Viscoelastic Properties and Morphological Characteristics of Polymer-Modified Bitumen Blends

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ABSTRACT: The state of dispersion, the viscoelastic properties and the mechanical properties (such as Young's modulus, ductibility, penetration, and Fraas breaking point) of polymer-modified bitumen are investigated. Bitumen was modified with low-density polyethylene from processed bags (PE_{bags}) and styrene-butadiene random block copolymer (SBR). The blends were characterized by optical microscopy, dynamic mechanical thermal analysis (DMTA), and other conventional methods. Photomicrographs indicated that different morphologies were obtained; PE_{bags} gave dispersions with almost spherical polymer particles; whereas in the case of SBR, fibrillar domains were observed. DMTA measurements indicated significant changes of the storage and loss moduli of modified bitumen; depending on the polymer content in the bitumen matrix, these values were three to four times higher compared with neat bitumen. Blends with SBR showed a significantly increased resistance to cracking at low temperatures due to decrease of the glass transition temperature from −14 to −34°C. Contrary, PE_{bags} gave better results at higher temperatures where as a result of the increased resistance to permanent deformation the softening point of modified bitumen was shifted from 52 to 73°C. It was also investigated the influence of mixtures of PE_{bags}/SBR on the properties of bitumen as function of the composition and ratio between PE_{bags} and SBR. It was found that the best improvement in deformation resistance, permanent deformation, and cracking of bitumen was achieved with the addition of PE_{bags}/SBR mixture as the rubber increased the bitumen properties at low temperatures and the polyolefin at high temperatures. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1320–1330, 2010

Key words: polymer-modified bitumen; morphology; rheology; viscoelastic properties

INTRODUCTION

Bitumen is a semisolid or solid thermoplastic colloidal material with a complex chemical composition and very complex rheological behavior. Because of its good adhesive and waterproofing properties, bitumen has a wide range of applications but still one of its most widespread uses is as a binder in road construction. Nowadays, the intensive growth of the traffic, increased axle loadings, and the rigorous climate changes require high-performance roads.[1] Road performances depend mainly on the rheological properties of the bitumen because in asphalt mixtures bitumen is the only deformable component and continuous phase. In this way, viscoelastic properties of bitumen are of great importance to predict road characteristics over a wide range of temperatures and loadings. The deformation properties of bitumen are determined mostly by its chemical composition and the structure of its molecules; but even when the ratio of asphaltenes to maltenes is optimal, there is a narrow temperature range in which pure bitumen exhibits suitable rheological behavior necessary for good road performance.[2–5] Therefore, a lot of research work has been devoted to the problem of extension of bitumen's workability. This will prevent road defects like thermal cracking and rutting at lower and higher temperatures, respectively.

There are different ways of bitumen modifications. The most attractive one is the process of bitumen modification with polymers, because it greatly improves the strength of bitumen and its resistance to aging. It should also be mentioned that only a small number of polymer products are suitable for bitumen modification, although a wide variety of them exist on the market. The complexity of this process arises from the different properties and molecular parameters of the polymer modifiers and the

different bitumen composition and nature.[6–9] The various factors, mentioned previously, produce different polymer network structures in bitumen generating different morphologies of these bitumen/polymer mixtures.

The aim of this article is to extend the service temperature range of bitumen by increasing the viscosity at higher temperatures and flexibility at lower temperatures. For this purpose, bitumen is modified with two types of polymers: one is a thermoplastic polymer (LDPE waste bags) which should increase the deformation resistance of bitumen at elevated temperatures and the other one is a thermoplastic elastomer (SBR) which is expected to improve the resistance to cracking at low temperatures. Also, a mixture of these two polymers is used as a third modifying agent. To determine the two material functions, viscosity and elasticity, which describe the viscoelasticity of the material under load, knowledge of the rheological behavior is required. Therefore, experiments were conducted to study the changes of these properties caused by the addition of polymers in bitumen. Recent literature shows that although numerous modifications on bitumen properties were carried out,[3,6,8–13] still there is a lack of a general quantitative expression capable to predict the ultimate properties of modified bitumen blends. To overcome this gap, it is necessary to perform a thorough analysis that will detect the main factors responsible for the formation of structure network in these blends. Assuming that the structure network has an essential role in the changes of the viscoelastic properties, this research was focused on finding the effect of the state of dispersion on rheological behavior of these modified bitumen blends.[14,15]

EXPERIMENTAL

Materials

A standard 50/70 bitumen was used as a base material obtained from the Institute for testing materials "Skopje." Bitumen was modified with two polymers: one of them is a thermoplastic polymer [low density polyethylene from processed bags (PE_{bags})] and the other is a thermoplastic elastomer [styrene-butadiene random block copolymer (SBR 1502)]. The properties of these materials are given in Tables I–III.

