Influence of Rubber Pre-Processing on the Rheological Behavior of SBS/Crumb Rubber-Modified Bitumen

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ABSTRACT

Mixing of SBS and crumb-rubber in bitumen requires high temperatures, as well as long mixing times and high shear deformations, for producing a satisfactory dispersion. Rubber pre-treating leads to a more efficient mixing process with reduced mixing time and improved dispersion quality. Bitumen modified with pre-treated rubber shows good stability and can be stored for reasonably long times without phase separation.

INTRODUCTION

Bitumen for asphalt cements is currently modified with polymers to improve its viscoelastic properties[1]. In a so-called wet process, small quantities of polymer are dispersed under high shear in hot bitumen to enhance the asphalt road performance. It is also common to add small quantities of rubber, such as 1%, but also higher quantities up to 9 % can be added[2-3].

Addition of polymers helps in delaying permanent deformations of roads, such as rutting at high temperatures, increases fatigue resistance and low temperature susceptibility. Due to these positive effects, addition of polymers increases the service time of paved roads[4]. Rubber is also incorporated in bitumen to produce asphalt roads with better mechanical properties, as addition of rubber allows an asphalt to retard low temperature cracking, which occurs when the binder is too stiff[5], and improves rutting resistance at high temperature[6]. However, the solubility parameters of the bitumen components (saturates, aromatics, resins and asphaltenes) are often different from those of the polymers and rubbers, retarding and even hindering the dispersion of polymers and rubbers in hot bitumen[7-8]. To achieve a good dispersion it is necessary to decrease considerably the particle size from millimetres or centimetres to micrometers[9]. The particle size reduction requires high temperature (160-210 °C) and long mixing times. Depending on the bitumen, the polymer and the polymer dispersion required, the mixing time can take from 1 to 6 h under shear as high as 6000 RPM[2,6,10-14]. In industrial applications, the highest possible shear is lower than that reached in laboratory due to the larger tank volumes, and thus the effective time to ensure a good mixture can be even longer. The above mentioned processing conditions have an environmental impact as well as lead to increased processing costs that should be considered when the mixing design is specified.

Tire scrap represents also an ecological problem if it is not treated properly, and the use of crumb-rubber in asphalts represents a good recycling solution. However, one of the greatest challenges is to produce a dispersion that is stable during hot storage without phase separation or creaming of the polymer.

To allow better dispersion and homogenization of the crumb-rubber modified bitumen, high mixing speeds and high temperatures have been suggested. However, the rubber particles do not resist long times at high temperatures, and degradation of the polymer[15] 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[16]. Therefore it is important to produce an efficient SBS dispersion in bitumen without compromising its quality and stability.

The storage stability of rubber-modified bitumen is a measure of the miscibility of the rubber particles and the bitumen matrix, and high storage stability is needed to ensure a homogeneous dispersion of the polymers in bitumen during long transportation times at high temperatures. Storage stability is critical to ensure the final Polymer-Modified Bitumen (PMB) quality[17].

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 saturates: 5.2%, aromatics: 44.9%, resins: 23.8%, asphaltenes: 26.1%.

Tire crumb-rubber, with particle size of ≤ 0.2 mm, was obtained from Genan GmbH (Germany). In addition rubber scrap from other sources was used.

Three commercial grades of SBS (SBS-A: S-411, SBS-B: S-1205 and SBS-C: H6120) for modifying bitumen were obtained from Dynasol (Mexico). SBS-A with a styrene content of 30% and a star molecular architecture is used in all the formulas presented here.

Two different oil grades where obtained from Sunoco (USA), the first one (Hydrolene H180T) is commonly used to control the viscosity in bitumen, and is referred to here as Oil-1. The second oil (Oil-2 Sunpar 2280) is commonly used in devulcanization processes of rubber in internal mixers.

2,2'-dibenzamidodiphenyldisulphide or DBADPDS with trade names Ultrapep 90 and Ultrapep 148 from Behn Meyer Europe were used as devulcanizing agents[18].

EXPERIMENTAL

All samples containing crumb-rubber were mixed "as supplied", except for sample G, for which the crumb-rubber was pre-treated by devulcanization with an internal Mixer (Brabender). To proceed with the devulcanization, the crumb-rubber was mixed with scrap rubber from other sources to form a mixture of 90% crumb-rubber and 10% scrap rubber. DBADPDS was used as devulcanization agent and Oil-2 as a lubrication aid.

