STORAGE STABILITY OF BITUMEN MODIFIED BY THE ADDITION OF GROUND RUBBER, SWOLLEN SBS AND POLYMERIC SHORT FIBERS

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ABSTRACT:
Bitumen is used as binder for asphalted roads worldwide. However the service life of asphalt roads is limited due to the viscoelastic properties of bitumen. The lack of yield stress and the flow behavior at high temperatures as well as the stiffness of bitumen at lower temperatures results in the main failure sources of asphalt roads. Many polymers have been used in industry to improve the rheological behavior of bitumen and consequently, service life of roads. The polymers are commonly added to hot bitumen under stirring in order to achieve a stable dispersion. However, most polymers show little to no miscibility in bitumen, which requires long dispersion times and may lead to oxidation of bitumen and degradation of the polymers. Poor miscibility of the dispersed polymer and the bitumen matrix can result in phase separation during transport of molten bitumen, leading to a heterogeneous binder and further failure of the paved road, which is a common problem in the paving industry. Rubber pre-treating leads to a faster mixing process without compromising dispersion quality and stability. Bitumen was modified with SBS, ground rubber and chopped fibers of polymers. These fibers, which showed good stability, can be considered for the future as bitumen modifiers. To evaluate the stability of the modified bitumen, we propose a stability index.

ZUSAMMENFASSUNG:
Bitumen wird als Bindemittel für asphaltierte Straßen weltweit eingesetzt. Allerdings ist die Lebensdauer von Asphaltstraßen aufgrund der viskoelastischen Eigenschaften von Bitumen beschränkt. Sowohl die Nichtexistenz einer Fließgrenze und das Fließverhalten bei hohen Temperaturen als auch die Sprödigkeit des Bitumens bei niedrigeren Temperaturen gehören zu den wichtigsten Versagensgründen bei Asphaltstraßen. In der Industrie sind viele Polymere versuchsweise eingesetzt worden, um das rheologische Verhalten von Bitumen und folglich die Lebensdauer des Asphaltbelags von Straßen zu verbessern. Die Polymere werden üblicherweise mit heißem Bitumen unter Rühren gemischt, um eine stabile Dispersion zu erreichen. Allerdings zeigen die meisten Polymere wenig bis keine stabile Mischbarkeit mit Bitumen, so dass für die Dispersion der Polymere im Bitumen lange Zeiten benötigt werden und dies zur Oxidation von Bitumen und zum Abbau der Polymere führen kann. Schlechte Mischbarkeit des dispergierten Polymers mit Bitumen kann zu Phasentrennung während des Transports von flüssigem Bitumen führen und als Folge zu einem heterogenen Binder und zu Schwachstellen im Asphaltbelag, was ein häufiges Problem im Straßenbau ist. Wie wir zeigen konnten, führt eine Vorbehandlung von Gummi zu einem schnelleren Mischvorgang ohne Qualitäts- und Stabilitätsverlust der Dispersion. Bitumen wurde mit SBS, gemahlenem Gummi und kurzen Polymerfasern modifiziert. Diese Fasern, die eine gute Stabilität zeigen, können zukünftig als Zusatzstoffe für Bitumen interessant werden. Um die Lagerstabilität des modifizierten Bitumens zu bewerten, schlagen wir einen Stabilitätsindex vor.

RÉSUMÉ:
Le bitume est utilisé dans le monde entier comme liant pour les routes asphaltées. Néanmoins, la longévité des routes asphaltées est limitée du fait des propriétés viscoélastique du bitume. Son manque d'élasticité et sa plasticité à haute température ainsi que sa rigidité à basse température, sont les sources principales des dégâts occasionnés sur ce type de routes. Plusieurs polymères ont été utilisés dans l'industrie afin d'améliorer le comportement rhéologique du bitume et de fait la longévité des routes. Les polymères sont généralement ajoutés au bitume à chaud sous agitation, dans le but d'assurer un homogénéisation stable. Toutefois, la plupart des polymères ont une faible, voir aucune miscibilité avec le bitume, ce qui requière des temps d'homogénéisation plus longs, qui peuvent induire une oxydation du bitume et une dégradation des polymères. Leur faible miscibilité ainsi que la matrice du bitume peuvent impliquer une séparation de phases lors du transport du produit fondu et former un liant hétérogène, qui générera à postériori des dégâts sur les chaussées, ce qui est un problème commun pour l'industrie du revêtement. Un pré-traitement avec du caoutchouc permet un mélange plus rapide en préservant l'homogénéité, ainsi que la qualité et la longévité du produit. Le bitume à été modifié avec du SBS, des caoutchouc naturels et des fibres de polymères hachées. Ces fibres montrant une bonne stabilité peuvent être considérés comme les modifiant futurs du bitume. Afin d'évaluer la stabilité du bitume ainsi modifié, nous proposons un index de stabilité.

KEY WORDS: rheology, bitumen, asphalt, storage stability

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1 INTRODUCTION

Bitumen is obtained from crude petroleum through fractional distillation, being the residual part of this process. Asphalt is a complex bituminous mixture of organic compounds including aliphatic, aromatic and naphthenic hydrocarbons, which can be divided into two main groups called maltenes and asphaltenes [1]. Asphaltenes form a dispersed phase in a continuous phase of maltenes; a typical classification of these groups is as follows: saturates (S), aromatics (A), resins (R) and asphaltenes (As). In this classification the different fractions present in a particular bitumen are grouped in percentages. The complexity, aromaticity and molecular weight of the fraction increases in the following order: S < A < R < As [2]. The bitumen acts as a binder (due to its cohesive properties) for the mineral aggregates which are laid down and compacted to form an asphalt road [3]. However, the roads can develop failures during their life time due to external factors. Though damaged asphalt roads can be repaired in many cases, the maintenance of roads represents high costs. Therefore there is great interest in modifying the rheological properties of bitumen and thereby obtaining paved roads with improved properties.