TABLE I
Physical Properties of a 50/70 Penetration Grade Bitumen

	Base bitumen	Aged bitumen
Penetration at 25°C (dmm)	45	44
Softening point (°C)	52	52
Fraas breaking point (°C)	−11	−10
Density (g/cm^3)	1.04	1.04

TABLE II
Characteristics of PE_{bags}

T_g (°C)	−22
T_m (°C)	110
Density (g/cm^3)	0.93

Preparation of polymer-modified bitumen blends

Blends of 50/70 base bitumen with 4, 6, and 8 wt % PE_{bags} and SBR were prepared by swelling each polymer in benzene and then added into the molten bitumen. The blends were mixed for 5 h with 1200 rpm and at constant temperature 120°C. Also, mixtures of these two polymers SBR/PE_{bags}, with different weight ratios 25/75, 50/50, and 75/25, were prepared and added into bitumen by 4, 6, and 8 wt %. The obtained bitumen blends were poured into metal containers and cooled to room temperature.

To exclude the effect of bitumen aging during mixing process and thus evaluate accurately the polymer effects, the base bitumen was treated under the same conditions as the modified blends. These results are reported in the third column of Table I.

Characterization of samples

To provide data on the state of dispersion and rheological properties, samples of neat and modified bitumen were analyzed by means of optical microscopy and DMTA, respectively. Also, conventional and mechanical tests were used for determining the penetration, softening point, Fraas breaking point, and tensile properties. Polymer modifying agents were additionally characterized with differential scanning calorimetry (DSC).

Morphological analysis

Samples of 0.5–1 mg of neat and modified bitumen were placed between microscope slides and pressed into a thin film. They were observed at room temperature with transmitted light by a Zeiss optical microscope. Photomicrographs of the obtained states of dispersion were taken.

Dynamic mechanical thermal analysis

The viscoelastic properties of samples in a solid state were measured using a DMT Analyzer (Pyris Diamond model). The experiments were performed on strip specimens (50 mm × 10 mm × 3 mm) in a bending mode with a heating rate of 4°C/min

TABLE III
Characteristics of SBR

T_g (°C)	−55
Density (g/cm^3)	0.94

Figure 1   Neat bitumen.

Figure 3   State of dispersion of 6% PE$_{bags}$ in bitumen.
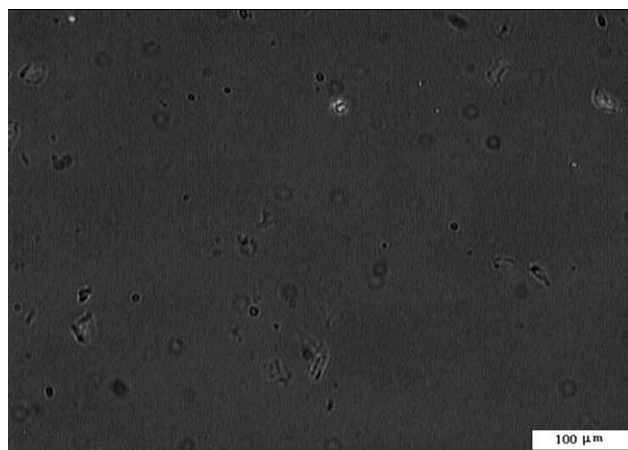
starting at $-60°C$ and ending when the sample became too soft to be measured. These tests were carried out at a constant frequency of 1 Hz.

Conventional tests

The conventional parameters such as the penetration, softening point, and Fraas breaking point were measured according to ASTM D5, ASTM D36–76, and IP 80, respectively.

Tensile measurements

Tensile measurements were carried out on a Shenck Tensile Tester at a rate of 200 mm/min at 10°C using specimens with a dumbbell shape. Strain–stress curves were obtained and tensile properties were evaluated.

Differential scanning calorimetry

Glass transition temperatures (T_g) and melting transitions (T_m) were tested by DSC. The measurements

were carried out with a Mettler DSC 822, using 5–10 mg of a sample in a hermetic aluminum pans and a heating rate of 20°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

The experimental results were processed and analyzed according the aim of this investigation and they are as follows.

State of dispersion

The state of dispersion of bitumen and bitumen/PE$_{bags}$ blends is presented in Figure 1 and Figures 2–4, respectively.

