

A performance grade of polymer - modified bitumen, according to SHRP specifications

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Summary

This paper present some results obtained on the evaluation of various bituminous binders used in rehabilitation, modernization and maintenance works, involving the SHRP/SUPERPAVE equipments and specifications, based on the performance criteria, in conjunction with the classical methods as those involving the thermal susceptibility, Fraass breaking point and chemical composition. The paper also includes recommendations concerning the improvement of the performance of these binders, by modification either with SBS or reactive polymers.

KEYWORDS: bitumen, performance grade, SBS polymer, reactive polymer, shear module, stiffness module.

1. INTRODUCTION

Bitumen is a visco-elastic material; its mechanical properties are influenced by time and temperature. During the service ability period, changes occur in the bitumen chemical composition, which lead to changes in the rheological behavior. In normal exploitation conditions, the behavior of the bitumen may be satisfying but in severe conditions the bitumen may suffer permanent deformations or cracks due to fatigue. In order to cope with the modern requirements, respectively obtaining a high plasticity limit, the bitumen can be modified by polymer addition.

Generally, polymers are used to modify bitumen for:

- increase the strength to permanent deformations (ruts) [1-6] by increasing the stiffness of the bitumen or by intensifying the elastic behavior;
- increase the strength to thermal and fatigue cracks [7];
- increase ageing and abrasion resistance;
- increase durability of asphalt pavement surface [2, 8].

Polyethylene, polypropylene, polystyrene and ethylene vinyl acetate copolymers are the main plastomers (synthetic polymers) studied for the modifying road binders; as for elastomers, the copolymers of styrene with butadiene are the best for modifying the bituminous binder [9]. These polymers are generally dispersed in the



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bitumen and if there isn't a good compatibility bitumen-polymer, a phases agglomeration may appear. To eliminate the problems of separation which may appear relative to storage stability of polymers modified bitumen, Du Pont Company produces an ethylene copolymer, respectively ethylene glycidyl acrylate (EGA), with the commercial name Elvaloy AM, which reacts easily chemically with bitumen and eliminates the problems regarding the phase separation [10]. This copolymer improves the properties of asphalt mixture at high temperatures, permanent deformation strength, susceptibility at temperature and also improves the creep compliance.

During the last decade, as in other European countries, the technical specifications regarding the road binders based on the performance criteria, elaborated within the American research program SHRP (Strategic Highway Research Program), produced a significant impact on the research directions as on the road technologies used in our country.

It is a well known fact that the main mechanisms which lead to deterioration of bituminous pavement surface are:

- permanent deformations and rutting phenomena at high exploitation temperatures, during summer time;
- fatigue phenomena under cycling load due to traffic, at normal temperatures;
- appearance of fissures on the road pavement surface at low exploitation temperatures, during winter time.

The SHRP specifications are able to evidence these mechanisms, as they are applicable to original bitumens as for modified bitumens with reactive or inert polymers.

Generally, most of the bituminous binders in initial state, regardless of their origin (made in /outside Romania) can't be considered proper for the high traffic roads. Consequently, specific research activities are initiated in our country, in order to improve the performance of bituminous binder requirements for the extremely severe climatic and traffic conditions specific to our national road network, using in this scope different polymers.

For this purpose, the bituminous binders having the penetration class D60/80 and D 80/100 have been modified with the SBS, respectively EGA polymers, evaluating their influence on the rheological characteristics and performance grade.

2. RESULTS AND DISCUSSIONS

The bitumen is a complex material, with a different behavior depending on temperature and time of loading (cyclic loads). At a high temperature and under



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long time loading bitumen behaves like a viscous liquid and flows (the response is instantaneous, without phase delay) but at low temperature and under short time loading, the bitumen behaves like an elastic solid (the response versus the loading is delayed with a 90° angle). At a corresponding temperature for service of most bituminous pavements under traffic, the bitumen behaves like a visco-elastic material, the delay between load and response is δ , from 0 to 90° .