Bitumen for asphalt cements is commonly modified with small quantities of polymers in order to improve its viscoelastic properties [4]. Through a technique known as wet process, polymers are added to bitumen at high temperatures (160 – 210°C) for a period of 30 minutes to two hours for ground-rubber, and 1 to 12 hours for other rubbers such as SBS and SBR [5]. A wet process requires molten bitumen that is mixed under high shear in large tanks [6]. To achieve a good dispersion, it is necessary to decrease considerably the particle size of the modifying polymers from millimetres or centimetres to micrometers [7], and this occurs for most polymers at high temperatures and long mixing times. Depending on the bitumen, the polymer and the quality of polymer dispersion, the mixing time can take from 1 to 6 h under shear as high as 6000 RPM [8 – 14]. The mixing time depends highly on the modifying polymer, the mixing speed and temperature, and these parameters have direct influence on the degree of dispersion of the polymers involved. It is common adding small quantities of rubber, such as 1 % in bitumen, but also higher quantities up to 9 % have been reported [13, 15]. However, by increasing the polymer content, the costs of raw material and processing can raise significantly. The price of SBS in Mexico during 2010 to 2012 was about 5 times higher than the price of bitumen.

Addition of polymers is valuable because it helps delaying permanent deformations of roads, such as rutting at high temperatures and low temperature cracking susceptibility besides it increases fatigue resistance. Due to these positive effects, addition of polymers increases the service time of paved roads [16]. Rubbers are incorporated in bitumen in order to produce asphalt roads with better mechanical properties, and delaying low temperature cracking, which occurs when the binder is too stiff [17], and help increasing rutting resistance at high temperatures [14]. However, the solubility parameters of the bitumen components are often different from those of the polymers, retarding and even hindering the dispersion of polymers in hot bitumen [18, 19]. In industrial applications, the highest possible shear is lower than that reached in laboratory due to the larger industrial tanks, and thus the effective time to ensure a good mixture can be even longer. In large mixing units a turbulent flow can be reached near to the impellers, but a laminar regime can be found away from them. The above mentioned processing conditions have an environmental impact due to energy consumption as well as increased processing costs that should be considered when the mixing design is specified. After bitumen is modified with polymers it usually remains in tanks at temperatures about 160°C in order to reach its final destination. This period is commonly known as hot storage and it is during this step that polymers can separate from bitumen by coalescence.

Tire scrap represents worldwide an ecological problem if this waste is not treated properly. Using ground-rubber in asphalts is considered as a good recycling solution to this problem. However, one of the greatest challenges is to produce a dispersion that is stable during hot storage. Grinding tires and obtaining relative constant particle sizes is state of the art in some countries, where small rubber particles can be purchased and included to a process that requires raw materials with constant quality. To allow better dispersion and homogenization of the ground-rubber modified bitumen, high mixing speeds and high temperatures are commonly used in the industry as in the case of SBS and SBR. However, rubber from tires does not dissolve or swell to a great extent in bitumen after hours of mixing due to its high cross-linking density [20]. Nevertheless, the rubber particles do not resist long times at high temperatures. Under these conditions degradation of the polymer [21] and ageing of the bitumen may occur. This ageing of bitumen during the mixing process, called primary ageing, impairs the bitumen properties during its service life [22]. Therefore it is important to produce an efficient dispersion of rubber in bitumen without compromising its quality and stability.

Improving the mixing time is a main topic for bitumen producers, because one of the primary causes of binder-related long-term-paved roads failures is the oxidative aging of asphalt binder. Where oxidation is a very complex process that changes both chemical and colloidal structure of bitumen [23, 24]. During the slow oxidation process viscosity increase, it loses its adhesivity and becomes brittle. The oxidation is indicated by formation of carbonyl groups [25] and Ketones [26]. The brittleness leads to the formation of cracks and these to ultimate failure of the paved surface. It is reported that the oxidation mechanism as well as the oxidation rate are temperature-dependent, and simple high-temperature oxidation tests may not accurately predict rheological changes in asphalt [27, 28] at service temperatures. A method for the rheological quantification of bitumen aging had been proposed recently. [29]

Polymers are in principle immiscible with other polymers and with most solvents. Blends of two polymers or a polymer with a solvent are often highly instable and tend to demix forming separated phases. The solubility of a rubber decreases with increasing of crosslinking density; however, rubbers swell if the solubility parameters (δF) of the polymer and bitumen are similar. The storage stability of rubber-modified bitumen is a measure of the miscibility of the rubber particles and the bitumen matrix, and a minimum of storage stability is compulsory to ensure a homogeneous dispersion after the required long transportation times at high temperatures. Storage stability is critical to ensure the final polymer-modified bitumen (PMB) quality [30]. The long time that is required to disperse the polymers into the bitumen reflect the high incompatibility of the polymers with the bitumen. Poly(ar-amide) and poly(ar-ester) chopped fibers are commonly used to reinforce materials by forming composites. These polymers are known due to its outstanding mechanical properties and stability even at hot temperatures. The storage stability of properly mixed PMB containing pre-treated rubber and chopped fibers was studied by rheological means. This results can provide the industry with useful background about processes that can be applied or not to design a suitable process for achieving desired results.

2 MATERIALS

Bitumen AC20 from the Salamanca refinery was obtained from Sem Materials, Mexico. The penetration grade of this bitumen is 79 1/10 mm at 25°C, and the bitumen chemical composition is the following: saturates: 5.2 %, aromatics: 44.9 %, resins: 23.8 %, and asphaltenes: 26.1 % (as reported by the supplier). This asphalt has a relatively high penetration grade and used for paving roads in Mexico. The physical properties of bitumen AC20 are listed in Tables 2 and 3.

Table 1 (above): Physical properties of Bitumen AC20 from Salamanca refinery as reported by Sem Materials Mexico.

Table 2 (middle): Physical properties of bitumen AC20 at different temperatures.

Table 3 (below): Processing conditions of rubber-modified bitumen.

Property	ASTM/Method	Salamanca
Viscosity 60 °C, (Poise)	D-2171	1700
Viscosity 135 °C, (cSt)	D-2170	987
Penetration, 100g-5 seg-25 °C, 1/10 mm	D-5	79
Melting temperature (°C)		120
Rolling thin film oven test (RTFO):		
Viscosity at 60 °C, (Poise)	*	3273
Ductility at 25 °C, (cm)	*	105

	Temperatures [°C]									
	15	25	50	100	150	160	170	180	190	200
Density [g/cm^3]	1.03	1.02	1.01	0.98	0.96					0.93
Viscosity [Pa-s]					0.1	0.07	0.06	0.04	0.04	0.03