Photomicrographs show that almost homogenous dispersions of spherical polyethylene particles (white regions) in the bitumen phase (black regions) are obtained. The increase in the polymer content does not change so much the shape of the particles but affects both the particle size and particle size distribution. It can also be seen that polyethylene particles swell absorbing the low-molecular components from
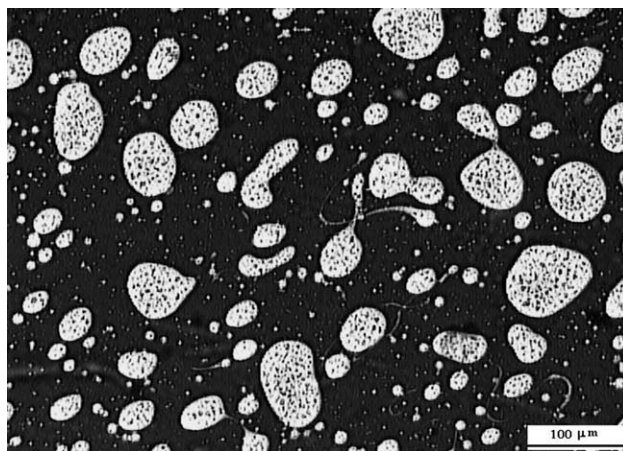

Figure 2   State of dispersion of 4% PE$_{bags}$ in bitumen.

Figure 4   State of dispersion of 8% PE$_{bags}$ in bitumen.

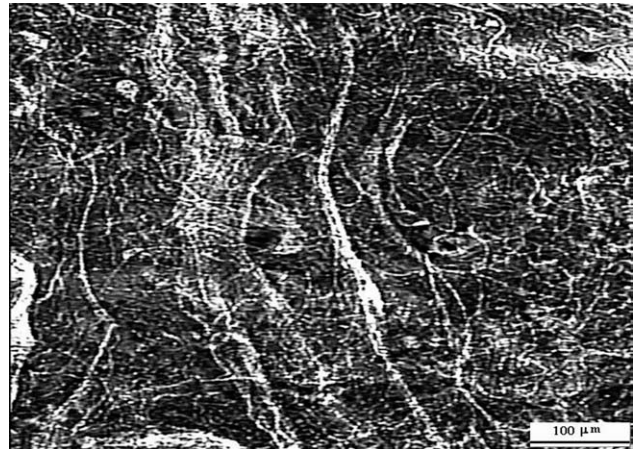**Figure 5** State of dispersion of 4% SBR in bitumen.

Figure 7 State of dispersion of 8% SBR in bitumen.

bitumen and as a result they form a new network structure with at least three detected phases: bitumen continuous matrix of the remaining components, polymer particles with trapped aromatic components, and solid asphaltene particles. It is assumed that the polymer network formed in such multiphase system is based on microcrystallites, which link together several polyethylene chains through the bitumen matrix, and act as reinforcement to the continuous bitumen phase.[11]

When bitumen/SBR blends with the same polymer content are analyzed, different morphologies are observed (Figs. 5–7). SBR is dispersed in a shape of fibrillar structures and forms three-dimensional network within the continuous bitumen phase as a result of its amorphous structure and rubbery behavior. By increasing polymer concentration, no significant changes in the state of dispersion of these systems are noticed.

The differences found in the states of dispersion when bitumen is modified with PE_{bags} or SBR are associated with the various intermolecular interactions occurring between the bitumen matrix and added polymer macromolecules. As it will be shown later, these new morphologies influence the rheological properties of the modified bitumen blends.

Also, the morphology of bitumen modified with a mixture of SBR and PE_{bags} was studied. From the photomicrographs presented in Figures 8–10, it can be seen that in all cases, the two polymers are spread in the continuous bitumen phase uniformly. Because of their mutual immiscibility, no interference between SBR and PE_{bags} particles is observed; SBR retains the fibrillar structure, whereas the PE_{bags} particles are still with spherical shape. As a consequence, the presence of the second polymer is not expected to influence the individual modifying effects of the other.

It should also be emphasized that no changes in the dispersed status in all cases were noticed when polymer-modified blends were processed at temperatures up to 130°C after several months of storage.
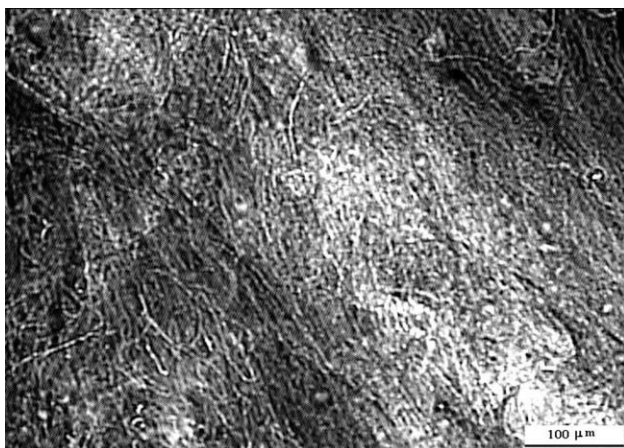

