

ESTUDIO COMPARATIVO DE LA ACCIÓN DE DOS COPOLÍMEROS TRIBLOQUE DE ESTIRENO-BUTADIENO-ESTIRENO (SBS) PARA LA MODIFICACIÓN DE LAS PROPIEDADES DE UN ASFALTO PERUANO

Wendy Herencia^a, Juan Carlos Rueda^{b*}

RESUMEN

Se prepararon asfaltos modificados con polímeros mezclando dos copolímeros lineales comerciales de bloque de estireno-butadieno-estireno (SBS-1 y SBS-2) con un asfalto de origen peruano (PEN 60/70). Se realizó un estudio comparativo de la influencia de SBS-1 y SBS-2 en las propiedades físicas y reológicas del asfalto. La caracterización de los copolímeros SBS se realizó mediante técnicas de RMN, FTIR y GPC. Mediante análisis de ¹H RMN, se determinó que la principal diferencia en la composición química de SBS-1 y SBS-2 radicaba en que el copolímero SBS-2 presentaba 36 % mol de grupos 1,2-vinilpolibutadieno, mientras que el copolímero SBS-1 solo 11 % mol. Las pruebas reológicas demostraron que el aditivo SBS-1 tuvo un mayor rendimiento que el aditivo SBS-2 en la mejora de las propiedades reológicas del asfalto modificado, como la resistencia a la deformación y elasticidad. Esto permitió que el asfalto modificado con polímero SBS-1 se clasifique para pavimentos de más altas exigencias.

Palabras clave: Asfalto modificado, copolímero tribloque-SBS, estabilidad del asfalto, propiedades reológicas.

COMPARATIVE STUDY OF THE ACTION OF TWO STYRENE-BUTADIENE-STYRENE (SBS) TRIBLOCK COPOLYMERS FOR THE MODIFICATION OF THE PROPERTIES OF A PERUVIAN ASPHALT

ABSTRACT

Polymer-modified asphalts were prepared by mixing two commercial linear styrene-butadiene-styrene block copolymers (SBS-1 and SBS-2) with an asphalt of Peruvian origin (PEN 60/70). A comparative study of the influence of SBS-1 and SBS-2 on the physical and rheological properties of asphalt was carried out. The characterization of the SBS copolymers was carried out using NMR, FTIR and GPC techniques. Through ¹H NMR analysis, it was determined that the main difference in the chemical composition of SBS-1 and SBS-2 was that the SBS-2 copolymer had 36% mol of 1,2-vinyl-polybutadiene

^a Materials Technology Group-TDM Asphalts, Lima, Peru

^b Polymer Laboratory, Physical Section, Research Department (DFI), Pontifical Catholic University of Peru (PUCP), Lima, Box 1761, Peru, *jrueda@pucp.edu.

groups while the SBS-1 copolymer only 11% mol. Rheological tests demonstrated that the SBS-1 additive had higher performance than SBS-2 additive in improving the rheological properties of the modified asphalt, such as creep resistance and elasticity, and this allowed the SBS-1 polymer-modified asphalt to be classified for more demanding pavements.

Keywords: Modified asphalt, SBS-triblock copolymer, asphalt stability, rheological properties.

INTRODUCTION

Asphalts are a complex mixture of hydrocarbons derived from the heavy fraction of crude oil distillation. Asphalts are thermoplastic and viscoelastic liquids that behave, at low temperatures, as a glass-like solid and at high temperatures as a viscous fluid¹. Being a viscoelastic material, asphalt exhibits both elastic and viscous properties and the relationships between the stress applied to the asphalt and the resulting deformations are temperature and time dependent².

Asphalts are mainly used to make road pavements. Pavements are composed of mineral aggregate and filler surrounded by an asphalt binder matrix. The performance of such pavement depends on the binding properties of asphalt, since asphalt is the continuous phase and is the only element of the pavement that can be deformed³.

Environmental conditions and increasing vehicle traffic can generate several problems in the pavement, the most frequent being: permanent deformation at high temperatures, cracking at low temperatures, fatigue associated with loads, among others³. For this reason, it is very important to study the asphalt binder in order to improve its physical and rheological properties and consequently its performance on the pavement. Currently, the use of linear styrene-butadiene-styrene copolymers (SBS triblock copolymers) are the most widely used polymeric additives, since they are capable of improving the properties of asphalt thanks to their chemical structure, and their degree of dispersion and compatibility with asphalt^{1,4,5}. It is essential to ensure the stability of the modified asphalt to avoid phase separation during storage, pumping, or asphalt application and thus obtain the desired properties in the pavement³. Stability testing can indirectly determine whether the interactions created between the asphalt and the polymers during the mixing process are strong enough to resist polymer separation under the conditions in which it is stored. One way to measure stability is to determine if there is a significant variation in the softening point, which would indicate phase separation⁶. The physical properties of a modified asphalt such as penetration, viscosity, linear elastic recovery, storage stability, etc. are important to determine the initial quality of the modified asphalt. However, the rheological properties of the asphalt are decisive because they allow to better determine the quality of the asphalt and allow to know more precisely what type of traffic the modified asphalt is suitable⁶⁻⁸. Rheological properties are measured with the dynamic shear rheometer and, for example, the Multiple Stress Creep and Recovery Test (MSCR, American Standard Testing Method-ASTM D-7405) is applied to study the rheological properties, which determines the degree of permanent deformation that an asphalt can undergo at high temperatures.

