

Turning challenges into solutions through innovation

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Abstract

Nowadays, safety and environmental concerns are acquiring increasing attention in our daily life. Asphalt industry is not an exception, and with more than 90% of the 5.2M Km of the Europe road network [1] this technology has to be adapted to these new challenges. For at least three decades, SBS modified bitumen has been used in paving with the aim of reducing road damages such as rutting, cracking and stripping. On the other hand, in roofing and waterproofing industry, SBS modified bitumen enhances the membrane elongation, increases elasticity, provides excellent low-temperature flexibility and high temperature resistance and more adhesive properties [2]. The specifications and properties of the SBS will impact noticeably in the performance of the modified binder in the final application. Different approaches have been developed to improve asphalt performance through the design of new SBS polymers based on a comprehensive study from polymer macro and microstructure to final application validation. These new SBS grades fulfil with the requirements to be used as modifiers for promising technologies such as Reclaimed Asphalt Pavement and shingles (RAP/RAS), warm-mix and porous asphalt pavement for rain drainage and noise reduction. References: [1] Alterpave project. Giteco. Unican <https://www.giteco.unican.es/proyectos/ALTERPAVE/index.html> [2] M. Davis, 2018. SBS modified bitumen roofing. https://continuingeducation.bnpmmedia.com/article_print.php?C=1649&L=514

1. INTRODUCTION

Bitumen is a material from the refining industry which is very important for paving and roofing industries. However, it is a brittle, solid material at low temperature and it is a viscous, deformable material at high temperature [1]. Therefore, failures like permanent deformation at high temperature and thermal cracking at low temperature may occur. Moreover, the increase in traffic loading can accelerate these pavement distresses [2].

Styrene-butadiene copolymers are elastomeric materials frequently used as asphalt modifiers in order to enlarge the temperature range of asphalt mixtures. Moreover, they improve the elastic behaviour of the bitumen, enhancing permanent deformation under traffic loadings [3]. The polystyrene domains give tensile strength and resistance to plastic deformation at high temperatures. On the other hand, the polybutadiene blocks give elasticity, fatigue resistance and flexibility at low temperatures. When the polymer is incorporated into the hot bitumen, the polystyrene blocks begin to soften and the polymer swells. When the mixture is cooled, the polystyrene blocks harden and form a polymer network interconnected by the butadiene phase. Figure 1 shows the chemical structure of styrene and butadiene.

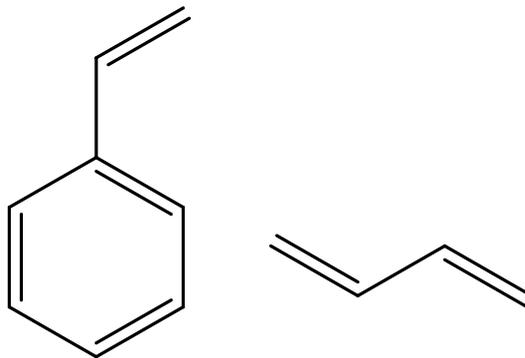


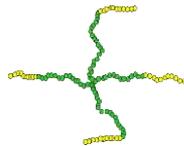
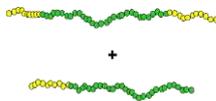
Figure 1. Chemical structures of styrene (left) and 1,3-butadiene (right)

There are different types of styrene-butadiene copolymers: styrene-butadiene rubber (SBR), linear styrene-butadiene-styrene (SBS) (sequential or dicoupled), radial SBS and styrene-ethylene-butylene-styrene (SEBS). In the past, SBR, which have a tapered structure, were the most frequently used polymer in paving. These polymers give excellent elastomeric properties and they require very low dispersion time. However, they require a crosslinking agent in order to form a polymeric network.

On the other hand, SBS (styrene-butadiene-styrene) triblock polymers are thermoplastic materials. In these copolymers, the crosslinking agent is not mandatory because the polystyrene (PS) blocks interact with each other forming polystyrene domains connected by polybutadiene (PB) chains, allowing a polymeric network. PS blocks are the hard segment and impart strength while PB blocks are the soft segment and enhance the elasticity. Among SBS, it is possible to differentiate different polymeric structures such as linear or radial polymers. Linear SBS are triblock polymers of styrene-butadiene-styrene. On the other hand, to obtain a radial SBS, four polymer chains of styrene-butadiene are joined together forming a branched structure. For the same molecular weight, a radial SBS has lower viscosity in comparison to a linear SBS. This permits to have product with high modification capacity but with adequate workability, which is very interesting for roofing applications.