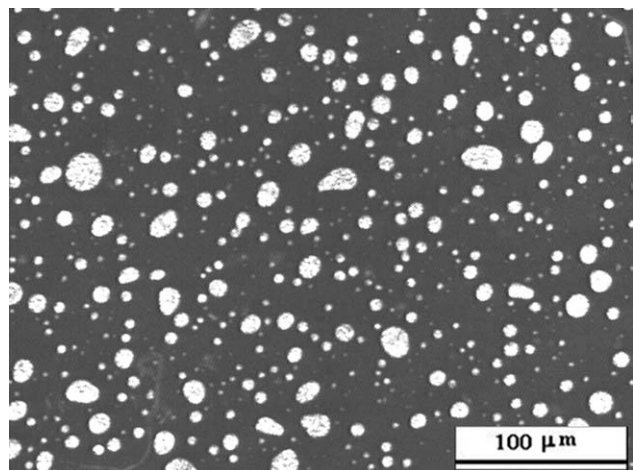
Figure 6 State of dispersion of 6% SBR in bitumen.

Figure 8 State of dispersion of bitumen/polymer mixture (SBR + PE_{bags}). The polymer ratio is (25/75), whereas the total polymer content in bitumen is 6 wt %.
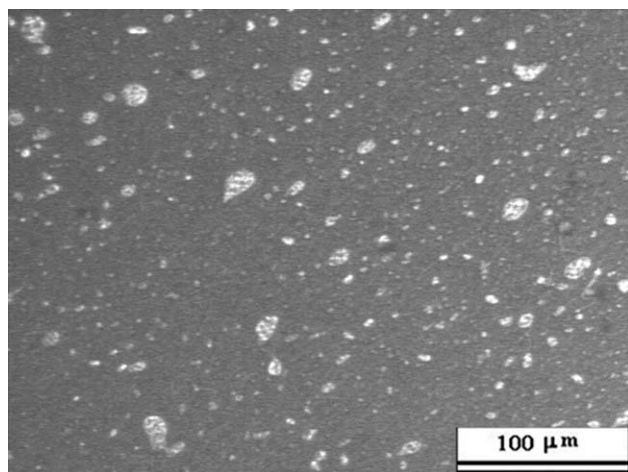
Figure 9 State of dispersion of bitumen/polymer mixture (SBR + PE$_{bags}$). The polymer ratio is (50/50), whereas the total polymer content in bitumen is 6 wt %.

Rheological behavior

Rheological measurements were carried out on samples of unmodified bitumen, polymer modifiers, and modified bitumen blends at constant frequency of 1 Hz over a sufficiently wide and appropriate range of temperature using DMTA to provide information on the three rheological characteristics: storage modulus (E'), loss modulus (E''), and loss factor (tan δ) defining the viscoelastic properties of the material. For illustration, a typical DMTA output only for the case of neat bitumen is given in Figure 11.

The resulting isochrones curves of $E' = f(T,f)$, $E'' = f(T,f)$, and tan δ $= f(T,f)$ from samples with different content of polymer modifier, SBR or PE$_{bags}$, were plotted in Diagrams 1–6. It can be observed that the obtained families of curves have the same shape and
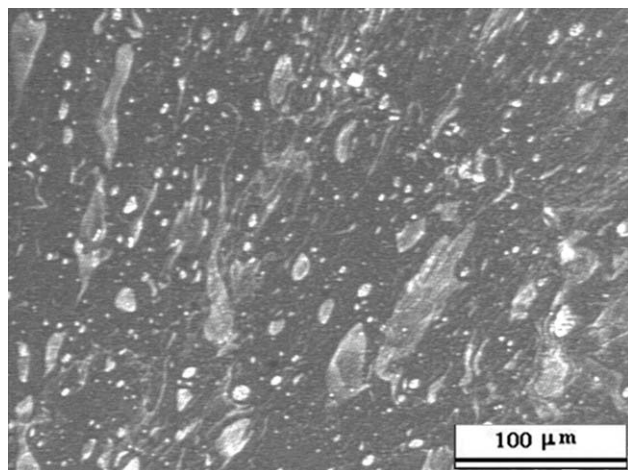

Figure 10 State of dispersion of bitumen/polymer mixture (SBR + PE$_{bags}$). The polymer ratio is (75/25), whereas the total polymer content in bitumen is 6 wt %.
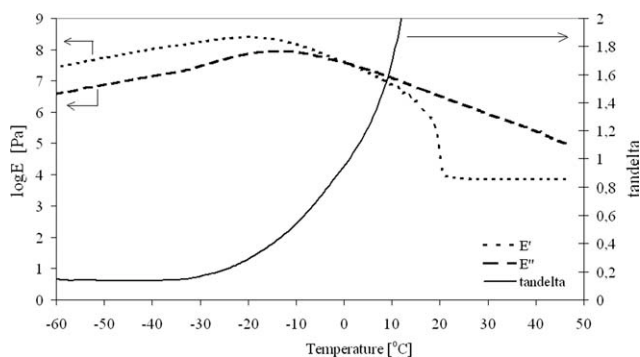
Figure 11 DMTA isochrone curves of neat bitumen.

follow a single loss process that terminates when the samples start to flow.