The objective of this work was to make a comparative study of the action of two linear SBS triblock copolymers in modifying the physical and rheological properties of an asphalt of Peruvian origin. For comparison purposes, the parameters of the current

Peruvian official standard for modified asphalts Type IC were used (Table 1). This standard is similar to the old USA ASTM D-5976 standard for modified asphalts. The rheological properties of modified asphalts were determined with the method mentioned above (ASTM D-7405) and ASTM D-7175.

We consider that this study could serve as a reference for the application of SBS additives in asphalts of other countries.

Table 1. Quality requirements for modified asphalt type IC (Peruvian standard, Highway Manual EG-2013, Ministry of Transport and Communications (MTC)-Peru, Table 431-01).

Test on asphalt		Test on rolling thin film oven test	
Penetration ^a , 25°C, dmm	50 – 75		
Absolute viscosity ^b , 60°C, P	5000 min.	Penetration ^a , 4°C, dmm	13 min.
Storage stability ^c , °C	2,2 max.	Linear elastic recovery ^d , 25°C, %	60 min.
Linear elastic recovery ^d , 25°C, %	60 min.	Storage stability ^c , °C	10 max.
Softening point ^e , °C	60 min.		
Kinematic viscosity ^f , 135°C, cSt	3000 max.		

^{a)-f)} The analysis methods of the *American Standard Testing Method (ASTM)* D-5, D-2171, D-7173, D-6084, D-36 and D-2170 were used for analysis of penetration, absolute viscosity, storage stability, linear elastic recovery, softening point and kinematic viscosity of the asphalts, respectively.

^{g)} *Rolling thin film oven residue*: is the asphalt residue after asphalt being subjected to aging in the thin film rotary oven at a temperature of 163°C for 85 minutes, according to ASTM D-2872.

EXPERIMENTAL PART

Materials

Two commercial linear styrene-butadiene-styrene block copolymers, SBS-1 and SBS-2 (Table 2) were used to modify a low-penetration asphalt of Peruvian origin (PEN 60/70, Petroperú Company-Conchán refinery in Lima, Peru).

Table 2. Characteristics of SBS-1 and SBS-2 block copolymers.

	Mn ^a	%PS ^b	%PB(C+T) ^c	%PB(1,2 V) ^d
SBS-1 ^e	99350	19	70	11
SBS-2 ^e	92650	21	43	36

a) Molecular weight (determined by Gel Permeation Chromatography (GPC), Agilent 1100, Column PL, Mixed B-LS with PS-Gel 10 um, CHCl₃, RI, 25°C). The Dispersity values were 1,47 and 1,57 for SBS-1 and SBS-2, respectively.

b) % molar polystyrene (PS) in block copolymer, determined by quantitative analysis ¹H NMR (NMR Spectrometer Bruker Ascend 500 MHz, 25°C, CDCl₃).

c) % molar (*cis* + *trans*)-polybutadiene (PB) in block copolymer, determined by ¹H NMR.

d) % molar 1,2-vinyl-polybutadiene (PB) in block copolymer, determined by ¹H NMR.

e) ¹H-NMR (CDCl₃) δ (ppm): 1,2-1,60 (CH₂-CH, polystyrene (PS)), 1,7-2,5 (CH₂, CH, polybutadiene (PB)), 4,9-5,1 (CH₂ 1,2-vinyl-PB), 5,3-5,5 (CH= (*cis* + *trans*) PB), 5,6 (CH=, 1,2-vinyl-PB) 6,3 – 7,4 ppm (aromatic protons, PS).

The chemical composition of the PEN 60/70 asphalt was determined by SARA (acronym for Saturated-Aromatics-Resins-Asphaltenes) chromatographic analysis (Table 3). This asphalt had an instability index (Ic) of 0,59.

Table 3. SARA-Chromatographic analysis of base asphalt PEN 60/70^a

Saturated (%)^b: 22,45; Aromatics (%)^b: 9,51; Resins (%)^b: 53,45; Asphaltenes (%)^b: 14,59;
Colloidal Index^c: 0,59

- a) Asphalt PEN 60/70 of Petroperú Company (Refinery Conchán-Lima, Peru).
b) Components weight percentages obtained by SARA-Chromatography Analysis using Iastrosan MK-6s chromatograph.
c) Colloidal Index (Ic)⁹ = (% asphaltenes + % saturated) / (% resins + % aromatics).
All are weight percentages obtained by SARA analysis.