Usually, up to their consistence, the road bitumens are divided in penetration classes (40/60, 60/80, 80/100). Since this classification isn't completely reflecting the viscous-elastic behavior of bituminous binder, a new classification methodology was established within SHRP, the performance grade (P.G.), depending on the maximum and minimum designed temperature for the road structures, considered as representative temperatures, as follows:

T max – the maximum designed temperature – represents the maximum average temperature measured in 7 days consecutively inside the road pavement, during the summer;

T min - the minimum designed temperature – represents the lowest temperature measured on the surface of the pavement, during the winter;

Example: PG: 64 - 28/the first number indicates the maximum temperature and the second indicate the lowest temperature at which the binder corresponds to the requirements taken into account during the design phase.

The parameters used for establishing the performance grade are: complex shear module G^* , phase angle δ , stiffness module S and the slope m .

Two shapes of G^* and δ have been used [11]:

- the ratio $G^*/\sin \delta$ which characterizes the behavior of bitumen at high temperature and may be used to evaluate the permanent deformations;
- the product $G^* \sin \delta$ which characterizes the behavior of bitumen at intermediate temperature and may be used to evaluate the fatigue cracking;

According with SHRP specifications [11]:

- the value $G^*/\sin \delta$ must be greater than 1,0 KPa for original bitumen and 2,2 KPa for aged bitumen; for a good resistance to permanent deformation, it is advisable that the value $G^*/\sin \delta$ to be as large as possible (G^* large values and $\sin \delta$ small values);
- the value $G^* \sin \delta$ must be smaller than 5000 KPa. To ensure good fatigue strength to cracking, the bitumen should behave like an elastic material. The 5000 KPa value is established because both the viscous and elastic parts may become too high and the bitumen would no longer be able to effectively resist to fatigue cracking;
- the value of the stiffness module must be max. 300 MPa. If the stiffness is too large, the bitumen behaves like a fragile material, at low temperatures



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cracking may appear. At low temperatures the values of stiffness module range are between 30 MPa and 300 MPa, so at the imposed value, 300 MPa the cracking phenomena is prevented.

- the slope m must have large values because at temperature changes and thermal efforts accumulation, the stiffness are changing relatively quickly and the bitumen may dissipate the efforts, such the cracking phenomena is avoided; SHRP specifies a minimum value of m at 0.3.

The values of the shear module and phase angle are determined for a temperature range between $46^{\circ}\dots 81^{\circ}\text{C}$ and the values to the stiffness module and the slope between $-6^{\circ}\dots -40^{\circ}\text{C}$; the performance grade represents the corresponding temperatures at which the parameters simultaneously equals the imposed values. In the case of negative temperatures, -10°C must be added to the test temperature when the imposed value is reached. The corresponding temperature which fulfills the previously specified requirements varies, regardless of the type of the bitumen (bitumen in initial state or modified).

In the present paper, binders with penetration class D 60/80 and D 80/100 (made in/outside Romania) are divided on their performance grade according to SHRP methods (Table 1), with the aid of previously mentioned parameters. The Fraass breaking point (the minimum temperature corresponding to appearance of cracks for a thin bitumen film in bending) is compared to the temperature corresponding to the maximum value of stiffness module of 300 MPa.

The temperatures from Table 1 represent the testing temperatures at which the values of the determined parameters correspond to the technical conditions imposed by SHRP specifications.

From the analysis of data specified in the Table 1 it results that some of the local binders (B), or imported (C) are divided in performance grade totally inadequate to the specific conditions to the public road network in our country. The studied binders show extremely low performance at negative temperature, results obtained with the SHRP tests (results in bending for B and C sample) and for the classical tests (Fraas). At high temperatures similar results are obtained. The penetration index PI reveals that the analyzed samples show significant thermal susceptibility at positive temperatures during the hot season.

The penetration index PI is a measure of susceptibility of bitumen on temperature; the negative or positive values of PI indicate susceptibility at positive or respectively negative temperatures [9]. The practice shows that binders having PI values in the range of $-1.0 < \text{PI} < +0.7$ ensure a satisfying behavior of asphalt mixtures in exploitation.



