RHEOLOGICAL CHARACTERIZATION OF BITUMINOUS COMPOUNDS FOR THE OPTIMIZATION OF ROOFING MEMBRANES

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ABSTRACT

Bitumen and polymer blends represent important compounds for the production of waterproofing membranes for the roofing industry. The addition of a polymer is fundamental to improve performance and mechanical characteristics. On the other hand, compatibility between asphalt and polymers is a crucial factor which deeply affect the thermo-mechanical and rheological properties of bituminous compounds. As a matter of fact, the low compatibility between polymer and bitumen is the root of many problems in the formulation of bituminous blends. A careful selection of the raw materials needed for the optimization of the final characteristics for the formulation of the bitumen-polymer compounds, used in the production of waterproofing membranes. Polyolefins and elastomers are commonly used in this kind of products, thanks to their compatibility with bitumen. The following study investigates the role of quantity and type of polymer to produce bituminous waterproofing membranes, by comparing the performance of different bitumen and polymer combinations (radial and linear SBS) through rheological tests. The bituminous compounds were tested with a strain-controlled rheometer by using a "temperature sweep" protocol, an oscillatory test in which both components of the moduli (G', elastic and G'', viscous) were evaluated by cooling the sample at a fixed frequency within the viscoelastic region. This kind of analysis gives an interesting insight into the behaviour of the bituminous compounds in a wide range of temperatures.

INTRODUCTION

Bituminous membranes consist primarily of bitumen, polymers, and an inert filler. The use of polymer-modified bitumen (PMB) is currently the standard choice for the production of bituminous water-proofing membranes, since the modification with a polymer significantly increases the viscoelastic properties of raw bitumen, especially at low temperatures.

However, the compatibility between bitumen and polymer is a critical factor in this kind of formulation; a careful selection of both components is necessary to achieve the desired final properties. Bitumen itself is a complex mixture of many components and each type of bitumen possesses a unique chemical composition, which determines different chemical interaction with the modifying polymer.

Additionally, the chemical nature of the polymer plays a key role. Commercially available SBS (styrene-butadiene-styrene) polymers with various structures—radial, linear, and diblock—and different PB/PS ratios are commonly employed to modify bitumen[1,2,3]. The structural differences among these polymers are highly significant, as they directly influence the performance level of the resulting PMB[4].

The degree of compatibility between bitumen and polymers is a critical factor in the production of bituminous membranes, as it directly affects the thermodynamic stability of the final product over time. Compatibility refers to the ability of bitumen to integrate intimately with a polymer, forming a biphasic morphological structure in which the polymer establishes a continuous and dominant phase, while the bitumen remains dispersed in a discontinuous phase[5].

Thermal susceptibility is another key aspect to understand the thermal stability of the compounds and their ability to maintain the desired properties under varying temperature conditions. This parameter significantly influences the performance of the modified material, making it a fundamental point to consider in PMB formulation. Classical laboratory tests performed at fixed temperatures provide only a limited perspective on the material's behaviour as a function of temperature. This limitation highlights the need to complement standard tests with advanced rheological and mechanical characterization techniques[6]. These advanced methodologies enable a deeper understanding of the modified bitumen's behaviour, facilitating the identification, optimization, and exploitation of the interactions between various bitumen types and polymers.

The following study investigates the role of quantity and structure of polymer to produce bituminous waterproofing membranes, by comparing the performance of different bitumen and polymer combinations (radial and linear SBS) through rheological tests.

MATERIALS AND METHODS

Materials

Bituminous membranes were prepared by using bitumen 160/220 mixed with 9% tall oil. To this mixture two different types of SBS (linear and radial SBS) were added in two different percentages (5% and 8%).

PMB compounds were prepared as follows: bitumen, previously heated in an oven, is placed on a heating plate. At 180 °C, the filler is gradually added stirring between 200 and 500 rpm. When the latter is completely dispersed, the modifying polymer is added. Then, the stirring is progressively increased up to a maximum of 2000 rpm at 180-190 °C.