The Ic value provides information on the instability of the polymer-asphalt system⁹. In general, an Ic greater than 0,3 predicts incompatibility (phase separation) between the asphalt and the SBS copolymer⁹.

For the characterization of the asphalt, conventional physical properties were used, such as, for example, penetration, softening point, ductility, penetration index, absolute viscosity, Brookfield viscosity and kinematic viscosity (Table 4).

Table 4. Conventional physical properties of the asphalt PEN 60/70^a

Penetration at 25°C (Pen _{25°C}):	62 dmm	Ductility at 25°C	>150 cm
Softening point:	49°C	Elastic recovery at 25°C:	30%
Penetration Index ^b (PI):	-1	Absolute viscosity at 60°C:	3,881 P
Pfeiffer and Van Doormal Correlation ¹⁰		Kinematic viscosity at 135°C:	429 cSt

a) ASTM methods were used in the analyses, which were mentioned in Table 1.

b) Pfeiffer and Van Doormal Correlation¹⁰.

PI = (1952-500logPen_{25°C}-20SP)/(50logPen_{25°C}-SP-120), where SP = Softening Point of asphalt.

Preparation of polymer modified asphalts

The polymer modified asphalts (PMA) were prepared by mixing 3% by weight of each of the SBS block copolymers relative to the weight of original PEN 60/70 asphalt.

Typical procedure: In a high shear mixer, 12 kilograms of PEN 60/70 asphalt were heated to 180°C and after, 360 grams of SBS additive were added. After mixing, a sample was taken to verify qualitatively, with the fluorescence microscope, that there were no undissolved polymer lumps in the mixture and, if positive, the additive AD-1 were added to the asphalt-polymer mixture according of recommendation of supplier and it was stirred at the same temperature. After this time, samples were taken to determine qualitatively the degree of dispersion of the polymer in asphalt, and performing physical, rheological and storage stability tests.

Stability of asphalt-polymer mixtures (ASTM D-7173)

The modified asphalt was placed in a pair of aluminum tubes and placed upright in an oven at 163°C for 48 hours. Once cooled, the tubes were cut into three sections, and samples were taken from the top and bottom (the middle part was discarded), then, the softening point test (Ring and Ball, Method ASTM D36) was performed with both samples to determine the degree of separation in the PMA.

Asphalt-polymer morphology

The degree of polymer dispersion in the asphalt samples was studied by total reflection optical fluorescence.

Rheology

Rheological tests of asphalts were carried out in a dynamic shear rheometer (DSR, TA-Instruments, Model DHR-2, ASTM D-7175 method). Typical procedure: The asphalt sample was placed between two 25 mm diameter parallel plates (with 1,0 mm test clearances) in the DSR and subjected to a temperature sweep at a frequency of 10 rad/sec. The dynamic shear modulus (G^*) and the phase angle (δ) of the asphalt binder were determined with ASTM D-7175 method. The complex shear modulus G^* is the ratio of the maximum shear stress and shear strain of linear viscoelastic materials under a continuous sinusoidal load and then is an indicator of the stiffness or resistance of the asphalt binder to deformation under load and the phase angle (δ) evaluates the relationship between the elastic and viscous response during the shear process. If phase angle (δ) is greater the elasticity of the asphalt decreases and vice versa. For original asphalt PEN 60/70 and for SBS-asphalt mixtures, applying the ASTM D-7405 method, temperatures 64°C and 76°C, respectively, were used.

Multiple Stress Creep and Recovery (MSCR) Test of asphalt binder (ASTM D-7405).

The test was used to analyze the high temperature performance of asphalt and was performed on the dynamic shear rheometer. The MSCR consisted of subjecting the asphalt, after being aged in a rolling thin film oven (RTFOT), to the maximum temperature (64°C (for PEN 60/70) or 76°C (for F-1 and F-2)). The aged sample was exposed to 20 deformation-recovery cycles, divided into two stages, the first of 10 cycles, at 0,1 kPa of stress and the second also of 10 cycles at 3,2 kPa of stress. Each cycle lasted 10 seconds: 1 second of creep and 9 seconds of recovery. MSCR test determines the elastic response (Re) and accumulated deformation (J_{nr}) of asphalt. The accumulated deformation (J_{nr}) is calculated with the following formula for each cycle: $J_{nr}(0,1 \text{ kPa}) = \varepsilon/100$ and $J_{nr}(3,2 \text{ kPa}) = \varepsilon/3200$, where ε = deformation of asphalt.

RESULTS AND DISCUSSION

The block copolymers styrene-butadiene-styrene, SBS-1 and SBS-2, were characterized by ^1H NMR and ^{13}C NMR spectrometry. Typical signals of styrene (e.g., aromatic protons at 6,3-7,4 ppm) and butadiene (e.g., *cis-trans*-vinyl protons at 5,3-5,5 ppm and 1,2-vinyl protons at 5,6 ppm) were identified (Figure 1).