Sample	Polymer	[PHB]	Swelling oil [x SBS]	Temperature [°C]	Speed [1/min]	Mixing time [min]	Reaction time [min]
A	SBS	2.5	4	180	900	10	30
B	Kneaded GR SBS	5.0 0.7	0 0	160	20 000	10	30
C	SBS	1.0	4	160	900	10	30
D	SBS	5.0	4	160	1400	10	30
E	GR SBS	10.0 0.7	0 0	200	1200	60	30
F	SBS Ground rubber	2.5 10.0	3.5	160	900	10	30
G	SBS Kneaded c-NR	0.7 5.0	3.5	180	1200	120+10	30
H	Poly(ar-amide)	0.5	0	180	600	120	-
I	Poly(ar-ester)	1.0	0	180	600	120	-

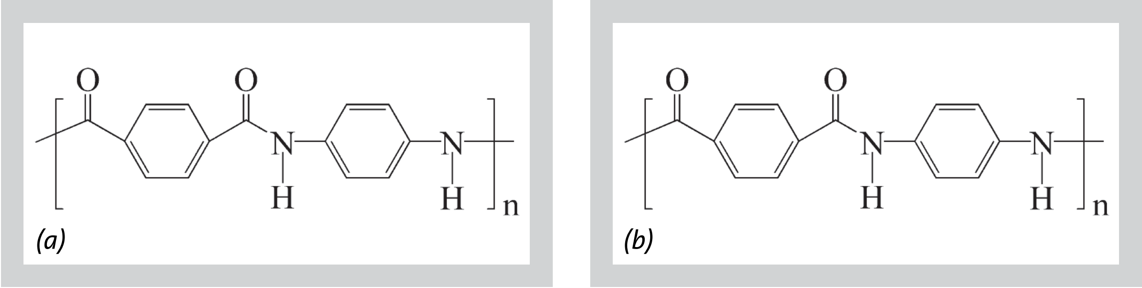


Figure 1: Skeletal formulas of monomeric units of (a) Poly(ar-amide) and (b) LCP Poly(ar-ester).

Tire ground rubber (GR), with particle size of ≤ 0.2 mm, was obtained from Genan GmbH (Germany). Rubber scrap from regular powder free natural rubber (NR) gloves was used as kneading aid for GR. Commercial grade SBS (Solprene 411) for modifying bitumen was obtained from Dynasol (Mexico). This thermoplastic co-polymer contains a styrene content of 30 % (ASTM D-5775) and a star molecular architecture (as reported by supplier). Two different oil grades where obtained from Sunoco (USA), the first one (Hydrolene H180T) is commonly used in the paving industry for controlling viscosity in bitumen, and is referred here as Oil-1. The second oil (Oil-2 Sunpar 2280) was used as lubricant during devulcanization of natural rubber by thermo-mechanical means in an internal mixer. Devulcanizing agent 2,2’-dibenzamidodiphenyldisulphide (DBADPDS) was obtained from Behn Meyer Europe. Ultra-Pep 148 is a blend of DBADPDS and fatty acid derivatives [31]. Two types of chopped fibers were used for bitumen modification. The first one is Poly(ar-amide) (Kevlar), provided by DuPont. This highly crystalline polymer has molecules presenting high rigidity due to the monomer units containing aromatic groups in the main chain, (Figure 1a). Kevlar fiber is though, impact resistant and fatigue resistant. According to DuPont, chopped Kevlar fibers induce tixotropy when added in solutions; furthermore, they are temperature resistant. Kevlar is inert to many common chemicals. These characteristics are desired in polymer-modified asphalt.

The second type are Poly(ar-ester) (Vectran) fibers, supplied by Kuraray. It is a thermoplastic liquid crystal (LCP) in the form of a spun yarn. According to Kuraray, this fiber possesses high strength (1 – 3 GPa), high tensile modulus (52 – 103 GPa), good impact resistance, high creep resistance, minimal moisture absorption, and chemical resistance. Due to its molecular characteristics (Figure 1b) its melting temperature is high ($T_m = 350°C$) and wont melt during mixing with hot bitumen.

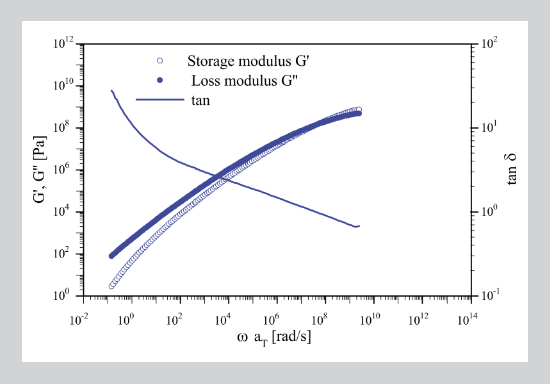
3 EXPERIMENTAL

Ground-rubber was mixed into hot bitumen “as supplied” in sample F. Samples B and G were modified with devulcanized ground-rubber. Devulcanization took place in an internal Mixer (Plasti-Corder PL2000 from Brabender). The rubber samples were mixed at 40 RPM and constant temperature of 80°C in batches of 50 g. The ground-rubber was mixed with scrap rubber (with lower vulcanization grade) in order to obtain a sticky material to be used as bitumen modifier, forming a mixture of 90 % ground-rubber and 10 % scrap rubber. Ultrapep 148 DBADPDS was used as devulcanizing agent (1 phr) and Oil-2 (2 phr) as a lubrication aid. In samples A, C, D, F and G, SBS was pre-treated before dispersing it in hot bitumen. The pre-treatment consisted in forming a gel with SBS and Oil-1 by a swelling process, which was carried out by immersing pellets of SBS in Oil-1 and placing them in an oven at 220°C. SBS and oil formed a gel-like material after a time shorter than 20 min without agitation and this will be further denoted as SBS gel.

The mixing of bitumen with polymer/rubber (all samples except sample B) was carried out with a tailor made impeller (six blades) coupled to a rotor-stator (IKA, Eurostar Power Control Visc.) with speeds from 900 to 1400 RPM in vessels of 200 g of bitumen capacity. Sample B was mixed with the same vessel using a high-shear dissolver Power Gen 1000 from Fischer Scientific at 20 000 RPM. The temperature of the bitumen was kept constant at ± 5°C during mixing time for all samples.

After the rubber was dispersed, sulfur was added to initiate cross-linking. When the vulcanization was completed, each sample was separated in 2 parts. The first part, containing only a few grams of bitumen, was analyzed rheologically without any further processing. The rheological behavior of rubber-modified samples was studied with a stress-controlled Rheometer (MCR301 Anton Paar Germany) using a nitrogen atmosphere in order to avoid oxidation during the measurements at high temperatures. A system of parallel plates with geometry of 25 mm and a gap of 1.0 mm for neat bitumen was used and a gap of 1.2 mm for samples containing GR. Frequency and temperature sweeps were carried out in oscillatory shear within the linear-viscoelastic regime.