Test methods

DMA: Thermo-mechanical properties of the polymers (linear and radial SBS) were evaluated using a dynamic mechanical analyser, which measures the elastic modulus (E') through oscillatory measurements. The polymeric samples were tested with a ramp from -150°C to 50°C at 2°C/min, with 30 μm displacement at 1 Hz, using the "single cantilever" geometry.

DSR: A strain-controlled dynamic shear rheometer (702e by Anton Paar) was used to measure the rheological properties of the samples. The linear viscoelastic region (LVR) was preliminarily evaluated at three different temperatures (120°C, 60°C and 20°C) with an amplitude sweep, to select a suitable shear strain for the subsequent temperature sweep test. The temperature sweep was performed from 150°C to 20°C with a cooling rate of 2°C/min, applying 0.1% shear strain at 1 Hz to measure the storage modulus (G') and loss modulus (G").

RESULTS AND DISCUSSION

The DMA characterization of the polymers was performed to highlight the influence of the different morphology on their thermo-mechanical properties. From **Fig. 1** it can be noticed that linear SBS possesses a higher rigidity at low temperatures, which becomes comparable to the radial one for temperatures higher than -100°C. Both polymers show the same glass transition temperature around -86°C; linear SBS presents also an additional peak at -110°C.

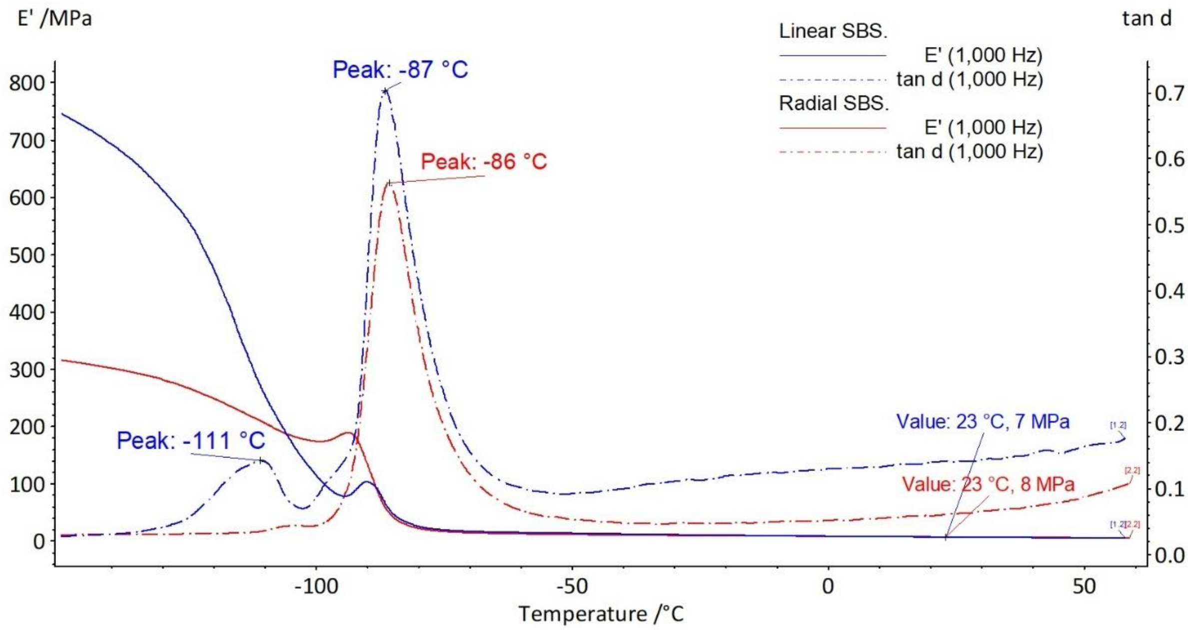

FIGURE 1: DMA characterization of linear and radial SBS

First, an amplitude sweep test was performed to evaluate LVR at different temperatures; one sample is shown in **Fig. 2** as an example. As expected, an increase in both G' and G'' moduli is observed by reducing the temperature; at the same time, the width of the linear viscoelastic region progressively decreases with temperature. The peculiar behaviour at 60°C, where the moduli values are almost overlapping, is confirmed by the temperature sweep test and discussed below.