Evaluation of storage and loss moduli

Storage modulus, E'

The storage modulus refers to the ability of the material to store energy and it is a measure of material stiffness. Diagrams 1 and 2 provide information on the elastic behavior of unmodified and polymer-modified bitumen with three different concentrations 4, 6, and 8 wt % of PE$_{bags}$ and SBR, respectively. For both systems, the storage modulus functions are above the curve of the neat bitumen. The ability of the modified material to store energy significantly changes with the temperature, polymer content, and particularly with the type of polymer used for this modification (Diagram 7). Also Diagrams 1 and 2 show that when bitumen is modified with PE$_{bags}$, the storage modulus curves lie between those of pure components; nevertheless such an observation is not possible with SBR, because the storage modulus function of pure SBR lies and terminates far in the negative temperature axis (Diagram 2, part C). It is expected that the two polymer modifiers will affect the elastic properties of bitumen in entirely different manner. Noticeable changes of more than one order of magnitude of the storage modulus were found at low temperatures (below −10°C) when bitumen modification was performed with SBR. An increase of the storage modulus with the polymer concentration in the range from −60 to −20°C is also obtained when the bitumen is modified with PE$_{bags}$ (Diagram 1). To see whether these changes enhance the resistance to cracking, the isochronos curves $E' = f(T)$ of the samples were differentiated and the glass transition temperatures (T_g) were evaluated. There is a great shift of T_g from −10°C (neat bitumen) to −35°C when bitumen is modified with SBR (Diagram 2, part B). The T_g's of bitumen/PE$_{bags}$ remained almost constant (around −10°C) (Diagram 1, part B).
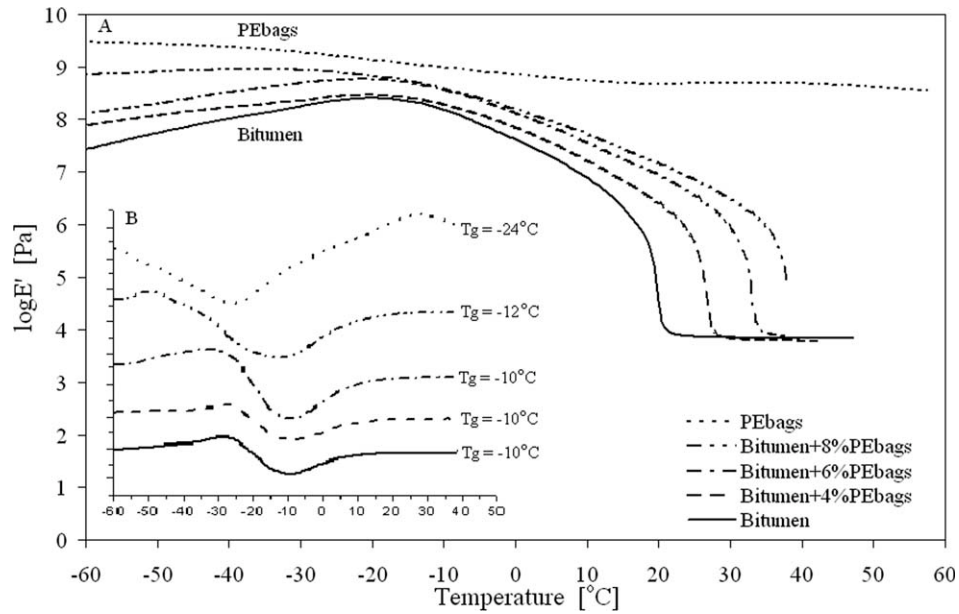
Diagram 1 Storage modulus curves of bitumen/PE_bags blends at different PE_bags content.
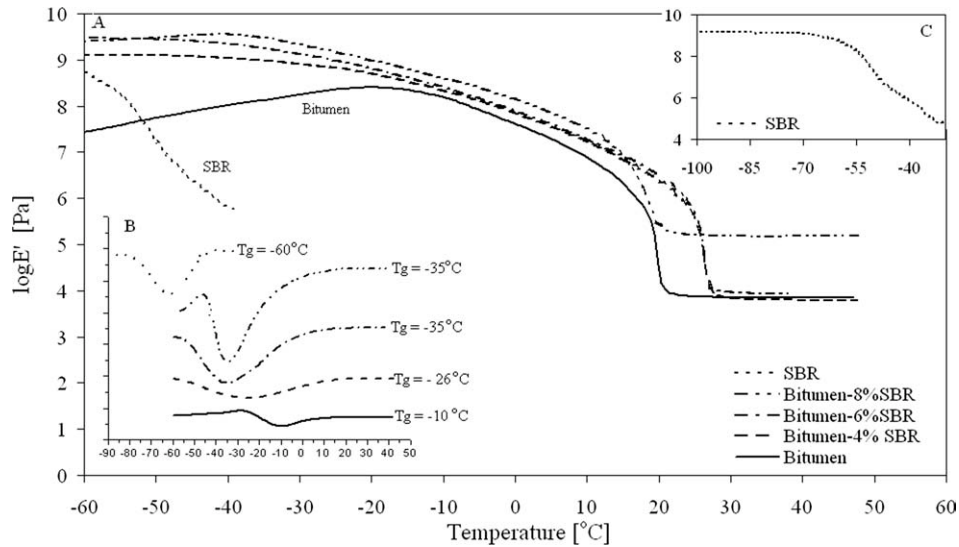