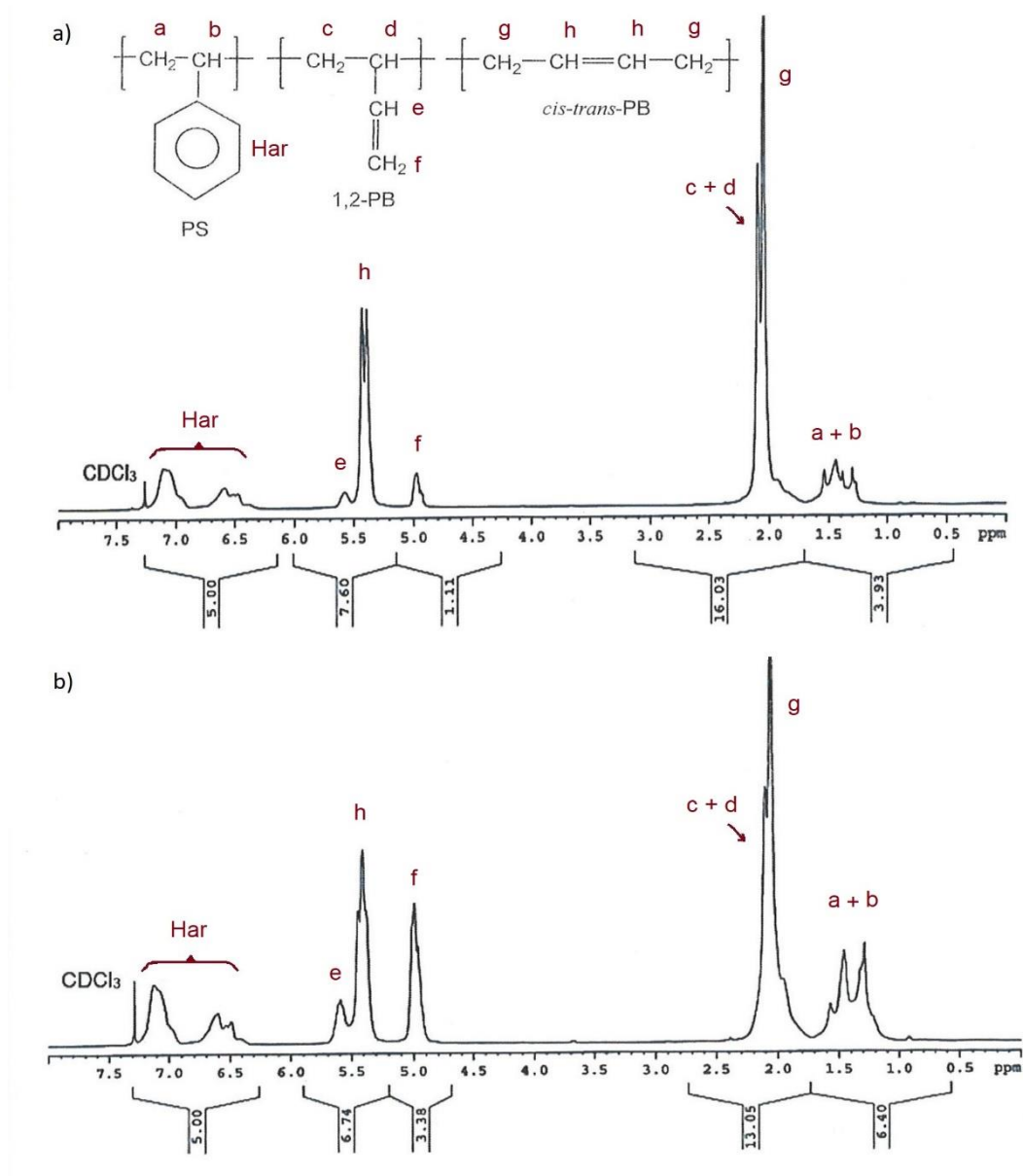


Figure 1. ^1H -NMR spectra of (a) SBS-1 and (b) SBS-2 block copolymer in CDCl_3 at 25°C .

By quantitative ^1H NMR analysis, comparing the "Har" signal versus "e", "f", and "h" signals of the mentioned spectra it was determined that the polystyrene content was 19,8 mol % and 21,8 mol % for SBS-1 and SBS-2, respectively. Likewise, was determined that SBS-1 and SBS-2 contained 70 mol % and 43 mol % of *cis-trans*-polybutadiene, respectively and comparing the integrals of the "e", "f" versus "h" signals (Figure 1) it

was determined that SBS-1 and SBS-2 contained 11 mol % and 36 mol % of 1,2-vinylpolybutadiene groups, respectively.