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Table 1: Evaluation of performance grade for indigenous (A, B) or imported (C) bitumen used in the road field

Source:	Technical Condition	A		B		C
Bitumen type		D60/80	D80/100	D60/80	D80/100	D60/80
Performance grade: PG X-Y		58 - 34	58 - 34	58 -16	52 - 16	58 -22
Breaking point Fraass, (°C)	max.-13	-23.7	- 24.1	- 16.5	- 15.1	- 10.1
Shear on original bitumen						
Temperature, (°C)	X	58	58	58	58	58
Ratio G*/sinδ, (kPa)	min.1.0	1.6	2.1	1.7	1.2	1.9
Shear on RTFOT ¹ aged bitumen						
Temperature, (°C)	X	64	64	58	52	58
Ratio G*/sinδ, (kPa)	min.2.2	3.98	2.4	3.5	5.1	3.7
Shear on PAV ² aged bitumen to 100°C						
Temperature, (°C)	-	19	13	22	19	22
Product G*x sinδ, (kPa)	max.5.000	1817.6	2271.1	4028.8	4793.1	4423.1
Bending on PAV aged bitumen to 100°C						
Temperature, (°C)	-Y	- 24	-24	-6	- 6	-12
Stiffness modulus S, (MPa)	max.300	181.96	161.13	108.3	101.2	287.1
Slope m	min.0.3	0.322	0.340	0.315	0.325	0.307
Penetration index IP, on original bitumen	-1<IP<+1	-0.83	-1.4	-0.98	-1.79	-1.75
Chemical composition (IATROSCAN) (%)						
Saturates	5...20	13.9	16.0	8.9	9.48	3.8
Aromatics	40...60	31.1	27.4	39.4	41.8	52.9
Resins	33...36	36.1	36.1	36.8	36.5	27.6
Asphaltenes	5...25	19.7	20.5	14.9	12.2	15.7
Coloidal instability index, Ic	max. 0.5	0.5	0.57	0.31	0.28	0.24

1 – rolling thin film oven test; 2- pressure aging vessel

In order to improve the qualities of these binders and getting them to the desired performance grade, researches were initiated regarding the use of different modifiers.

For improving the qualities of bitumen in initial state for the climate conditions in our country the modifiers should fulfill more conditions: improve the performances at high and low temperatures, ensure the stability of binder-modifier mixture during its stocking and preparation of the asphalt mixture.



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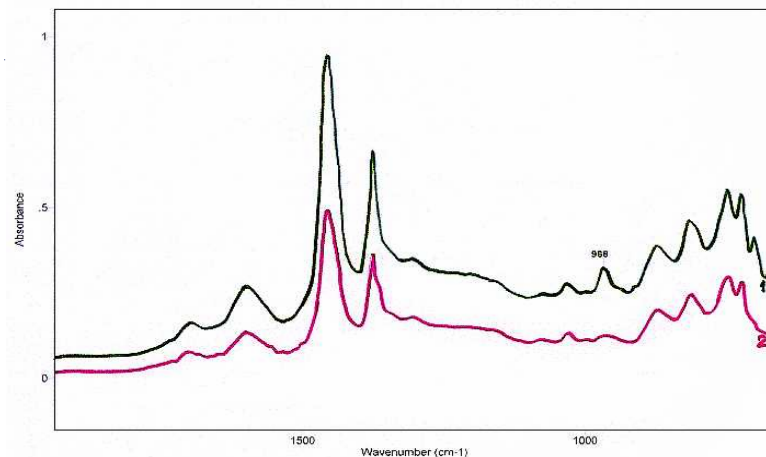


Fig. 1 – IR spectra of the bitumen in initial state (2) and SBS polymer modified bitumen (1)