Frequency sweeps were performed in a frequency range of 0.01 – 390 rad/s under isothermal conditions. Temperature sweeps at 10 rad/s



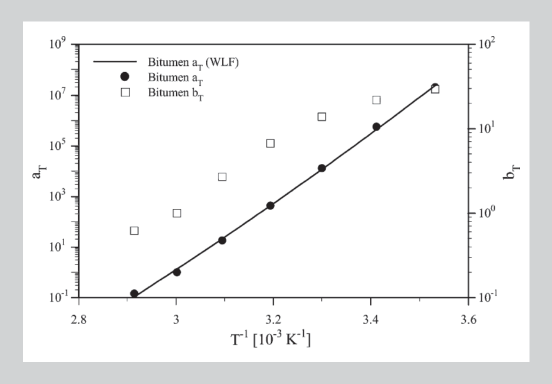


Figure 2 (left above): Mastercurve of storage G' and loss modulus G'' as a function of frequency of non-modified bitumen measured at temperatures between 10 and 70°C.

Figure 3 (Right above): WLF Horizontal a_T and vertical b_T shift factors as a function of temperature T^{-1}. The shifted data show a good correlation with the WLF equation horizontal shift factor.

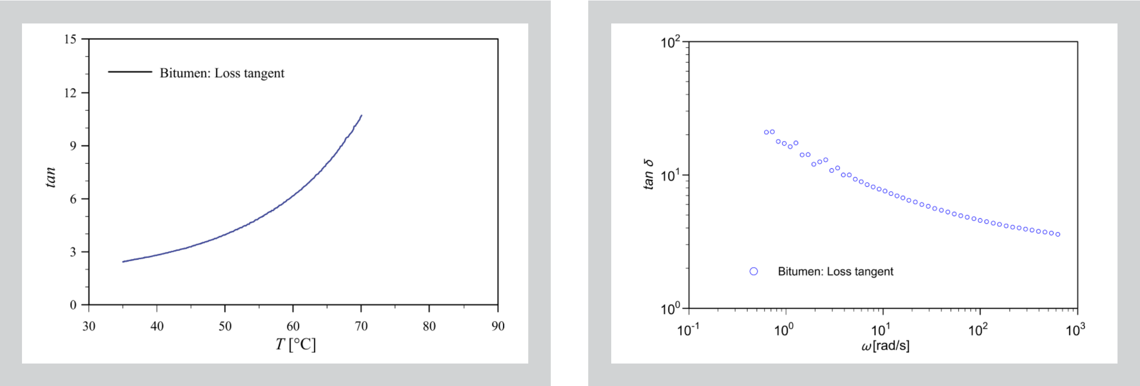


Figure 4 (middle left and right): Temperature and frequency sweep of bitumen before addition of polymers. The values of tan δ increase significantly at higher temperatures as well as low frequencies.

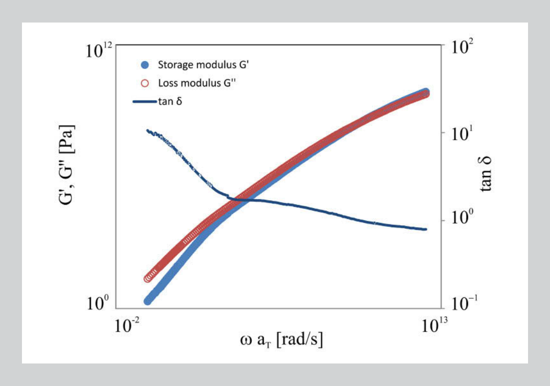


Figure 5 (below): Mastercurve at T_{Ref} = 60°C of sample A.

according to AASHTO-TP5 [32] were made within the linear-viscoelastic regime in order to obtain measurements of the rutting parameter $G^*/\sin\delta$, complex viscosity η^*, and loss tangent $\tan\delta$. Creep tests with a constant shear stress σ_o of 50 Pa for 5 min and a relaxation time of 10 min were carried out at 40, 50, 60 and 70°C, analogous to Desmazes [33]. All the samples reached a steady state, after which the elastic recovery and the zero-shear viscosity η_o were determined.

In order to test the storage stability of the modified bitumen the industrially well-known tube-test was used [34]. The PMB samples were poured in aluminum tubes having a diameter of 38 and a length of 220 mm. The tubes were firmly closed avoiding air entrance, and placed in a vertical position in an oven at 160°C for 96 hours, as reported by Isacsson [3]. After the storage was completed, the samples where carefully cooled-down in order to avoid any agitation of the hot bitumen that could influence the results. After cooling, the samples were slowly frozen at - 10°C and cut in three parts keeping the specimens from the top and bottom of the tubes for characterizing the storage stability in a similar way as described by Becker [12]. The middle part was kept frozen but not analyzed. The processing parameters for the modified samples are shown in Table 1, where the temperature indicates the measured mixing temperature of polymer and bitumen. Mixing time indicates the processing time required in order to achieve the designed dispersion; in the case of sample G, the times given are the mixing time for ground rubber, and the mixing time after addition of SBS gel.

4 RESULTS

The linear viscoelastic region of non-modified bitumen was analyzed prior to the modification with polymers. Figure 2 shows a mastercurve of non-modified bitumen. Storage and loss moduli were shifted to the reference temperature T_{Ref} = 60°C. From the shifted values it was possible to obtain the complex viscosity. The shifted moduli and tan δ in the curve present a very good fit with the WLF equation. The fitting of the mastercurves was corroborated using the IRIS software [35], where a horizontal and a vertical shift factor a_T and b_T were obtained (Figures 3 and 4).