SBS-1 and SBS-2 copolymers were also characterized by FTIR-ATR. The presence of styrene and butadiene was detected, for example (SBS-2), with the signals at 3005 cm^{-1} (aromatic) and 966 cm^{-1} ($=\text{CH}$, *trans* 1,4), respectively. The presence of 1,2-vinylpolybutadiene groups in SBS-1 and SBS-2 copolymers was detected at 909 cm^{-1} (Figure 2).¹¹⁻¹³

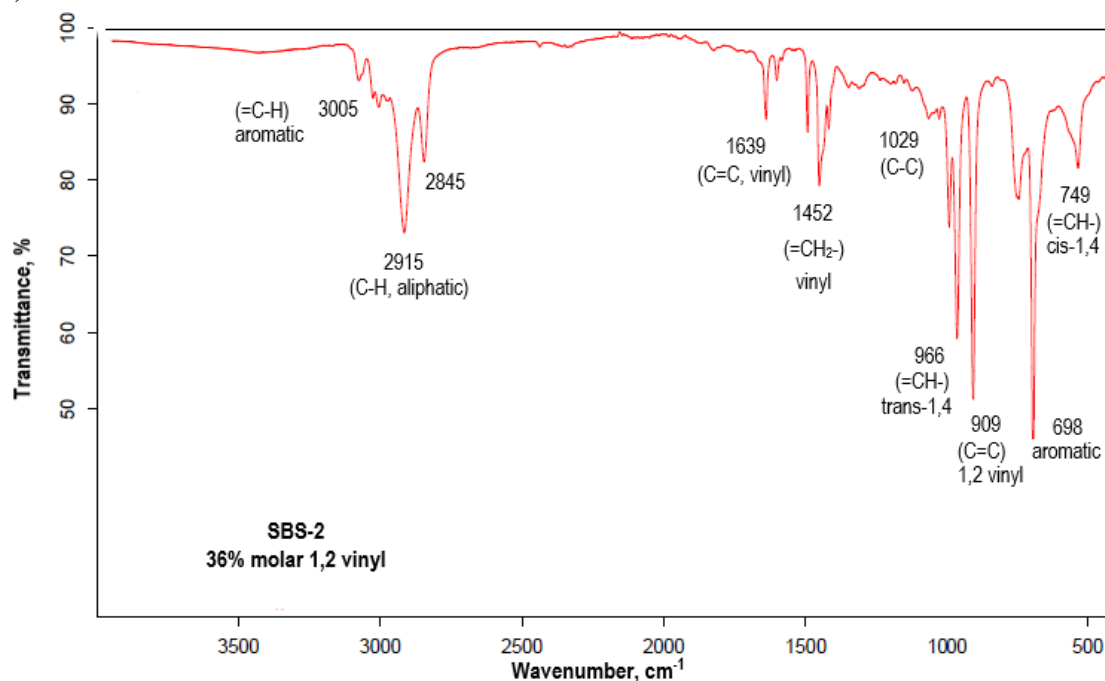


Figure 2. FTIR-ATR spectra of SBS-2 copolymer at 25°C.

The number average molecular weight of the SBS-1 and SBS-2 copolymers, obtained by GPC, were 99350 and 92650, respectively and both had a relative narrow molecular weight dispersion (1,5), which is consistent with anionic polymerization, the method by which these copolymers are made in the industry^{3, 14}.

Through SARA-chromatographic analysis it was determined that the original PEN 60/70 asphalt had an instability index I_c of 0,59 (Table 3) greater than maximum 0,3 and therefore there should be an incompatibility between asphalt and SBS copolymers due to the lower degree of solubility of the SBS copolymer in asphalt due to the low content of aromatic compounds in asphalt^{3,9,15}.

In general, when asphalt is modified with SBS copolymer, a three-dimensional network is formed that produces greater viscosity, and an increase in the complex modulus (G^*), greater elastic response (Re) and better mechanic behavior at high and low temperatures^{3, 5}.

Due to the high Colloidal Index of PEN 60/70 asphalt selected ($I_c = 0,59$), the formulations of modified asphalt used additive to improve asphalt polymer compatibility (interaction between polymer and asphalt), both formulations (F-1 and F-2) meet all the requirements of Table 1.

Table 5. Physical properties of asphalts modified with SBS-1 and SBS-2 block copolymers

Test on asphalt	F-1	F-2
Penetration ^b , 25°C, dmm	56	52
Absolute viscosity ^b , 60°C, Px10 ³	17,39	12,76
Kinematic viscosity ^b , 135°C, cSt	1588	1350
Storage stability ^b , °C	1,6	2,0
Elastic recovery ^b , 25°C, 10 cm, %	82	85
Softening Point ^b , °C	61,4	61,7
<i>Rolling Film Oven Test^c,</i>		
Elastic recovery ^c , 25°C, 10 cm, %	77	78
Penetration ^c , 4°C, dmm	24	20
Storage stability ^c , °C	0,6	2,8

a) F-1, F-2: Prepared modified asphalt formulations. In both formulations (F-1 and F-2) 3% by weight of SBS-1 or SBS-2 copolymer was used relative to the weight of original PEN 60/70 asphalt.

b) Requirement of minimum or maximum values contained in the Peruvian standard for IC modified asphalts (see Table 1).

c) Rolling thin film oven test: is the asphalt residue after original asphalt being subjected to the thin film rotary oven at a temperature of 163°C for 85 minutes, according to ASTM D-2872.

d) The analysis methods of the *American Standard Testing Method (ASTM)* D-5, D-2171, D-2170, D-7173, D-6084 and D-36 were used for analysis of penetration, absolute viscosity, kinematic viscosity, storage stability, linear elastic recovery and softening point of the asphalts, respectively.

