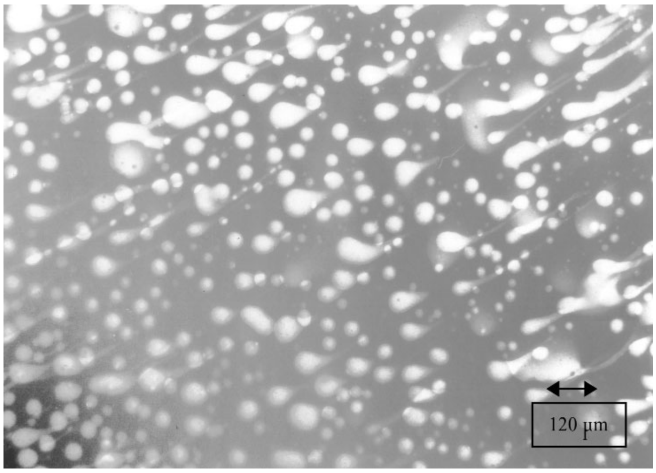


Figure 5. The state of dispersion of 5% SMR 20 in base bitumen.

CONCLUSION

Four different types of rubber including synthetics were introduced in bitumen and their properties were studied. Based on the obtained results, polybutadiene forms a continuous phase in bitumen and improves the performance of bitumen at high temperature via increasing its consistency. SBRs are different from each other. SBR1712 improves the high temperature properties, whereas, it makes bitumen more brittle at low temperature. This could be the result of the additive's presence such as carbon black etc., in this copolymer. However, this copolymer increases the performance of the bitumen at high temperatures. SBR1502 recovers all properties of the base bitumen with exception of the increasing its performance at high temperatures. Natural rubber stiffens bitumen, which results in better performance at high temperatures and it makes bitumen brittle at low temperatures. All these observations show a necessity for addition of proper oil fraction such as heavy vacuum slops and vacuum bottom to compensate the part of bitumen ingredient that are absorbed by polymer. This will reduce low temperature brittleness of bitumen. The blends of softer bitumen (60/70) with these rubbers are of higher penetration and softening point with respect to those of harder bitumen. Regarding the PG of two series of blends those of the second series are better. The proposed equations are very easy to use and by justification it could be used to estimate bitumen performance using non-expensive equipment.

ACKNOWLEDGEMENTS

The author wishes to acknowledge Iran Polymer and Petrochemical Institute for assisting to purchase and donate some raw materials and mixing equipment. The author also appreciates all efforts of Mr Sadeq Ehsani for his essential helps in preparing the blends.

REFERENCES

1. Yousefi A.A., PhD dissertation, "Preparation and rheological behavior of polymer-modified asphalts", Department of Chemical Engineering, Laval University, Canada (1999).
2. Walter H.F., Ed., *Use of Waste Materials in Hot-mix Asphalt,* ASTM Special Technical Publication, 1193 (1993).
3. Routes/Roads, "Modified binders, binders with additives and special bitumens", World Road Association, PIARC, No. 303, III (July 1999).
4. Liants Hydrocarbonés, École Nationale des Ponts et Chaussés, Québec, January 21-24 (1992).
5. Yousefi A.A., Ait-Kadi A., and Roy C., "Effect of used-tire derived pyrolytic oil residue on the properties of polymer modified asphalts", *Fuel*, **70**, 975-986 (2000).
6. Yousefi A.A., Ait-Kadi A., and Roy C., "Composite asphalt binders: Effect of modified recycled polyethylene on asphalt", *J. Mat. Civil Eng.*, **12**, 113-123 (2000).
7. Ait-Kadi A. and Yousefi A.A., "Stable paving composition having improved low and high temperature properties", *U.S. Patent*, 6,359,033, March 19 (2002).
8. Dealy J.M. and Wissbrun K.F., *Melt Rheology and its Role in Plastics Processing: Theory and Applications*, Van Nostrand Reinhold, New York (1990).

9. Yousefi A. A., "Polymer-modified paving bitumens", Iran Polymer Institute's Research Project Report No. 798CH366 (2001).
10. Heitzman M., "Design and construction of asphalt paving materials with crumb rubber modifier", Transport Research Record, No. 1339, 1-8 (1992).
11. Abdelrahman M.A. and Carpenter S.H., "Mechanism of interaction of asphalt cement with crumb rubber modifier", Transport Research Record, No. 1661, 106-113 (1999).
12. Yousefi A.A., "New polymeric blends for bitumen modification", 1st Statewide Seminar on Building Membranes (in Persian), Mashad, Iran, October 16-17, 19-27 (2001).
13. Polymers, Petrochemical Commercial Co., (2000).
14. Nazarbeigi A.E., MSc. dissertation (in Persian), Amir Kabir University of Technology, Tehran, Iran (1992).