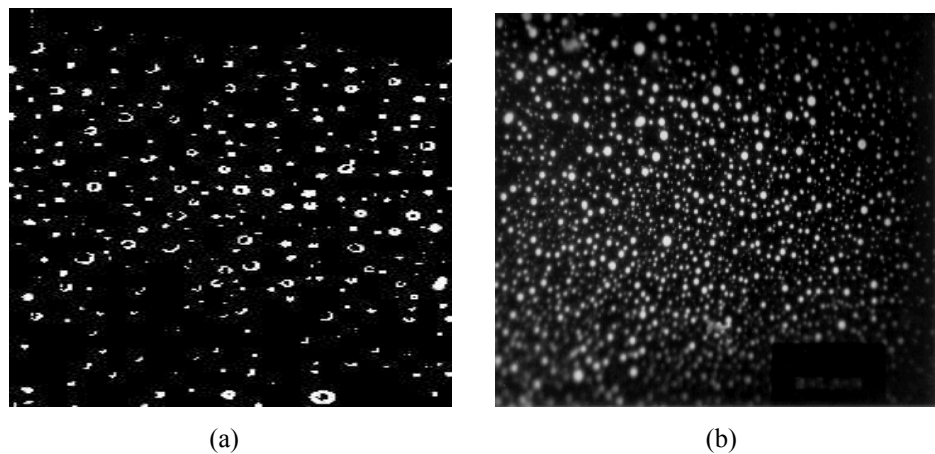


Fig.2 –Bitumen A 60/80 (a) and bitumen B 60/80 (b) modified with SBS polymer

For this purpose polymer SBS, respectively reactive polymer EGA – Elvaloy AM were used. The polymer was added as grains/powder in the preheated bitumen mass (175° - 180°C); the mass is continuously mixed with a speed to 250 rotations/min for 2,5 hours.

In the case of SBS the modification was evidenced by recording the IR spectra (Fig. 1) of original and modified bitumen (the absorption strip corresponding to the 965 ± 5 nm wavelength and a vibration of $=\text{C-H}$ bond outside the plane of 1,4 trans butadiene in SBS, the missing strip in the unmodified binder) and also by



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fluorescent microscopy, evaluating the polymer dispersion degree within the bitumen (Fig. 2).

Notice that in the case of bitumen having an increased aromatic content (B), and accordingly a lower colloidal stability index (increased bitumen-polymer compatibility), the dispersion of the polymer within the bitumen is better (Fig. 2, b).

The evaluation of performance grade of SBS and Elvaloy AM modified bitumens is shown in Tables 2, 3.

Table 2: Evaluation of performance grade for indigenous bitumen A and modified with SBS polymer B bitumens

Source Bitumen type	Technical Condition	A D 60/80		A D 80/100	B D 60/80
SBS polymer content		+4%	+5%	+4%	+4%
Performance grade, PG X-Y		76-34	76-34	76-34	70-28
Breaking point Fraass, (°C)	-	-24	-24	-24	-18
Shear on original bitumen					
Temperature ⁽¹⁾ , (°C)	X	76	76	76	70
Ratio G*/sinδ, (kPa)	min. 1	1.47	1.50	1.30	2
Shear on RTFOT aged bitumen					
Temperature ⁽¹⁾ , (°C)	X	76	76	76	70
Ratio G*/sinδ, (kPa)	min.2.2	2.8	3.4	2.50	4.3
Shear on PAV aged bitumen to 100°C					
Temperature ⁽¹⁾ , (°C)	-	13	13	13	19
Product G*x sinδ, kPa	max.5000	3769	2843	3425	4800
Bending on PAV aged bitumen to 100°C					
Temperature ⁽¹⁾ , (°C)	Y	-24	-24	-24	-18
Stiffness modulus S, (MPa)	max.300	178	121	168	280
Slope m	min.0.3	0.367	0.367	0.300	0.320

1. (1) Temperature of testing for reached corresponding value of impose technical condition.