Table 1 summarize the different types of styrene-butadiene copolymers suitable for bitumen modification, their polymeric structures and the main performance features.

Table 1. Styrene-butadiene copolymers for bitumen modification

POLYMER	STRUCTURE	PERFORMANCE
SBR		<ul style="list-style-type: none"> - Very low dispersion time and good storage stability - Improvement in rutting parameter - High elasticity - Adhesive properties: - Main applications: pavements and emulsions
LINEAR SBS		<ul style="list-style-type: none"> - Improvement in rutting, cracking and fatigue parameter - High elasticity - Main applications: pavements
RADIAL SBS		<ul style="list-style-type: none"> - High improvement in modulus, fatigue and rutting parameter - High elastic recovery - Main application: roofing
SBS + SB		<ul style="list-style-type: none"> - Improvement in rutting, cracking and fatigue parameter - Adhesive properties: autoadhesive membranes - Good dispersion - Main applications: pavements and emulsions
SEBS		<ul style="list-style-type: none"> - Excellent aging, thermal stability and weatherability - Main applications: roofing, mooping, sealants

Similar to radial SBS products, it is possible to obtain linear SBS via coupling agents. In this case, a dicoupling agent joints two polymeric arms of styrene-butadiene. This synthesis route has structural and performance advantages, such as a perfect symmetry of the two polystyrene blocks, a better control of the kinetic reaction and, therefore, a better control of the micro and macrostructure of the polymer. Also, it is possible to not couple all the polymeric chains, allowing the presence of styrene-butadiene diblock polymer chains. This diblock have adhesive properties, which could be interesting for some applications, such as autoadhesive membranes for roofing industry. The final polymer properties and performance will depend on the final composition of the polymer.

Regarding their synthesis, styrene-butadiene block copolymers are obtained by anionic polymerization. The polymerization starts with the polymerization of a styrene block followed by the addition of butadiene. When 1,3-butadiene is introduced, it may be linked as 1,4-butadiene (forming cis and trans groups) or 1,2-butadiene (forming vinyl groups, where the remainder double bond is located as a pendant group). Using polar modifiers it is possible to change the structure of the polybutadiene segment, promoting the formation of vinyl groups. This modification has a significant influence on bitumen performance: the polymer has lower viscosity at equivalent molecular weight due to it lower hydrodynamic volume, higher compatibility with bitumen and reactivity, higher resistance to oxidation and better thermal stability [4][5]. The reason why these high vinyl copolymers have higher thermal and oxidative resistance is the location of the remainder double bond. If the polymer is exposed to degradation, the main polymer chain will not be affected.

The viscosity of the polymer has a significant impact on the properties of the Polymer Modified Bitumen (PmB). In general, it allows a higher modification degree. However, the PmB is more instable to storage.

Moreover, it is possible to selectively hydrogenate a SBS polymer in order to saturate the remainder double bond (cis, trans, vinyl) of the polybutadiene chain. The saturation of double bond, especially in the polymer main chain, enhances significantly the thermal stability and weatherability of the polymer [6].

Nowadays, the society is increasing focus on sustainability, especially on the reduction of fossil fuels consumption greenhouse gases emission and reduction of raw materials. Traditional hot-mix asphalt technologies are responsible for a large amount of energy consumption and the release of pollutant gases. For this reason, warm-mix and cold-mix asphalt technologies, which require lower production temperature, are being encouraged due to their lower energy consumption and lower emissions [7].

The aim of this work is to develop different strategies modifying the polymer structure to fulfil the requirements of the different scenarios of bitumen modification.

2. RESULTS

Three SBS with different molecular weight were blended with a 70/100 bitumen during 2 h at 4000 rpm, 180 °C and different polymer concentrations. The softening point results are shown in figure 2. It is observed that, at the same polymer concentration, the higher molecular weight the higher softening point. Moreover, the softening point increases as the polymer content increases up to a point in which the softening point remains constant.