Obtaining mastercurves for the non-stored sample A (Figure 5) as well as the bottom (B) and top (T) part is possible. A difference between the bottom and top part is not straightforwardly observed. However, from the frequency sweep shown in Figure 6b it can be observed that the value of tan δ at low frequencies differs between

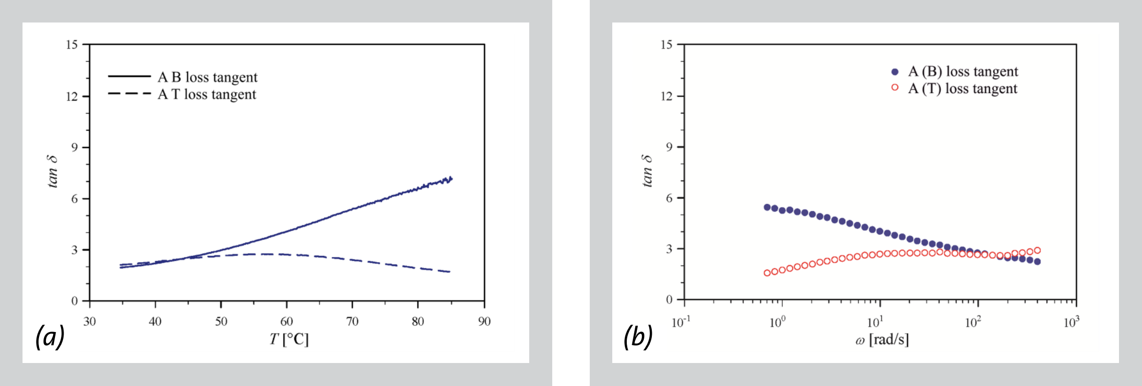


Figure 6 (above): Loss tangent tan δ of bottom and top parts of sample A obtained by temperature (a) and frequency (b) sweeps within a single measurement at (a) 10 [rad/s] and (b) 60 °C

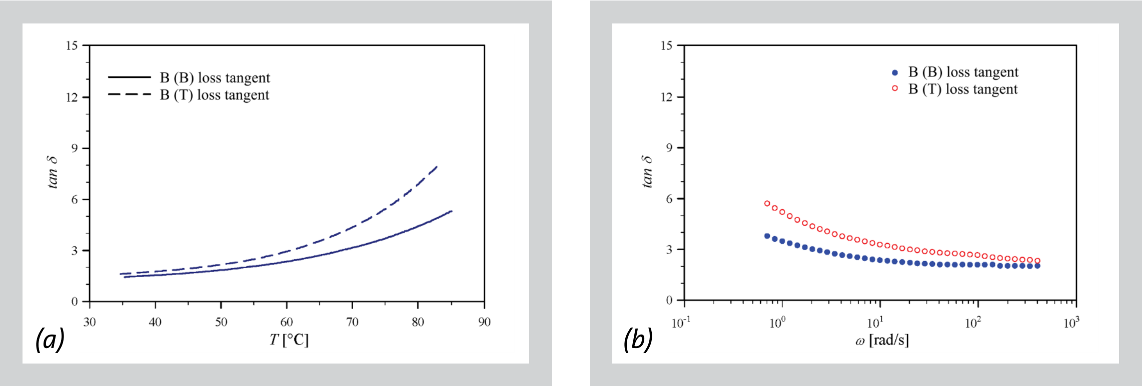


Figure 7 (middle): Loss tangent (tan δ) of bottom and top parts of sample B obtained by temperature (a) and frequency (b) sweeps with in a single measurement at (a) 10 [rad/s] and (b) 60°C.

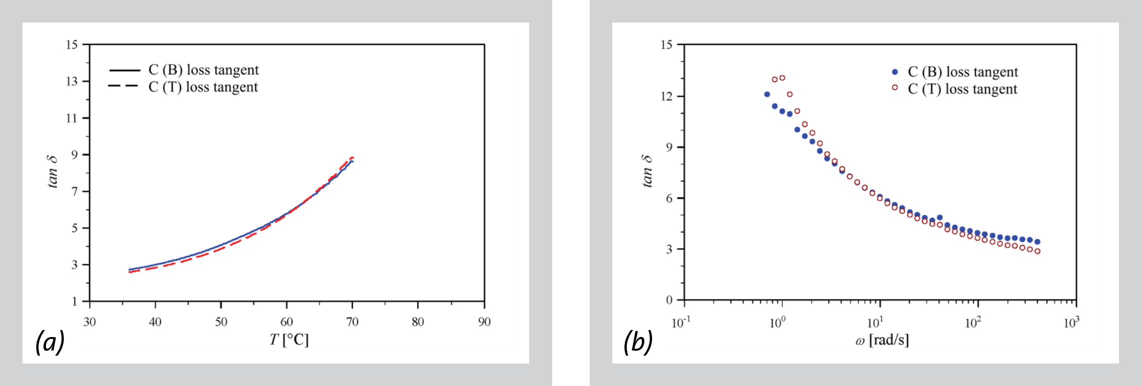


Figure 8 (below): Dependence of tan δ as a function of temperature (a) and frequency (b) of Sample C. The values at very low frequencies in (b) are clearly out of the measuring range of the rheometer.

the bottom (B) and top (T) part. The sensitivity of tan δ to differences in polymer content of bitumen allows characterizing the storage stability of the samples using of a simple and fast technique. Similarly in Figure 6a it is observed that tan δ from the bottom and top part are very similar at lower temperatures, while above 60°C, the difference in the values of tan δ between the bottom and top part increases. This sample is not stable and it will not last during transport until final lay down of the paved road, resulting in inhomogeneous quality of the binder.

Figure 7 shows the values of tan δ obtained with sample B, which was modified with ground-rubber devulcanized by thermo-mechanical means. This sample shows poor storage stability. At higher temperatures and lower frequencies it is observed that the tan δ values measured for bottom and top part separate from each other, indicating that this is a non-stable sample and therefore, it will develop phase separation if transported for long distances. Sample C presents higher storage stability and is within the acceptable storage tolerances. Both oil and gel of SBS lead to a decrease in viscosity and density. Maintaining the amount of oil at a low level can help developing improved stability with SBS gel which requires short time for dispersing. Other bitumen types than the one used in this study, which have a better toleration of high oil proportions, can, however lead to different results. Bitumen in Sample C was modified with 1.0 phb of SBS gel, and showed an acceptable stability. Compared to sample D, with a concentration of 5.0 phb of SBS gel, Sample C has improved stability. This is reached with concentrations of ≤ 1.0 phb SBS gel. Higher concentrations of oil tend to impair the viscosity of bitumen. Therefore it can be considered producing the SBS gel by mechanical means.