Diagram 2 Storage modulus curves of bitumen/SBR blends at different SBR content.
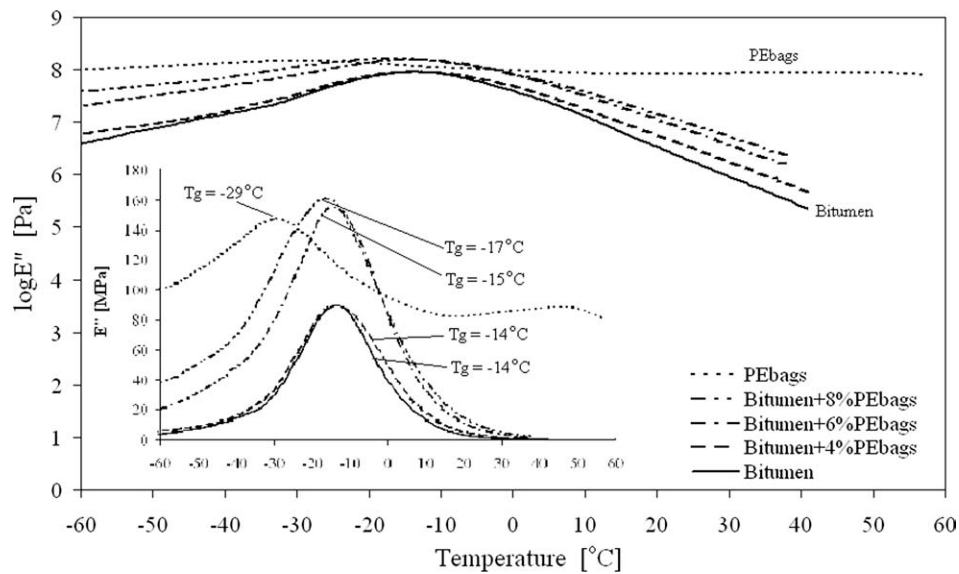