Table 2. Influence of softening point, penetration and cold bending

Polymer	MW	% diblock
A	315000	12
B	310000	27
C	342000	10

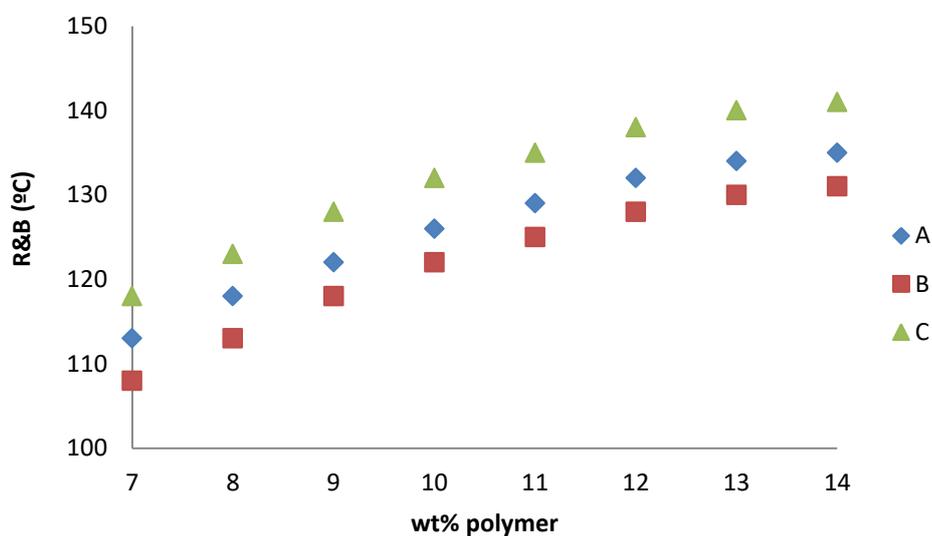


Figure 2. Influence of molecular weight and polymer content on softening point

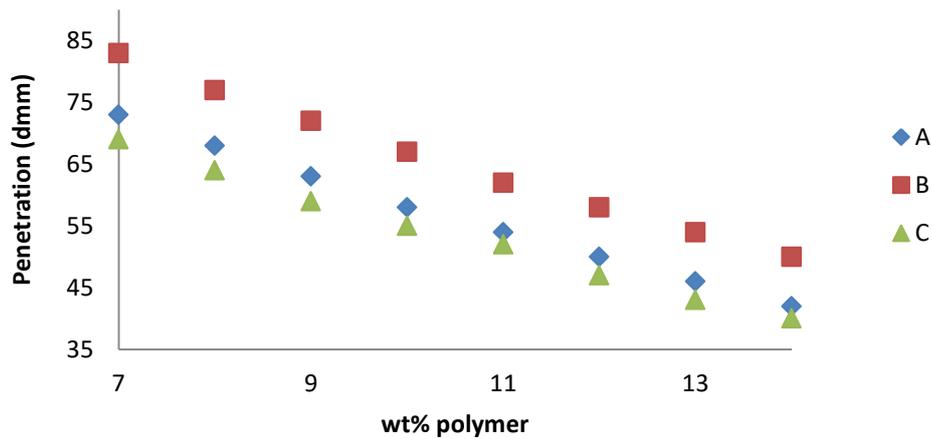


Figure 3. Influence of molecular weight and polymer content on penetration

Similarly, figure 3 shows the effect on penetration. The penetration decreases as the polymer content and molecular weight increase, as a result of the hardening of the bitumen. Another important parameter to be considered, especially for roofing applications, is the cold bending test, which gives an indication about the cold flexibility of the PmB. It is worth noting that the most flexible PmB is achieved with the polymer with lower molecular weight and higher diblock content..

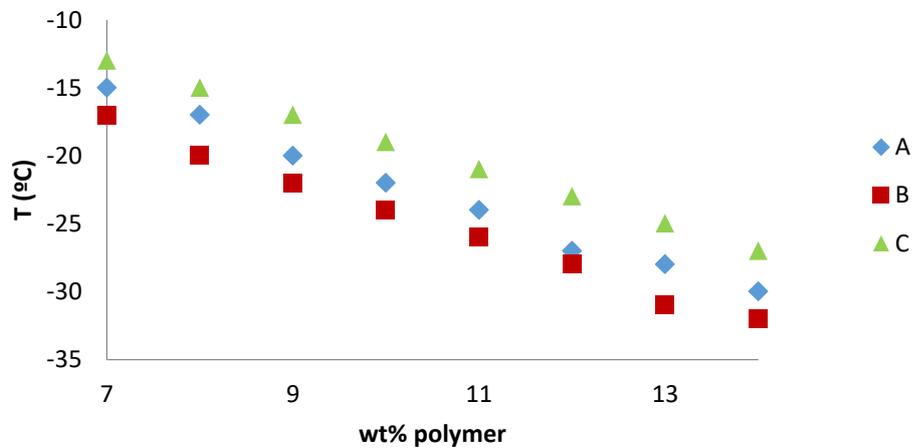


Figure 4. Influence of molecular weight and polymer content on cold bending

As it was aforementioned, the market is demanding new polymer configurations with better aging properties and reactivity with different types of bitumen, without sacrificing the PmB workability. Two SBS with equivalent molecular weight but different vinyl content (table 3) were evaluated according their Brookfield viscosity at different polymer content (figure 5).