Sample D formed an extremely elastic material, and due to this high elasticity and yield stress, handling of this sample was extremely difficult. In order to be able to dose it into the sta-

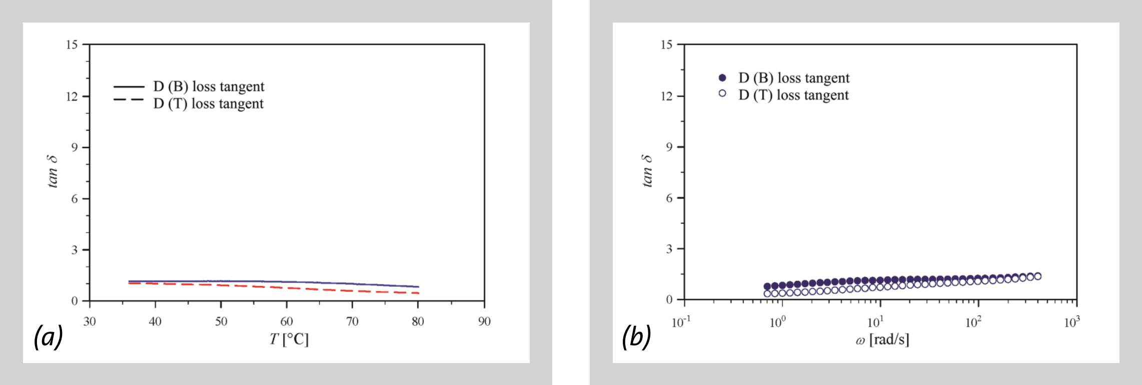


Figure 9 (above): Loss tangent tan δ of bottom and top parts of sample D obtained by temperature (a) and frequency (b) sweeps with in a single measurement at (a) 10 [rad/s] and (b) 60°C.

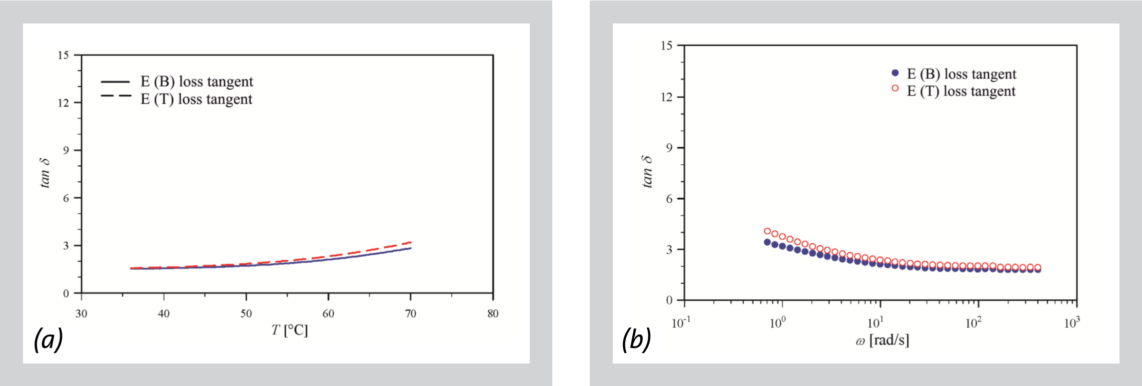


Figure 10 (middle): Loss tangent tan δ of bottom and top parts of sample E obtained by temperature (a) and frequency (b) sweeps with in a single measurement at (a) 10 [rad/s] and (b) 60°C.

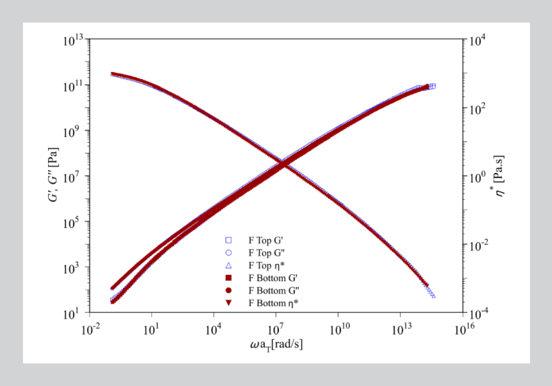


Figure 11 (below): Storage and loss moduli and complex viscosity of sample F. containing 2.5 % SBS and 10 % ground rubber (reference temperature 60°C).

bility test tubes, the sample was frozen by immersion in liquid nitrogen during 2 minutes, and afterwards was broken into pieces with a hammer. The pieces were placed into the storage stability test tubes and remelted, subsequently the storage stability test was carried out, as with the other samples. The curves of tan δ from the bottom and top parts of Sample D from temperature and frequency sweeps are very similar (Figure 9). Such a PMB can be difficult to be pumped with a standard pump, however mixing it can be easily mixed with the mineral aggregates. In extreme cases, such as this formulation the high viscous technology used for polymers can be applied. The curves of sample E (Figure 10) showed similar values of tan δ for bottom and top parts in both temperature and frequency sweeps. The storage stability index of both samples is found within the criterion of stability. This indicates that non-treated SBS and GR can form a stable dispersion under certain proportions of SBS/GR/bitumen.

The moduli of sample F (85), *G'* and *G''*, show very similar values at all frequencies in the mastercurve (Figure 11). Storage stability from this mastercurve is not clearly observed. However, slight differences in the tan δ values from the bottom and top parts can be observed in the plots of temperature and frequency sweeps (Figure 12), similarly to the previous samples. Both graphics show in a single measurement enough information about the stability of the sample. The Samples F and G were both modified with a combination of Swollen-SBS and ground-rubber. Sample F was modified with 2.5 phb of SBS gel (formed with SBS plus 3.5 times its weight of Oil-1 at 220°C for 30 min without stirring). As observed for sample 80, a concentration of 2.5 phb of SBS could lead to instability of the dispersion during hot storage. However, samples F (85) and G (91) showed to be stable. Sample 91 was loaded with 0.7 phb of SBS gel, and with 5.0 phb kneaded (devulcanized) and swollen ground-rubber. This GR-to-SBS proportion is commonly used in Mexican road construction and therefore of industrial interest. Mastercurves of sample 91 showed slightly similar slopes to those of sample 85, with lower values of *G'* and *G''* and η^*. However, the storage stability of both samples is significant.