On the basis of the results shown in Table 2 it is observed that the temperature at which the corresponding technical SHRP parameters are fulfilled is improved by using SBS polymer. For the bitumen sample at initial state the ratio $G^*/\sin\delta$ (the elastic component) reaches the imposed value at 58°C; in the case of modified bitumen, the corresponding temperature for reaching the imposed value is 76°C for A bitumen and 70°C for B bitumen; the performance grade at higher temperature increases for all the bitumen types (from PG 58 to PG 76, in the case of A bitumen and from PG 58 to PG 70 in the case of B bitumen) (Fig.3 and 4).

In the case of SBS polymer modified bitumen its behavior improves at high temperatures, the elastic component improves the strength to permanent deformations. By modification with polymer the viscous component, $G^*\sin\delta$,



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increase for a given temperature, this meaning a lower fatigue strength. Regarding the behavior at low temperature, the Fraas breaking point is improved in the case of indigenous bitumen B (from -16.5°C to -18°C) and practically remains constant for the A bitumen (-24°C).

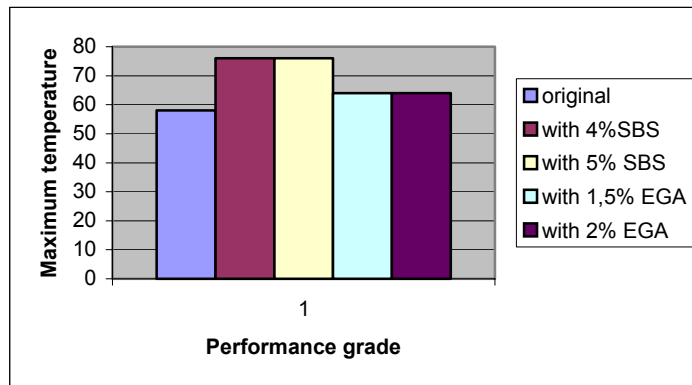


Fig.3 – Original and modified indigenous bitumen type A60/80. Performance grade to high temperature

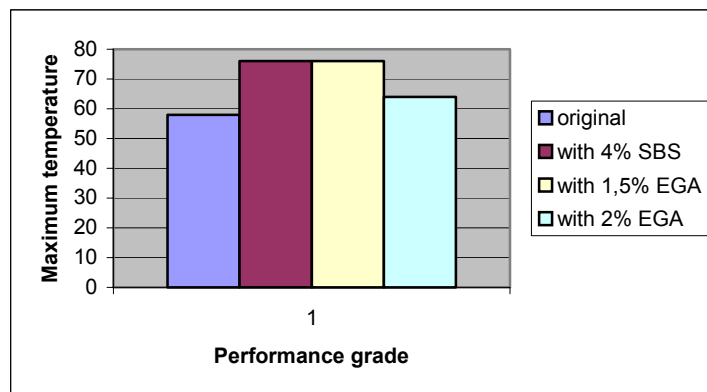


Fig.4 – Original and modified indigenous bitumens type A80/100. Performance grade to high temperature

This fact is correlated to the results obtained from bending, the temperature corresponding to the SHRP imposed value of stiffness module is -18°C in the case of B bitumen, and -24°C for A bitumen. So, adding the polymer improves also the performance grade at low temperature in the case of B bitumen (from PG -16 to PG -28).



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Even though the modification with polymer does not improve the performance grade at low temperature for all the studied bitumens, the SBS modified bitumen versus the original one show a lower stiffness; the polymer improves the relaxation of bitumen under effort.

Table 3: Evaluation of the performance grade for indigenous bitumen A/B and imported bitumen C modified with reactive polymer Elvaloy AM