From the data in Table 5, it was determined that the additives SBS-1 and SBS-2, have a practically equal effect in improving the physical properties of the asphalt-SBS copolymer mixture. However, the SBS-1 additive produced much better rheological properties in the modified asphalt than the SBS-2 additive, as will be seen later.

For PEN 60/70 and asphalt mixtures the standard temperature used for measurement was 64°C and for F-1 and F-2 were 64°C and 76°C. This is because the Performance Grade of Peruvian asphalt PEN 60/70 is normally PG 64-22, while modified asphalt is typically PG 76-22.

Rheological tests of asphalts (PEN 60/70, F-1 and F-2) were carried out in a dynamic shear rheometer (DSR) applying the ASTM D-7175 method. The dynamic shear modulus (G^*) and the phase angle (δ) of the asphalts were determined under the conditions mentioned in the experimental part. The $G^*/\sin(\delta)$ increased for F-1 and F-2 when the asphalt was modified with SBS polymers (Table 6), and therefore, the creep resistance of F-1 and F-2 was better than that of PEN 60/70 asphalt. Of the two modified asphalts, formulation F-1 presented a lower phase angle (δ) at both temperatures and therefore, it will be a more elastic asphalt than F-2 and PEN 60/70 at these conditions. It was also determined that the modification of asphalt with SBS polymers increased the failure temperature in the original asphalt from 69,1°C to 83.6°C (F-1) and to 80.4°C (F-2) respectively (Table 6). The failure temperature is where $G^*/\sin \delta$ is equal to 1 kPa and above this temperature the asphalt loses its properties as a binder.

The F-1 formulation presented a lower phase angle (Table 6). Therefore, it will be more elastic against deformations⁷.

Multiple stress creep recovery (MSCR) tests were used to determine the high-temperature performance of original PEN 60/70 and SBS-modified asphalt. The stress levels of the test were 0,1 kPa and 3,2 kPa, and each stress condition consisted of 10 loading cycles, each loading cycle with constant stress for 1 s and loading recovery for 9 s. According to the characteristics of asphalt, 64 and 76°C was selected as the test temperature in the study, and the creep recovery test results of SBS-modified asphalt were compared to the original asphalt (Table 7 and 8).

Table 6. Dynamic shear modulus of asphalts, ASTM D-7175

Asphalt	$G^*/\sin \delta^a$ (kPa)	Phase angle ^b (δ)	Fail.Temp. ^c (°C)
PEN 60-70	1,91 (64°C)	81,5 (64°C)	69,1
F-1	5,91 (64°C)	62,9 (64°C)	
F-2	4,75 (64°C)	66,8 (64°C)	
F-1	1,93 (76°C)	67,2 (76°C)	83,6
F-2	1,49 (76°C)	72,4 (76°C)	80,4

a) $G^*/\sin \delta$: dynamic shear modulus of asphalt obtained by Dynamic Shear Rheometer (DSR)

b) Phase angle of asphalt obtained by Dynamic Shear Rheometer.

c) Fail temperature of asphalt.

Creep recovery percentage (Re (%)) is used to characterize the ratio between the rebound deformation and the total deformation of asphalt materials at different stress levels to obtain the elastic properties of asphalt. The non-recoverable creep compliance (Jnr) is used to represent the viscous residual deformation of asphalt materials, and the higher its value, the worse the high temperature resistance of the materials.

As can be seen of Table 7, due to the poor high-temperature resistance of the original asphalt PEN 60/70 itself, this material had a creep recovery rate (Re) of the original asphalt at 0,1 and 3,2 kPa is only 23,7% and 13,3%, respectively. Compared with original asphalt, the creep recovery rate of F-1 and F-2 asphalt mixture was significantly higher and also there is a smaller difference (< 8%), between the elastic response at 0,1 kPa and at 3,2 kPa of the modified asphalts compared to the original asphalt (greater than 43%). This is an indicator that the modified asphalts are more resistant and stable than the original asphalt PEN 60/70 under the high stresses to which they were subjected and, therefore, is an indicator of their improved quality^{7, 16, 17}.

Figure 3 shows that, at 64°C, 70°C or 76 °C the elastic recovery (Re(%)), at 0,1 kPa or 3,2 kPa pressure, of F-1 and F-2 is greater than the original PEN 60/70 asphalt and that Re(%) of F-1 is always greater than that of F-2 at any of these conditions (temperature, pressure).