Before dispersion in bitumen, SBS was pre-treated to form a gel with Oil-1 using an oil amount of 2 to 3 times the weight of the SBS without mechanical stirring.

The mixing of bitumen with polymer/rubber was carried out with a tailor made impeller (six blades) coupled to a rotor-stator (IKA, Eurostar Power Control Visc.) under constant temperature ±5 °C. The dispersions were made at speeds from 900 to 1400 RPM in vessels of 200 g of bitumen capacity.

After the dispersion of rubber was achieved, sulfur was added to cross-link the dispersed rubber. When the vulcanization was completed, each sample was separated into 2 parts. The first part, containing only a few grams of bitumen, was analyzed rheologically without any ageing process. The rheological behavior of rubber-modified samples was studied with a stress-controlled Rheometer (MCR301 Anton Paar Germany) under nitrogen atmosphere to avoid oxidation during the measurements at high temperatures. A plate-plate system was used

Table 1. Processing conditions of rubber-modified bitumen.

Sample	Polymer	[%]	Temperature [°C]	Speed [1/min]	Mixing time [min]	Reaction time [min]
A	SBS	2.5	180	900	10	30
B	SBS	0.7				
	Crumb-rubber	10.0	160	1200	10	30
C	SBS	1.0	160	900	10	30
D	SBS	5.0	160	1400	10	30
E	SBS	2.5	160	1400	20	30
F	SBS	2.5				
	Crumb-rubber	10.0	160	900	10	30
G	SBS	0.7				
	Kneaded c-NR	5.0	180	1200	120+10	30

with geometry of 25 mm and a gap of of 1.0 mm for neat bitumen and 1.2 mm for crumb-rubber/SBS modified bitumen. Frequency and temperature sweeps were carried out in oscillatory shear within the linear-viscoelastic regime.

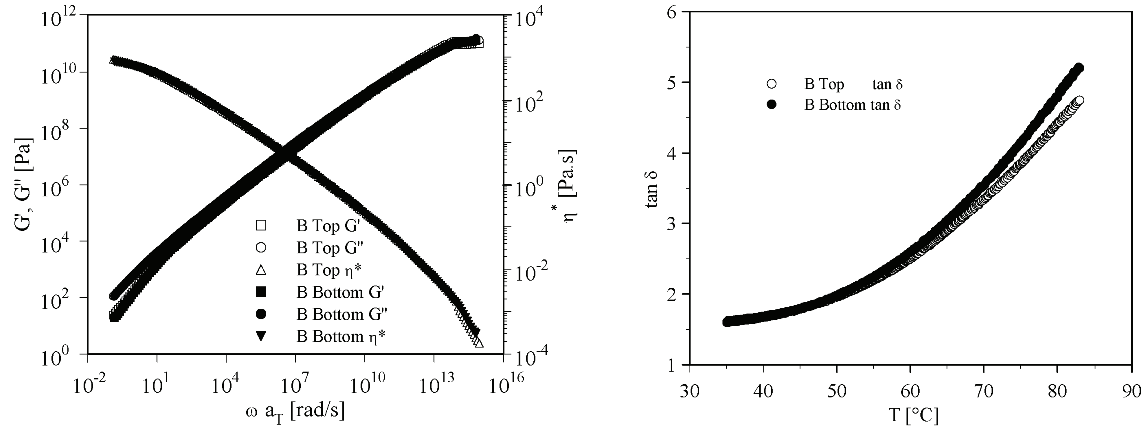
Frequency sweeps were performed in a frequency range of 0.01 – 390 rad/s under isothermal conditions. Temperature sweeps at 10 rad/s according to AASHTO-TP5[19] were made within the linear-viscoelastic regime in order to obtain measurements of the rutting parameter $G^*/\sin(\delta)$, complex viscosity η^*, and loss tangent tan δ.

Creep tests with a constant shear stress (σ_0) 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[20]. All the samples reached a steady state, after which the elastic recovery and the zero-shear viscosity (η_0) were determined.

For the storage stability tests, the PMB samples were poured in aluminum tubes having a diameter of 38 and a length of 220 mm. The tubes were firmly closed to avoid 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 time, the samples where carefully cooled down to avoid any agitation of the hot bitumen. After cooling, the samples were frozen and divided in three parts in order to take specimens from the top and bottom of the tubes for characterizing the storage stability of the different samples in a similar way as described by Becker[12]. The processing parameters for the modified samples are shown in Table 1. The temperature indicates the mixing temperature of polymer and bitumen. Mixing time indicates the processing time to achieve the designed dispersion; in the case of sample G, the times given are the mixing time with crumb-rubber, and the mixing time after addition of SBS gel.