Diagram 3 Loss modulus curves of bitumen/PE_bags blends at different PE_bags content.
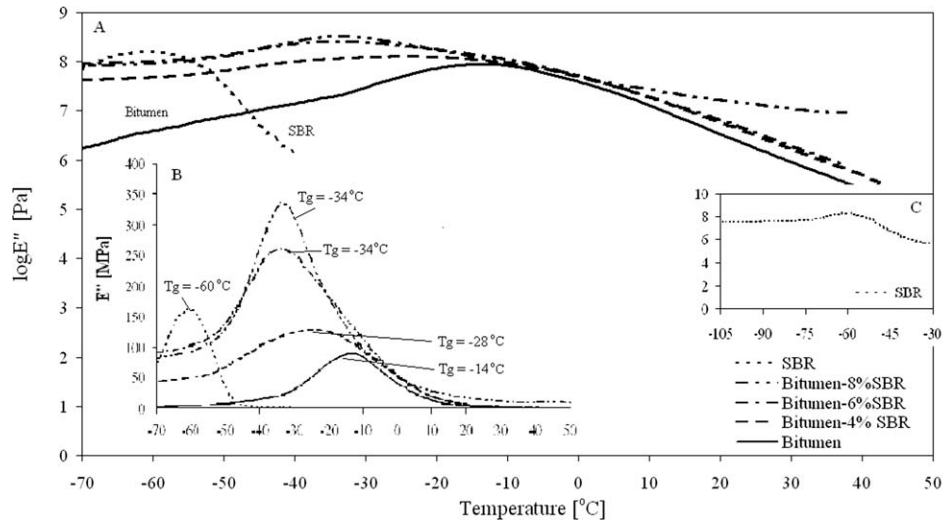
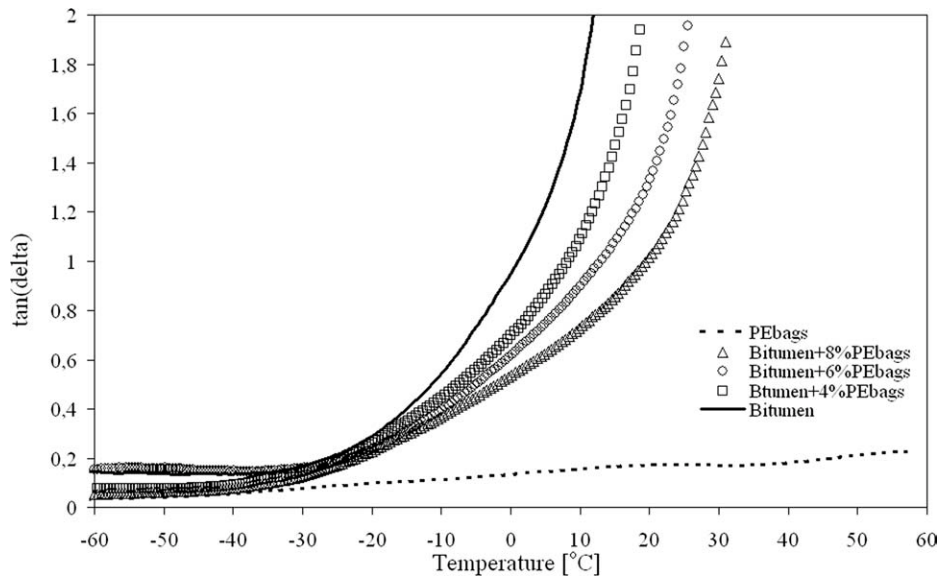**Diagram 4**   Loss modulus curves of bitumen/SBR blends at different SBR content.

Diagram 5   tan δ = *f*(*T*) curves of bitumen/PE$_{bags}$ blends at different PE$_{bags}$ content.
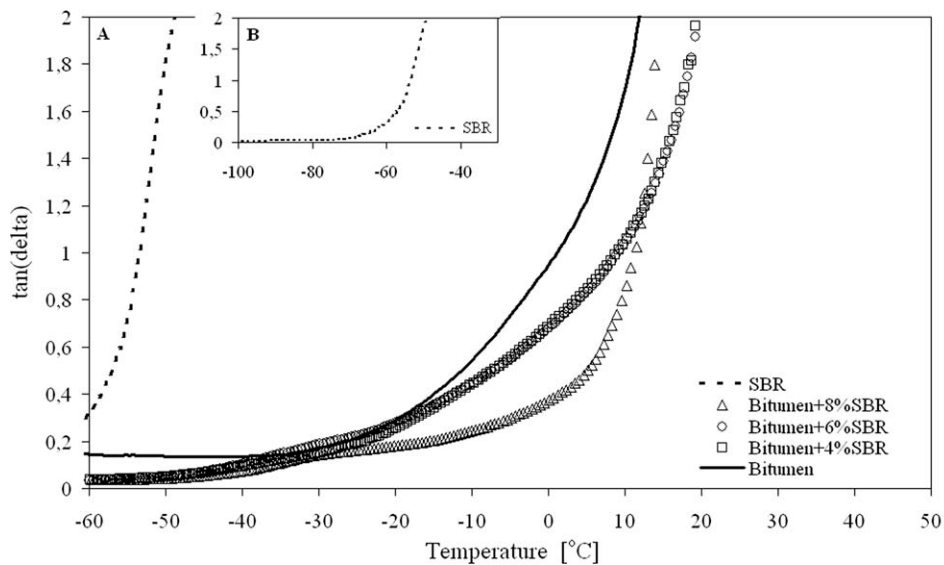
Diagram 6   tan δ = *f*(*T*) curves of bitumen/SBR blends at different SBR content.
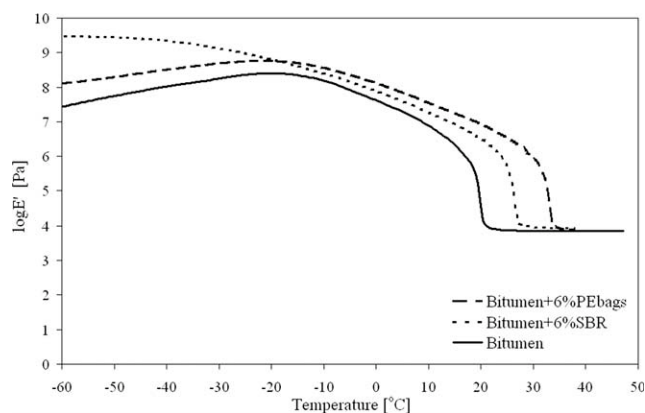
Diagram 7 Storage modulus curves of bitumen/PE_{bags} and bitumen/SBR blends with total polymer content in bitumen 6 wt %.