Table 3. Influence of vinyl content on Brookfield viscosity

Sample	Vinyl (%)
D	12
E	35

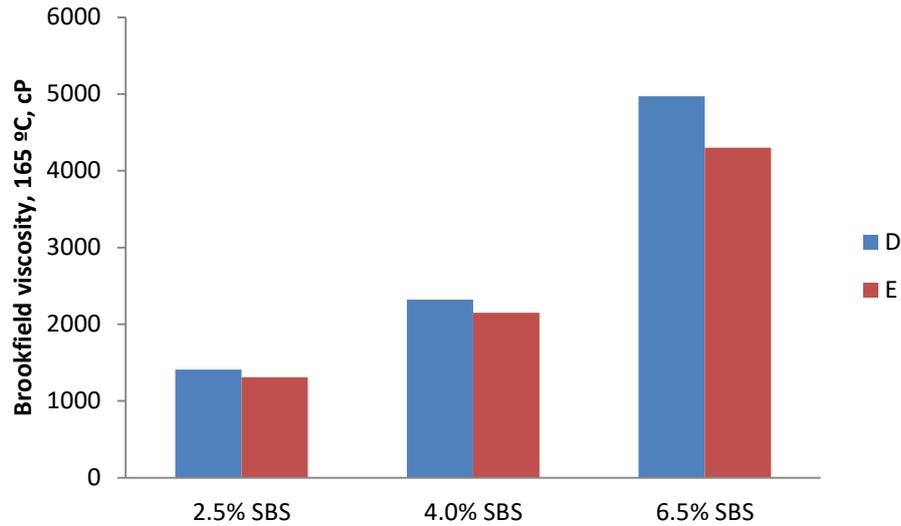


Figure 5. Influence of vinyl content and polymer content on Brookfield viscosity

As expected, as the polymer content increases the viscosity also increases exponentially. However, the polymer with higher vinyl content has lower viscosity. This difference is more remarkable at higher polymer content. This is an advantage for highly modified mixtures, making them more workable without compromising the degree of modification. Moreover, These high vinyl copolymers are more reactive with bitumen and they have better aging resistance compared to conventional low vinyl copolymers.

In figure 6 the thermal stability of a bituminous mixtures with 12% SEBS and SBS is represented. For this purpose, the evolution of Brookfield viscosity at 220 °C with time was registered. As it can be observed, the viscosity of the SBS starts to increase at 600 minutes, indicating the beginning of the degradation of the polymer. On the other hand, the viscosity of the mixture with SEBS remains constant demonstrating the superior thermal stability of these hydrogenated polymers.