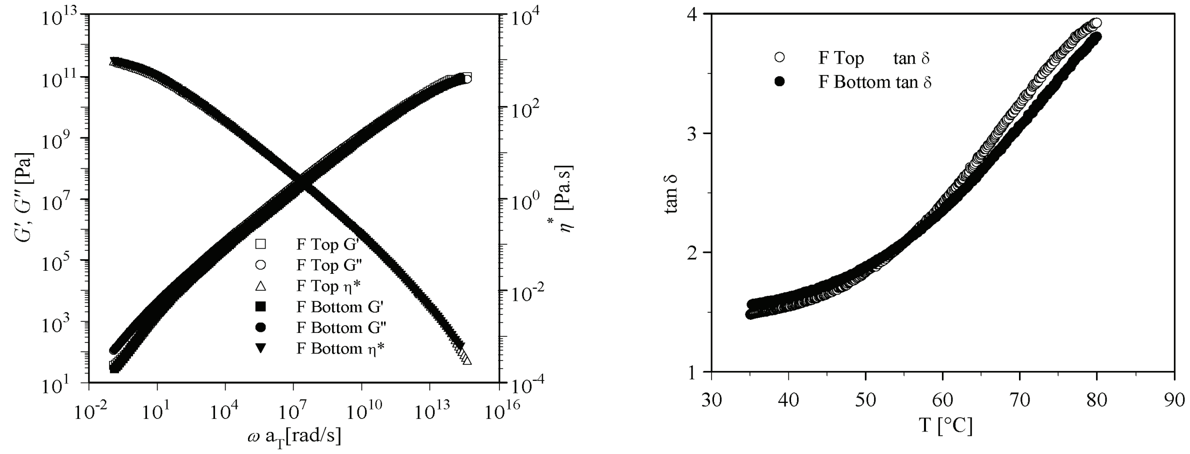
RESULTS

Samples F and G in Figs. 2 and 3 show a similar behavior as sample B: G’ and G’’, as well as η^*, from the bottom and top parts are very similar, and therefore, these samples can be considered as stable. From the frequency sweeps in Figs. 1-3 it is observed that tan δ is very similar at lower temperatures, while above 60 °C the difference in the values of tan δ between the bottom and top part increases.



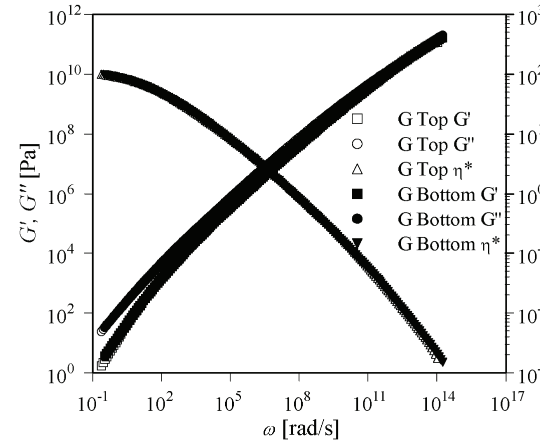
(a) (b)

Figure 1. (a) Storage and loss moduli and complex viscosity of sample B containing 0.7% SBS and 10% crumb-rubber (reference temperature 60°C) and (b) Loss tangent tan δ of bottom and top parts obtained by temperature sweep tests.

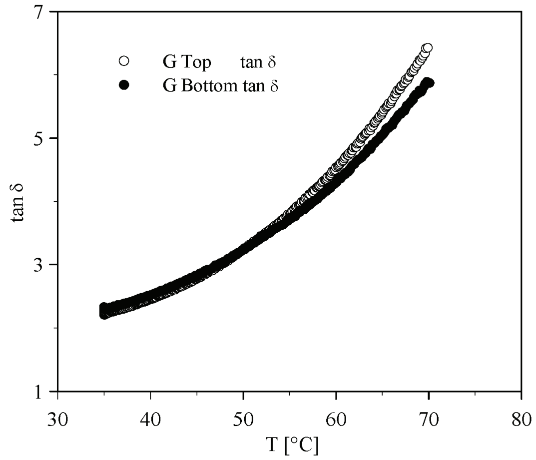


(a) (b)

Figure 2. (a) Storage and loss moduli and complex viscosity of sample F. containing 2.5% SBS and 10% crumb-rubber (reference temperature 60°C) and (b) Loss tangent, tan δ of bottom and top parts obtained by a temperature sweep.