The non-recoverable creep flexibility (Jnr) for F-1 and F-2 was significantly reduced compared to PEN 60/70 (Table 8).

Table 7. Asphalt deformation resistance (Re) at 64°C

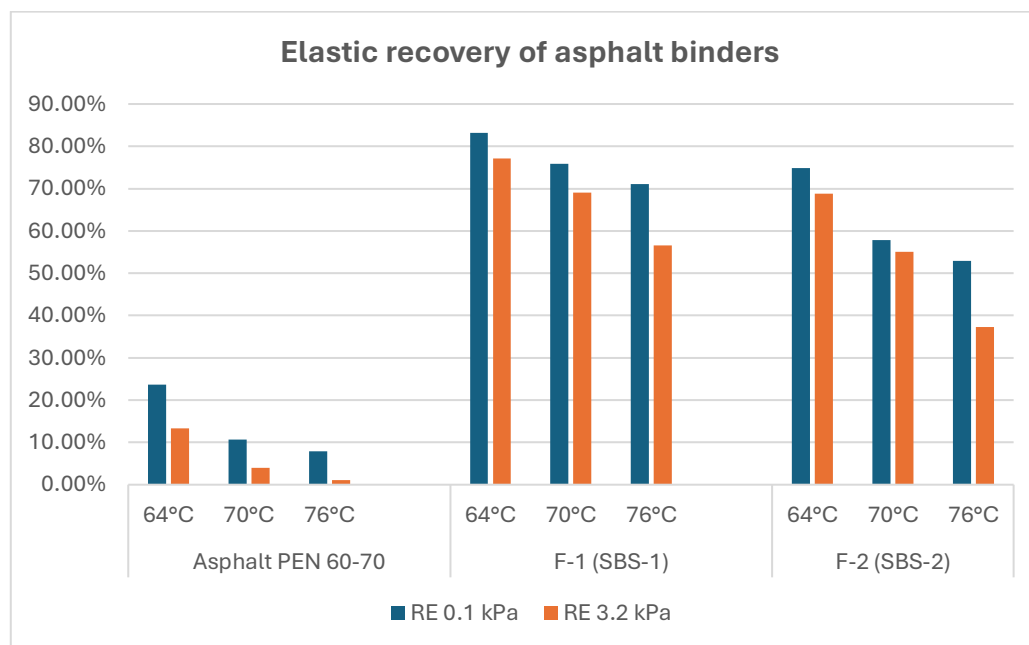
Asphalt	Re, 0,1 kPa ^a , (%)	Re, 3,2 kPa ^b , (%)	Re, dif. ^c , (%)
PEN 60-70	23,7	13,3	43,7
F-1	83,2	77,1	7,3
F-2	74,8	68,8	8,0

a) Average percent recovery of asphalt at a creep stress of 0,1 kPa.

b) Average percent recovery of asphalt at a creep stress of 3,2 kPa.

c) Percent of difference in recovery of asphalt between 0.1 kPa and 3.2 kPa.

It was used the MSCR Method, ASTM D-7405 Method.

**Figure 3.** Elastic recovery of asphalt binders at 64°C, 70°C and 76°C

This indicates that the addition of SBS-1 (F-1) and SBS-2 (F-2) enhanced the rutting resistance of asphalt. Then F-1 and F-2 had a lower permanent deformation than the original asphalt (without SBS copolymer). So we can conclude that with respect to elasticity and resistance to deformation, the SBS-1 additive produces better properties in asphalt than the SBS-2 additive.

From the results in Table 8, F-1 and F-2 were classified for “Very Heavy” and “Heavy” traffic, respectively.

Table 8. Non-recoverable creep compliance (Jnr) of asphalts at 76°C. (MSCR, ASTM D-7405)

Asphalt	Jnr, 0.1 kPa ^a , kPa ⁻¹	Jnr, 3.2 kPa ^b , kPa ⁻¹	Jnr, dif. ^c , %	Type of traffic ^d
PEN 60-70	4,12	5,40	31,20	NC
F-1	0,325	0,515	58,48	(V)
F-2	0,707	1,090	53,62	(H)

- a) Non-recoverable creep compliance (Jnr) of asphalt at a creep stress of 0,1 kPa.
 b) Non-recoverable creep compliance (Jnr) of asphalt at a creep stress of 3,2 kPa.
 c) Percent difference between non recoverable creep compliance of asphalt at 0,1 kPa and 3,2 kPa.
 d) NC: does not classify for any type of traffic at 76°C,
 H: Traffic Heavy, 10-30 millions of ESAL.
 V: Traffic Very Heavy, >30 millions of ESAL.
 were ESAL: number of equivalent load repetitions of a standard load dual wheel single axle of 18000 lb.