Source Bitumen type	Technical condition	A D 60/80		A D 80/100		C D 50/70
Reactive polymer content		1.5 %	2 %	1.5 %	1.75%	1.5%
Performance grade: PG X-Y		64-34	64-34	76 -34	64 -34	64 -22
Breaking point Fraass, (°C)	-	-27	-27.5	- 28	- 29	- 17.3
Shear on original bitumen						
Temperature ⁽¹⁾ , (°C)	X	64	64	76	64	64
Ratio G*/sinδ, (kPa)	min.1.0	1.7	1.8	1.2	1.9	1.2
Shear on RTFOT aged bitumen						
Change of mass, (%)	-	0.186	0.148	0.242	0.236	+ 0.112
Temperature ⁽¹⁾ , (°C)	X	64	64	76	70	64
Ratio G*/ sinδ, (kPa)	min.2.2	4.3	4.5	4.0	3.7	2.4
Shear on PAV aged bitumen to 100°C						
Temperature ⁽¹⁾ , (°C)	-	13	13	19	16	19
Source Bitumen type	Technical condition	A D 60/80		A D 80/100		C D 50/70
Product G*x sinδ, (kPa)	max.5.00 0	3530	3363	2156.4	2156.4	4546.9
Bending on PAV aged bitumen to 100°C						
Temperature ⁽¹⁾ , (°C)	-Y	-24	-24	-30	-24	-12
Stiffness modulus S, (Mpa)	max.300	236.5	243.3	288.5	137.5	299.0
Slope m	min.0.3	0.361	0.326	0.347	0.381	0.304
Penetration index PI, original bitumen	-1<PI<+1	+0.3	-0.42	+ 0.57	-0.62	-0.2
Chemical composition (IATROSCAN) (%)						
Saturates	5...20			8.3	21.8	3.5
Aromatics	40...60			37.0	19.2	52.1
Resin	33...36			26.2	30.6	27.7
Asphaltene	5...25			28.5	28.4	16.6
Coloidal instability index, Ic	max.0.5			0.6	0.94	0.25

(1) – Temperature of testing for reached corresponding value of imposed technical condition.

From the results shown in Table 3, we notice that using reactive polymers for modifying the bitumen at initial state gives the advantage of a simpler technology; this implies a smaller polymer content (1...2;%); the polymer reacts with



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asphaltene from the bitumen at initial state and the result is a stable combination, bringing the bitumen to the desired performance grade and also improving the thermal susceptibility (improved penetration index).

Modified bitumen with reactive polymer shows smaller values of ratio $G^*/\sin\delta$ corresponding to SHRP method, at higher temperatures than those corresponding to bitumen at initial state, this leads to improvement of performance grade at positive temperatures from PG: 58 to PG: 64 and PG: 70, in the case of indigenous bitumen, respectively from PG: 58 to PG: 64, in the case of imported bitumen. This classification shows that the bitumens modified with reactive polymer EGA versus bitumens in initial state, have a better strength to permanent deformations.

Even if Fraass breaking point is improved by adding the reactive polymer EGA (from -24°C to $-27^{\circ}\text{C}/-29^{\circ}\text{C}$, in the case of indigenous bitumen and from -10°C to -17°C , in the case of imported bitumen), the temperature for SHRP, the corresponding values of stiffness module, and the slope m remain the same in the conditions of an unimproved performance grade (PG: -34 for indigenous bitumen and PG: -22 for import bitumen). Even more, the stiffness module recorded at the classification temperature shows higher values for the modified bitumen, so the EGA reactive polymer shows a lower ability of improving the relaxation of bitumen under effort, in comparison to the SBS polymer.

3. CONCLUSIONS

SHRP specifications based on the rheologic parameters (parameters completely reflecting the viscous-elastic behavior of bitumen) determined for the climate and traffic conditions in our country, proved to be a very important instrument in the evaluation of the performances of indigenous and import bitumens and also in quantifying the effect of different techniques for improving their quality.

SHRP tests on unmodified and modified bitumen prove the increase of performance in the case of bitumen modification with polymer.

Bitumen modified with SBS and EGA polymer show improvement of the performance grade at high temperature, leading to a better strength to permanent deformations. Depending on the type of the bitumen base, these polymers also improve the performance grade at low temperature.

Use of bitumen modified with reactive polymer, compatible to all studied bitumen types implies simplified technology and reduced production cost.

The adequate bitumen, with the required performance grade, may be selected according to the different climate and traffic conditions in our country.



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