(a)



(b)

Figure 3. (a) Storage and loss moduli and complex viscosity of sample G. with 0.7% SBS and 10% crumb-rubber (reference temperature 60°C) and (b) Loss tangent, tan δ of bottom and top parts obtained by a temperature sweep

To quantify the stability of the rubber-modified bitumen samples, two indexes are proposed. Both stability indexes are obtained from temperature sweeps $\overline{S}_{i-T}$ as shown in Eq. 1 and from frequency sweeps at 60 °C $\overline{S}_{i-\omega}$ as shown in Eq. 2. The stability indexes take into account measurements from the bitumen obtained from the bottom and the top parts of the test tubes stored at high temperature.

$$\overline{S}_{i-T} = \frac{\sum_{T_0}^{T_f}\left[\left|1-\left|\left(\frac{\tan\delta_T - \tan\delta_B}{\tan\delta_T}\right)\right|\right|\right]}{N} \quad (1)$$

$$\overline{S}_{i-\omega}\Big|_{T=60^\circ C} = \frac{\sum_{\omega_0}^{\omega_f}\left[\left|1-\left|\left(\frac{\tan\delta_T - \tan\delta_B}{\tan\delta_T}\right)\right|\right|\right]}{N} \quad (2)$$

The loss tangents tan δ_B and tan δ_T were measured at the same temperature, and using the same frequency sweep test parameters. N is the total number of measurements.

Stability indexes for all the samples from temperature and frequency sweeps are presented in Table 2. Values of $\overline{S}_{i-T} = 1.00$ or $\overline{S}_{i-\omega}$=1.00 indicate a sample that is completely stable during storage. However, values between 0.90 and 1.10 would indicate a satisfactory stability of the sample.

Table 2. Stability Indexes from temperature and frequency tests.

	Stability Index	
Sample	$\overline{S}_{i-T}$ (tan δ)	$\overline{S}_{i-\omega}$ (tan δ)
A	0.75	0.70
B	0.97	0.96
C	0.95	0.93
D	0.59	0.53
E	0.50	0.53
F	0.96	0.96
G	0.96	0.91

CONCLUSIONS

Pre-processing of both crumb-rubber and SBS has a positive influence on the mixing efficiency and the rheological behavior of polymer-modified bitumen (PMB). By pre-processing the rubber, the mixing time, temperature, and shear needed for obtaining a satisfactory dispersion can be significantly reduced. Rheological behavior of pre-processed rubber-modified bitumen shows a more flexible binder at low temperatures, which can retard cracking of pavements. Other rheological properties such as moduli, tan δ, complex and zero-shear rate viscosity, show an improved rutting resistance of the paved asphalt at high service temperatures.

Rubber particles in gel form are faster incorporated into bitumen than SBS “as supplied”, without impairing its dispersion grade. Rubber dispersion were shown to be stable even when mixed at processing temperatures as low as 160°C, under low shear conditions (900-1400 RPM) and for less than 20 min of mixing.

The storage stability of SBS/crumb-rubber is satisfactory for the rubber-modified samples under certain processing conditions, and the inclusion of crumb-rubber seems to increase the stability of the SBS-bitumen dispersions.

The suggested stability indexes $\overline{S}_{i-T}$ and $\overline{S}_{i-\omega}$ show good correlation between each other, and can be used to characterize quantitatively the stability of modified bitumen in temperature and frequency sweep tests. The loss factor tan δ is highly sensitive and is highly reproducible, and it can be easier measured in practice than the commonly used parameter η_0 in a wide temperature range.

Crumb-rubber modified bitumen, i.e. samples B, F and G, showed higher stability than modified-bitumen without it: even samples with a very high viscosity (sample D) due to a high content of SBS showed lower stability without crumb-rubber. Samples containing a small amount of SBS, such as 1.0 wt%, showed good stability (sample C), which means that the stability of SBS-modified bitumen could depend not only on good dispersion, but also on the density differences and the lack of compatibility (solubility parameter differences) between SBS or crumb-rubber and bitumen.

Due to the high mixing efficiency of SBS in gel form, future work can be focused on a modification in semi-continuous CSTR reactors instead of large batch reactors.

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