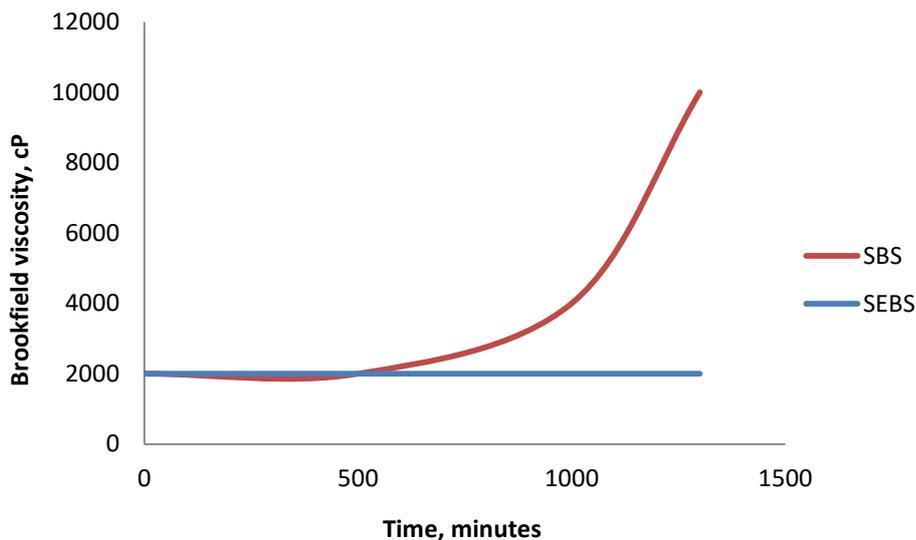


Figure 6. Thermal stability SBS vs. SEBS

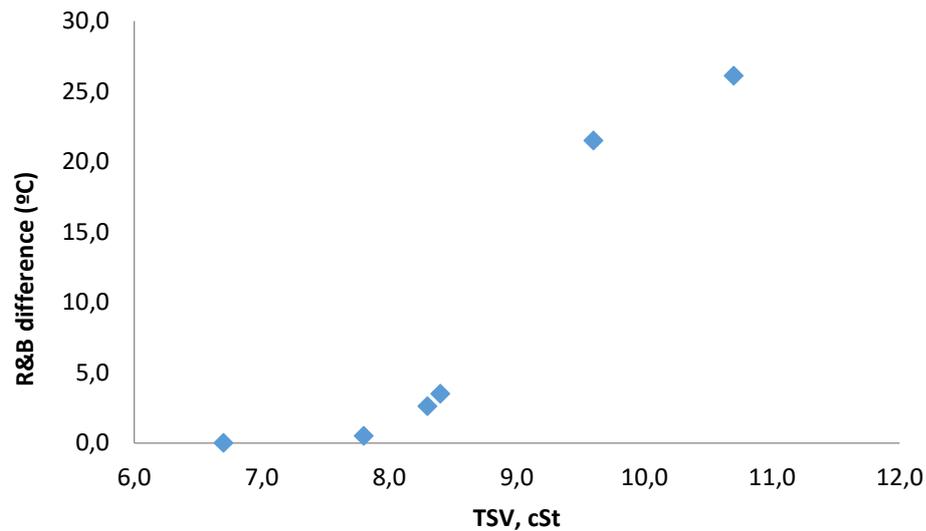


Figure 7. Influence of viscosity on storage stability, R&B difference.

As it was aforementioned, the viscosity of the polymer has a significant impact on the storage stability of the bituminous mixture. Mixtures with 5 wt% of different SBS with viscosities ranging between 6.5 and 11 cSt were produced at 180 °C and 3 hours. The effect of storage stability, expressed as the difference in softening point between the top and the bottom part of the test tube, is represented in figure 7.

The mixtures are more instable as the polymer viscosity increases. It is worth noting that there is an inflexion point at 8-9 cSt, probably associated to the formation of the polymeric network. Around this point, a small variation in the viscosity has a big impact on the stability of the mixture.

CONCLUSIONS

The softening point of the Polymer Modified Bitumen (PmB) depends on the molecular weight and the polymer content. These two variables can increase the softening point parameter. However, it can compromise the storage stability. One approach to increase the molecular weight of the polymer without reducing the storage stability is the use of high vinyl polymers which allow PmB with lower viscosity. Moreover, it is expected that the ageing of these polymers is better than conventional SBS.

It is also important to consider the properties at low temperatures, at which the PmB is more rigid and brittle. SBS polymers with lower molecular weight and medium-high diblock content result in a PMB more flexible at lower temperatures.

For applications in which the thermal stability is required, it is advisable the use of hydrogenated polymers (SEBS) which have superior resistance in comparison with SBS.

The micro and macrostructure of the polymers have a strong impact on the final properties of the PmB. It is possible to design copolymers specifically to fulfil the changing requirements of this industry.

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Annex

1. INTRODUCTION

The awakening of environmental consciousness is changing the traditional asphalt modification processes, not only in the mixing procedure towards less energy demanding conditions but also in terms of maintenance and transport of the mixes [1].

Polymer design plays a major role in this strategy. By means of specific combinations between micro and macrostructure is possible to obtain more reactive polymers with low viscosity, which can be concentrated in bitumen mixes, allowing a high level of modification, excellent Polymer Modified Bitumen (PmB) properties and ease of transport [2-3]. Among the polymer characteristics, the polybutadiene 1,2-vinyl percentage is essential for improving compatibility with different bitumen qualities, increasing durability and reducing the use of crosslinking agents.