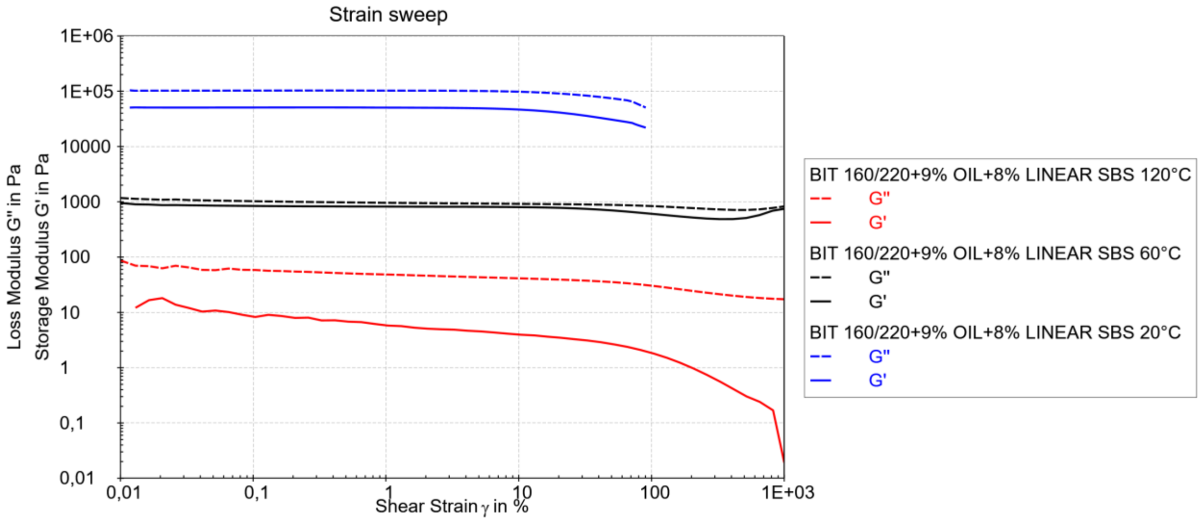

FIGURE 2: Determination of LVR at different temperatures

Then, the temperature sweep test was performed on all samples. The rheological profile obtained for the unmodified bitumen sample (**Fig. 3**) is characteristic of a system with no distinct texture, exhibiting a predominantly viscous response, with the loss modulus (G") much exceeding the storage modulus (G') in the entire temperature range. In the same graph a sample of raw bitumen, without the addition of oil, is also shown for a comparison. Tall oil is commonly used as a modifier for bitumen, since it is widely available as a by-product and it can significantly increase the viscous response of asphalt binders, resulting in better low-temperature properties but reduced high-temperature properties[7].