CONCLUSIONS

Two linear triblock copolymers styrene-butadiene-styrene (SBS copolymers) were used as additives to improve the performance of Peruvian asphalt PEN 60/70 and obtain modified asphalts for paving. The mentioned asphalt had an instability index $I_c = 0,59$, which is higher than the maximum expected value of 0,3 due to the low content of aromatic compounds in the asphalt, which implied a low solubility of the SBS copolymers in it.

The main difference in the chemical composition of SBS-1 and SBS-2 was the higher content of 1,2-vinyl-polybutadiene groups presents in SBS-2 copolymer. However, rheological tests demonstrated that the SBS-1 additive outperformed the SBS-2 additive in improving the rheological properties of the modified asphalt, such as resistance to deformation and elasticity. This allowed the SBS-1-modified asphalt to be classified for use in pavements with greater demands.

ACKNOWLEDGMENTS

The authors would like to thank TDM Asphalts, a company from the Materials Technology Group in Lima, Peru, for funding this research. They also thank the Pontifical Catholic University of Peru (PUCP), Lima, Peru, and the Leibniz Institute for Polymer Research in Dresden, Germany, for providing polymer characterization analysis.

REFERENCES

1. Airey G. D. Styrene-butadiene-styrene polymer modification of road bitumens. *J Mater Sci.* 2004; 39: 951-959.

2. Zhang J, Bao. Determination of asphalt mixture's viscoelastic constitutive parameters for pavement response analysis using dynamic modulus transformation. *Constr Build Mater.* 2021; 315 (10): 125729. doi: 10.1016/j.conbuildmat.2021.125729.
3. Zhu JB. Polymer modification of bitumen: advances and challenges. *Eur Polym J.* 2014; 54: 18-38. doi: 10.1016/j.eurpolymj.2014.0.005.
4. Wu W, Cavalli MC, Jiang W, Kringos N. Differing perspectives on the use of high-content SBS polymer-modified bitumen. *Constr Build Mater.* 2024; 411: 134433. doi: 10.1016/j.conbuildmat.2023.134433.
5. Wang Y, Guo S, Pei Z, Zham S, Lin S, Li J. Study of the properties and modification mechanism of SBS-modified asphalt by dry process. *Materials (Basel).* 2024;17(7):1454. doi: 10.3390/ma17071454.
6. Wen G, Zhang Y, Sun K, Fan Y. Rheological characterization of storage-stable SBS-modified asphalts. *Polym Test.* 2002; 21: 295-302. doi: 10.1016/S0142-9418(01)00086-1.
7. Chen JS, Huang CC. Fundamental characterization of SBS-modified asphalt mixed with sulfur. *J Appl Polym Sci.* 2006; 103(5), 2817-2825. doi: 10.1002/app.24621.
8. Mielczarek M, Formalczyk S, Slowik M. Evaluation of rheological properties of polymer-modified asphalt binders and mastics with organic additive-imidazoline. *Sustainability.* 2024; 16 (4): 1434. doi: 10.3390/su16041434
9. Polacco G, Filippa S, Merusib F, Stastnac G. A review of the fundamentals of polymer-modified asphalts: Asphalt/polymer interactions and principles of compatibility. *Adv Colloid Interface Sci.* 2015; 224: 72-112. doi: 10.1016/j.cis.2015.07.010
10. Pfeiffer JH, Van Doormal PM. The rheological properties of asphaltic bitumens. *J Inst Pet.* 1936; 22: 414-440.
11. Günzler H, Gremlich HU. *IR Spectroscopy- An Introduction.* First edition. Weinheim, Germany: Wiley-VCH; 2002.
12. Behera P, Mandal T, Maiti M, Jasra R. Insight into preparation of vinyl polybutadiene via cobalt-based catalyst: tuning its properties by thiol-ene modification of vinyl group. *Rubber Chem Technol.* 2016; 89(2): 335-348. doi: 10.5254/rct.16.84832.
13. Ciampelli F, Morero D, Cambini M. Some remarks on the infrared analysis of polyisoprenes. *Makromol Chem.* 1963; 61: 250. doi: 10.1002/macp.1963.020610122.
14. Koltzenburg S, Maskos M, Nuyken O. *Polymer chemistry.* Second edition. Berlin, Germany: Springer; 2023. doi: 10.1007/978-3-662-64929-9.
15. Airey GD. Rheological properties of styrene-butadiene-styrene polymer modified road bitumens. *Fuel.* 2003; 82: 1709-1719. doi: 10.1016/S0016-2361(03)00146-7.
16. Al-Adham K, Al-Abdul Wahhab H. Influence of temperature on Jnr values of polymer modified asphalt binders. *Int J Pavement Res Technol.* 2018; 1: 603-610. doi: 10.1016/j.ijprt.2018.01.001.
17. Lesueur D. The colloidal structure of bitumen: consequences on the rheology and on the mechanism of bitumen modification. *Adv Colloid Interface Sci.* 2009; 45(1-2): 42-82. doi: 10.1016/j.cis.