For this purpose, two polymers with different structure were designed and evaluated at high concentration in bitumen modification. Moreover, one of them was also evaluated at lower mixing temperature (warm-mix asphalt) in order to explore the feasibility of the use of these polymers in more sustainable approaches.

2. EXPERIMENTAL

2.1. Materials

The base bitumen was EKBE PG 64-22, except for the warm-mix evaluation which was a 70/100 penetration grade from Repsol.

Two SBS polymers with different micro and macrostructure were designed and synthesized at pilot plant scale. The differences between them are related to styrene content, molecular weight, coupling degree and 1,2-vinyl content. A qualitative comparison is shown in table 1. The polymer structure was confirmed by FTIR, GPC and H-RMN.

Table 1. SBS qualitative characterization

Property	SBS A	SBS B
Styrene, %	medium-high	medium
MW, daltons	medium	low
Coupling degree, %	low	medium-low
1,2-vinyl, %	high	low

2.2. Bitumen mixing procedure

Bitumen blends were obtained at different concentration of SBS (6% and 3% diluted from 6% blend) at 190 °C, 3 h, 2500 rpm using a high-shear mixer. Warm-mix evaluation was carried out at 4% SBS concentration, 4000 rpm, 135 °C and 2h using a high-shear mixer.

2.3. Testing methods

Polymer modified asphalt blends were characterized by means of their softening point according to ASTM D36; penetration was determined using a Koheler penetrometer model K95500 according with ASTM D5; dynamic viscosity was obtained with a Brookfield viscometer model RDVS-II+ according with ASTM D4402, and rheological properties were studied according to SHRP and AASHTO T315 methods with a Paar Physica rheometer MCR-300-SP model.

3. RESULTS

Table 2 shows the evaluation of the two SBS in bitumen modification at 6% and 3% diluted from the 6% mixture.

High concentrated mixes achieved excellent performance, showing high modification at lower viscosity values. This low viscosity value are more prominent with SBS B, with almost the half of Brookfield viscosity at 135°C than SBS A. However, despite the fact that the standard European characterization is equivalent for both product, the Superpave Performance Grading is broader for SBS A probably due to the higher molecular weight and vinyl content. This high vinyl SBS permits high polymer concentration in PMB increasing the stiffness and elastic recovery without detriment in mix workability

On the other hand, the dilution at 3% of both modified bitumens obtained the same PG, proving the feasibility of working with concentrated mixes and subsequent dilution.

Table 2. Bitumen evaluation at high SBS concentration and subsequent dilution

Property	3% diluted		6%	
	SBS A	SBS B	SBS A	SBS B
R&B, °C	61	62	82	81
Pen. 25°C, dmm	44	45	38	40
Brookfield 135°C, cP	950	671	2206	1226
ER torsion, %	33	34	52	76
Ductility 25°C, cm	67	150	50	50
ER duct. RTFOT, 25°C, %	80	53	93	88
PG grade, °C	70-16	70-16	82-16	76-6

As SBS B is a low molecular weight polymer, it was explored for bitumen modification at lower temperature (135 °C) as a more sustainable mixing procedure. Table 3 showed the results of bitumen modification with SBS B at 180 °C and 135 °C. No undissolved particles were observed after mixing at 135 °C, demonstrating the ease of dispersion of this polymer. Moreover, similar performance was obtained at both temperatures confirming the possibility of working at less energy-demanding conditions.

Table 3. Bitumen evaluation at lower mixing temperature

Property	SBS B (180°C)	SBS B (135 °C)
Fraass, °C	-16	-16
Penetration 25 °C, dmm	48	56
R&B, °C	58,1	58,1
Brookfield 180 °C, Cp, 200 rpm	130	131
Elastic recovery 25°C, %	70,6	47,6
Storage stability, 180 °C, 3 days		
Top: Pen 25°C, dmm	48	50
Top: R&B, °C	60	59
Bottom: Pen 25°C, dmm	49	52
Bottom: R&B, °C	60	59

4. CONCLUSIONS

More environmentally friendly bitumen modification processes can be accomplished by tailored polymer designs. Low viscosity SBS can be dosed at higher concentration in bitumen mixes, achieving good PmB properties and transport benefits. Among the polymer characteristics, the polybutadiene 1,2-vinyl percentage is essential for an outstanding compatibility between SBS and bitumen even in absence of a crosslinking agent. Moreover, this low viscosity SBS strategy permits modification at more sustainable conditions.

5. REFERENCES

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