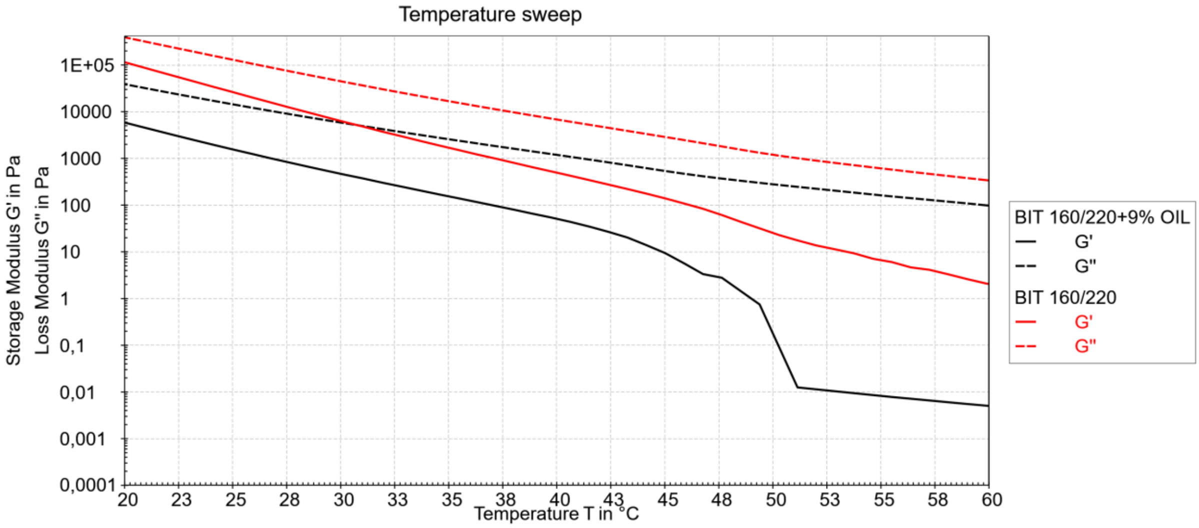

FIGURE 3: Effect of tall oil on the temperature sweep test

Modification with SBS significantly enhances the viscoelastic response of the bitumen, as testified by an increase in both components of the modulus, G' and G'', as can be easily observed from the values reported in **Tab. 1**. The viscoelastic properties of the PMBs are determined by the polymer morphology, the chemical composition of the bitumen, and the nature of their interactions. When SBS copolymers are incorporated into the bitumen, intermolecular interactions occur between the bitumen and the PS (polystyrene) and PB (polybutadiene) blocks of the SBS[8]. This leads to the formation of a rubbery supporting network within the modified bitumen, which contributes to increased moduli, particularly by enhancing the elastic response.

TABLE 1: G' and G'' values at different temperatures

	40°C		**70°C**		**90°C**		**120°C**		**T cross/ °C**
	G'/Pa	**G''/Pa**	**G'/Pa**	**G''/Pa**	**G'/Pa**	**G''/Pa**	**G'/Pa**	**G''/Pa**	
Bitumen + 9% oil	54	1242	$2\cdot10^{-3}$	41	$5\cdot10^{-4}$	9	$9\cdot10^{-5}$	2	-
5% radial polymer	2775	4725	482	509	130	252	12	55	-
8% radial polymer	12778	6908	2176	3303	349	947	30	170	30; 63
5% linear polymer	606	2996	3	116	$1\cdot10^{-3}$	28	$3\cdot10^{-4}$	5	-
8% linear polymer	2879	4663	727	466	272	294	2	19	55; 90

From the comparison of **Fig. 4** and **Fig. 5** it emerges that both the quantity and the morphology of the modifying polymer deeply affect the viscoelastic properties of the system.

An increasing percentage of the polymer leads not only to an increase of the moduli value, but also to a different relation between G’ and G’’; this is especially apparent in the case of linear SBS. In fact, a different degree of modification of the PMB is associated to a change in the microstructure of the material.

The morphology of SBS also plays a pivotal role: thanks to is architecture, radial SBS is more likely to form a rigid and robust three-dimensional network within the bituminous matrix. On the other side, linear SBS has weaker interactions with the bitumen. In fact, 5% of linear SBS has much less impact on the rheological behaviour compared to 5% of radial SBS.

It can be observed that 8% of modifying polymer induces a structural change that radically influences the rheological properties at intermediate temperatures (approximately 40°C-70°C for radial SBS and 50°C-90°C for linear SBS). In this temperature range, the response become more elastic and the storage modulus G’ prevails over G’’. This surprising behaviour is probably ascribable to the complexity of the PMB structure, especially with SBS as a modifying polymer; the different glass transition temperatures of polystyrene and polybutadiene blocks must be taken into consideration.