Samples H and I contain the maximum possible concentration of poly(ar-amide) and poly(ar-ester) that could be reached without agglomeration of fibers around the impeller. Figure 15 and Figure 16 show the viscoelastic functions of bottom and top parts of both stored

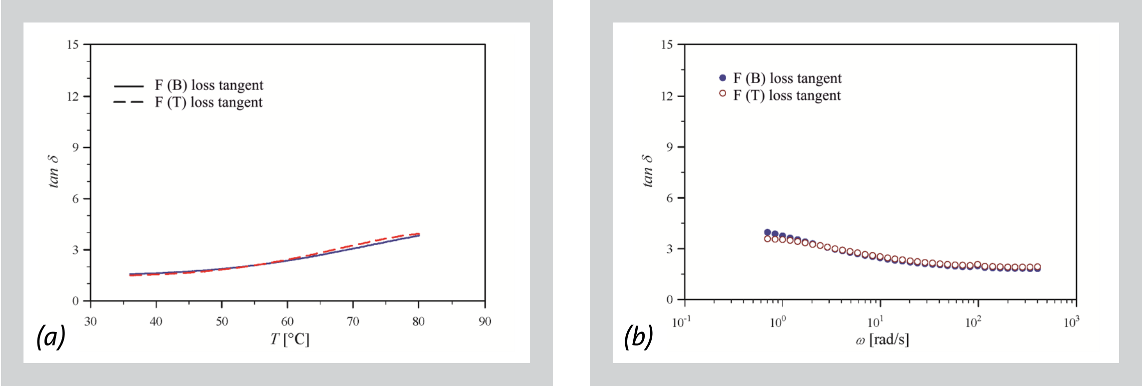


Figure 12 (above): Loss tangent tan δ of bottom and top parts of sample F obtained by temperature (a) and frequency (b) sweeps with in a single measurement at (a) 10 [rad/s] and (b) 60°C.

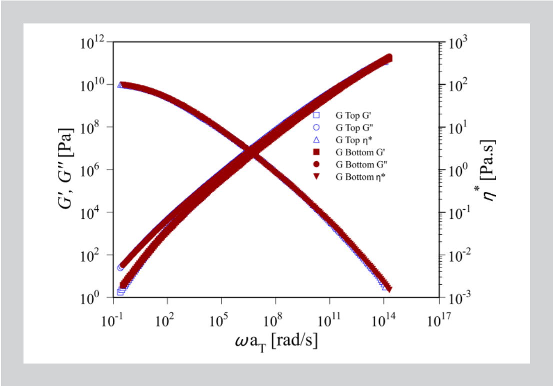


Figure 13 (below): Storage and loss moduli and complex viscosity of sample G. with 0.7 % SBS and 10 % ground rubber (reference temperature 60°C).

samples. Both rheological curves of sample H, resulted in a horizontal lines of tan δ against temperature and frequency. The poly(ar-amide) chopped fibers provided bitumen with enhanced rheological properties. Comparing the curves of Figure 15 with those of Figure 16 it is observed that the original slope of tan δ can be considerably changed by addition of a small amount of polymer. Chopped fibers have a significant effect on the viscoelastic properties of bitumen. Under the optical microscope, the fibers of poly(ar-amide) appeared as yarn, while the chopped fibers of poly(ar-ester) appeared as single fibers showing a more rigid-like structure and a smooth surface.

Figures 15 and 16 show that the stability performance of bitumen can be of interest when chopped fibers of poly(ar-amide) and poly(ar-ester) are used. However, this property enhancement is observed only within the temperature range of the non-modified bitumen, which is limited by the performance grade. This can be understood due to the rheological behavior of bitumen: Once the bitumen is softened, near its melting point (about 100°C), the fibers can no longer act as reinforcement, even when the chopped fibers have a noteworthy effect on the viscoelasticity of bitumen. Sample H was modified with the same weight of chopped fibers as Sample I. However, the poly(ar-ester) fibers from sample 4 resulted in poorer storage stability. Though, both storage stability index values as discussed below, present acceptable tolerances, as shown in Table 3.

It was observed that at higher temperatures, the tan δ of non-modified bitumen increases. With polymer addition, however the values of tan δ at higher temperatures remain lower. Therefore, tan δ not only can be used as a measurement of the storage stability, but also of the efficiency of the modifying polymer. Frequency as well as temperature sweep tests allow characterizing the storage stability of modified samples. In order to quantify and classify the storability of different samples modified by various polymers and diverse mixing procedures, two storage stability indices are proposed. The first one, the temperature stability index $\bar{S}_{i\text{-}T}$, takes into account the values of tan δ as a function of temperature at 10 rad/s as shown in Equation 1.

$$\bar{S}_{i-T} = \frac{\sum_{T_o}^{T_f}\left|1-\left|\frac{tan\delta_T - tan\delta_B}{tan\delta_T}\right|\right|}{N} \qquad (1)$$

The second one, the frequency stability index $\bar{S}_{i\text{-}\omega}$ takes into account the values of tan δ as a function of frequency at 60°C (Equation 2), at frequencies from 0.1 to 400 rad/s.

$$\bar{S}_{i-\omega}\Big|_{T=60^\circ C} = \frac{\sum_{\omega_o}^{\omega_f}\left|1-\left|\frac{tan\delta_T - tan\delta_B}{tan\delta_T}\right|\right|}{N} \qquad (2)$$

The stability indices consider the rheological properties of the polymer-modified bitumen obtained from the bottom and the top parts of the test tubes, which were stored at high temperature. Equation (1) takes into account the values obtained from the temperature sweeps between 35 and 70°C, a temperature range selected due to the fact that higher temperatures would require the use of 50 mm diameter parallel plates instead of 25 mm plates in the rheometer. This range can vary for other bitumen grades. It was possible to measure certain modified bitumen samples at temperatures higher than 70°C without using larger parallel plates because the *G'* was significantly increased by polymer addi-

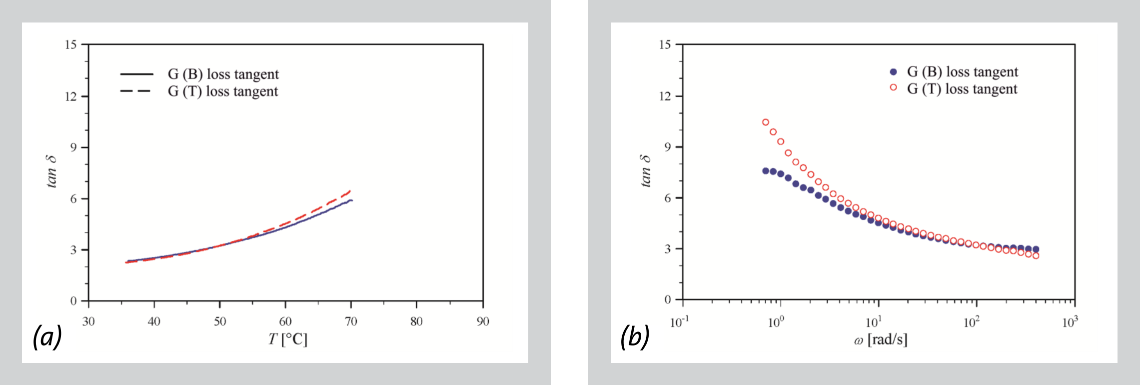


Figure 14 (above): Loss tangent tan δ of bottom and top parts of sample G obtained by temperature (a) and frequency (b) sweeps with in a single measurement at (a) 10 [rad/s] and (b) 60°C.