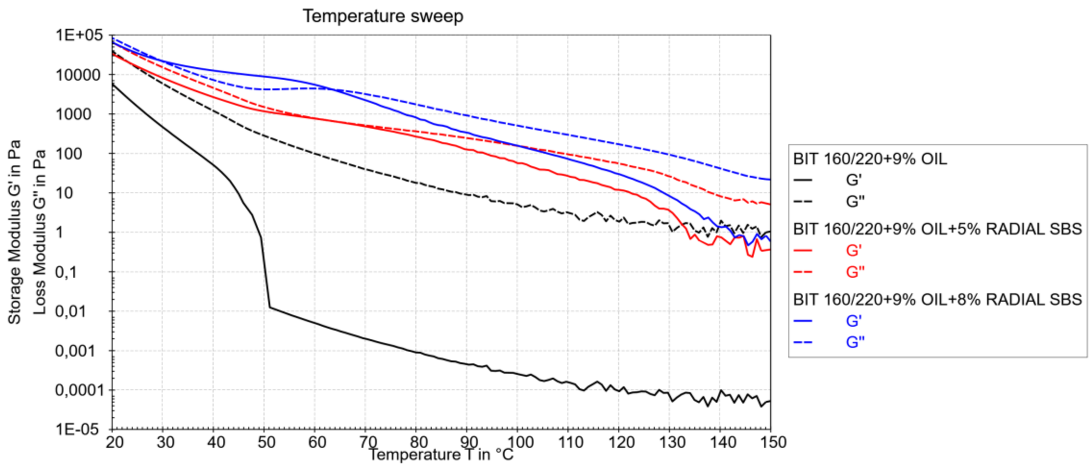

FIGURE 4: Effect of radial SBS on temperature sweep test

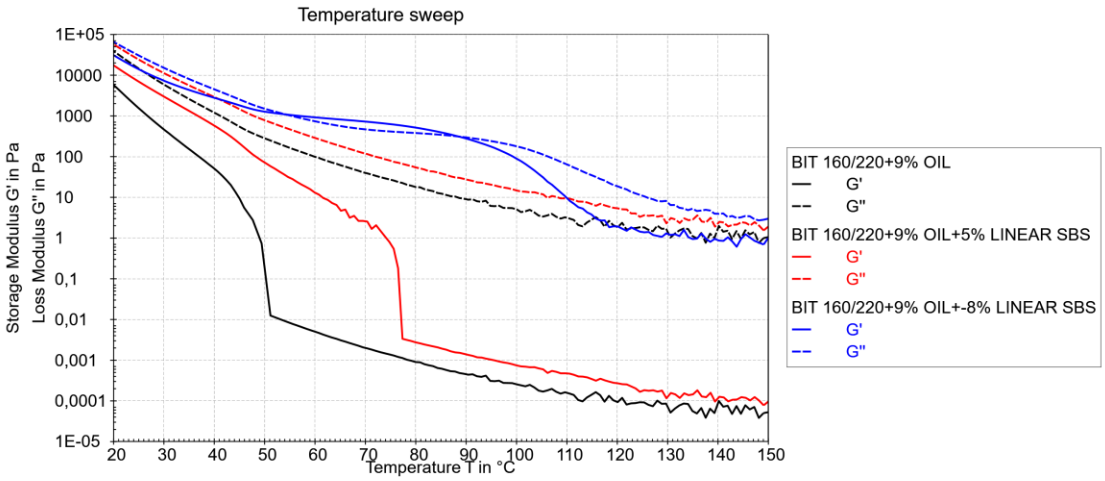

FIGURE 5: Effect of linear SBS on temperature sweep test

CONCLUSION

The rheological analysis conducted on SBS-modified bitumen compounds provided a deep and complex description of the material behaviour over a wide temperature range. The results demonstrate that the incorporation of SBS polymers significantly enhances the viscoelastic properties of bitumen. However, the degree of compatibility between the bitumen matrix and the SBS polymer plays a pivotal role in determining the overall performance of the composite material.

The different architectures of SBS polymers—linear and radial—have a substantial influence on the rheological response of the compound, leading to different performance characteristics that must be carefully considered during the formulation of bituminous membranes. These findings are particularly pertinent to the design and optimization of waterproofing membranes, where both thermal and mechanical properties are critical for ensuring the long-term durability and reliability of the final product.

The appropriate selection of SBS polymer types is crucial from an applicative point of view, since bituminous membranes require a precise balance between thermal stress resistance and adhesion to the substrate[6]. Rheological evaluations further affirm that achieving optimal performance necessitates the careful selection of bitumen and SBS polymer combinations, tailored to the specific demands of the application and local climatic conditions.

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