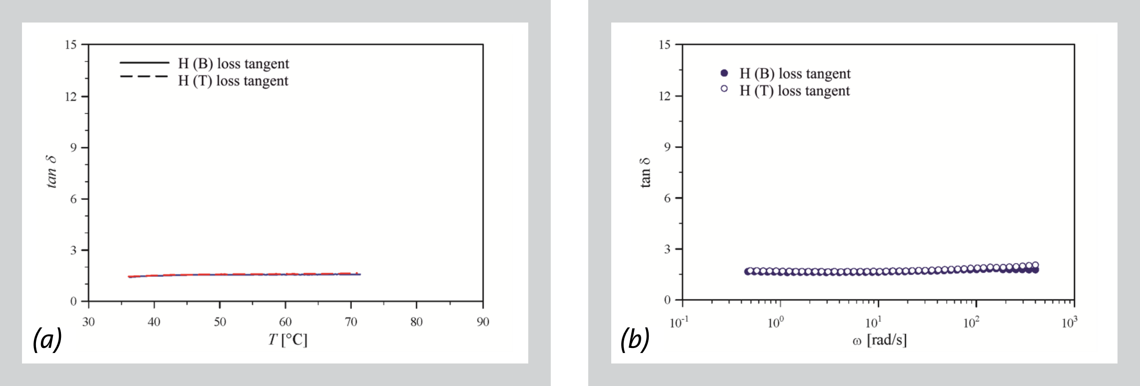


Figure 15 (middle): Loss tangent tan δ of bottom and top parts of sample H obtained by temperature (a) and frequency (b) sweeps with in a single measurement at (a) 10 [rad/s] and (b) 60°C.

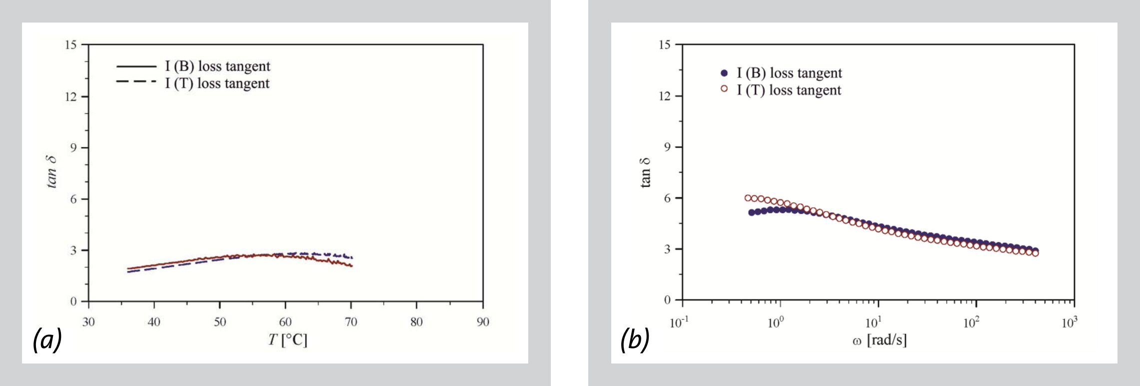


Figure 16 (below): Loss tangent (tan δ) of bottom and top parts of sample I obtained by temperature (a) and frequency (b) sweeps with in a single measurement at (a) 10 [rad/s] and (b) 60°C.

tion. However, in order to standardize the temperature stability index only the temperature range from 35 to 70°C is considered. The loss tangent as a function of frequency from the bottom (tan δ_B) and top (tan δ_T) parts of the storage test tubes were measured for all the samples at 60°C, using the same frequency sweep test parameters for $0.1 > \omega > 400$ rad/s. *N* is the total number of measurements. Values of $\bar{S}_{i\text{-}T} = 1.00$ or $\bar{S}_{i\text{-}\omega} = 1.00$ indicate that a sample is completely stable during hot storage. However, values between 0.90 and 1.10 would indicate acceptable stability of the modified bitumen, and therefore its suitability for being transported at 160°C, with little de-mixing until the lay down process. Stability indices from temperature and frequency sweeps are presented in Table 3.

5 CONCLUSIONS

We have studied the effect of pre-processing of both ground rubber and SBS with oil. It has a positive influence on the mixing efficiency and the rheological behavior of polymer-modified bitumen (PMB). By pre-processing the modifying rubbers, the required time to obtain a stable dispersion of SBS and GR in bitumen was effectively reduced from 1–12 h to 20–40 min, developing samples which were stable during hot storage; even when they were processed at 160°C, 900 to 1400 RPM, and for less than 40 min. Swollen Rubber particles are fast incorporated into bitumen than non-treated SBS. The suggested stability

Table 4: Stability Indices defined in Equations 1 and 2 from temperature and frequency tests.

Sample	$\bar{S}_{i-T}$	$\bar{S}_{i-\omega}$
A	0.75	0.70
B	0.76	0.65
C	0.95	0.93
D	0.59	0.53
E	0.92	0.90
F	0.96	0.96
G	0.96	0.91
H	0.98	0.96
I	0.93	0.93

indices $\bar{S}_{i-T}$ and $\bar{S}_{i-\omega}$ show good correlation between each other, and can be used to characterize quantitatively the stability of modified bitumen in temperature and frequency sweep tests. These indices can be simply used for quality control purposes with less uncertainty than the commonly used parameter η_o. Devulcanizing of ground-rubber did not showed conclusive advantages in rheological properties. Therefore, it is not suggested mechanical kneading of ground rubber. Bitumen modified with polymeric fibers showed fair to good stability, however, the addition of chopped fibers of poly(ar-amide) and poly(ar-ester) is limited to low concentrations. Due to the high mixing efficiency of pretreated SBS, future work should be focused on bitumen modification in a continuous or semi-continuous process, such as twin-screw kneader/reactors.

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