Regarding the shape of the storage modulus curves (Diagrams 1 and 2), the curve of neat bitumen shows that the storage modulus increases as the temperature rises from −60 to −20°C. According to the literature,[16–20] this phenomenon is attributed to physical hardening as a result of reorientation of some aromatic structures present in bitumen and crystallization of waxes possible to happen at lower temperatures (below T_g of bitumen). When bitumen is modified with PE_{bags}, this unusual behavior decreases with PE_{bags} composition and it disappears for the sample containing 8% of PE. In fact, it is observed a conspicuous increase of the storage modulus in the range from −60 to −30°C with the addition of PE_{bags}. When bitumen is modified with SBR, the addition of 4% is already sufficient to have the effect to increase the storage modulus so that the unusual behavior is already not visible on the curve in Diagram 2. A possible explanation could be that the two polymer modifiers are able to absorb most of the aromatics and saturates responsible for these physico-mechanical changes. However, this phenomenon is still not well understood and further investigation is needed.

Loss modulus, E''

As the loss modulus reflects the amount of mechanical energy dissipated by the material, viscous effect were assessed in Diagrams 3 and 4 where rheological functions of the loss modulus $E'' = f(T)$ are presented at a constant frequency of 1 Hz with three different concentrations 4, 6, and 8 wt % of PE_{bags} and SBR. It can be observed that the isochronos curves of E'' of all samples are above the curve of neat bitumen. The viscous behavior of modified bitumen blends changes similar to the elastic one in terms of temperature, polymer content, and type of modifier, but with much smaller intensity. At low

temperatures (from −60 to −20°C), bitumen/SBR samples show higher values of E'' than bitumen/PE_{bags} blends, whereas at temperatures higher than −10°C, it is the opposite (Diagram 8).

The linear loss modulus in function of temperature curves $E'' = f(T)$ is also used to find T_g's of the investigated samples (Diagrams 3 and 4, part B). The T_g of modified blends, calculated from the maximum of these curves, are between those of pure components. The obtained numerical values and observations about the shifting of T_g with respect to neat bitumen are the same as that previously discussed in the part of storage modulus (Diagrams 1 and 2, parts B).

Loss factor, tan δ

tan δ is another useful parameter related to the material viscoelasticity as it is a ratio of the loss modulus (viscous component) and the storage modulus (elastic component) tan $\delta = E''/E'$. The polymer addition in all cases caused a reduction in the tan δ values indicating that viscoelastic properties of modified bitumen are improved. In the case of bitumen blends with PE_{bags}, the changes are more expressed at higher temperatures than at low where the decrease of the loss factor is negligible (Diagram 5). It is noticeable that significant effect on tan δ curves is obtained in terms of PE_{bags} content. The increase of PE_{bags} concentration caused a considerable reduction in tan δ values signifying an improvement in polymer-modified asphalt binder (PMB) elastic response and stiffness. These enhanced viscoelastic properties resulted in a shift of tan $\delta = f(T)$ curves toward higher temperatures for more than 25°C (difference between neat and modified bitumen with 8% PE_{bags}). As a consequence, materials with greater resistance to permanent deformation or rutting under load were obtained.
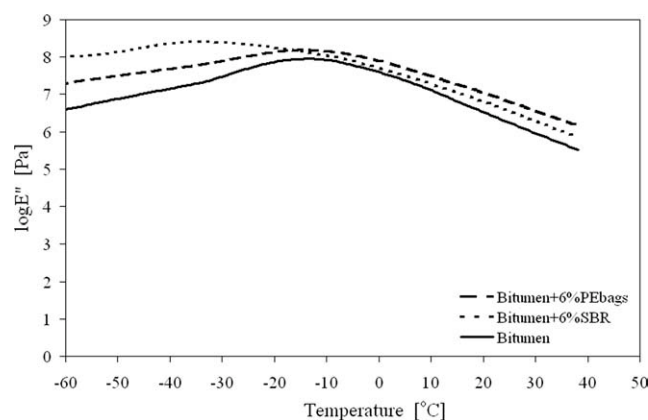

Diagram 8 Loss modulus curves of bitumen/PE_{bags} and bitumen/SBR blends with total polymer content in bitumen 6 wt %.
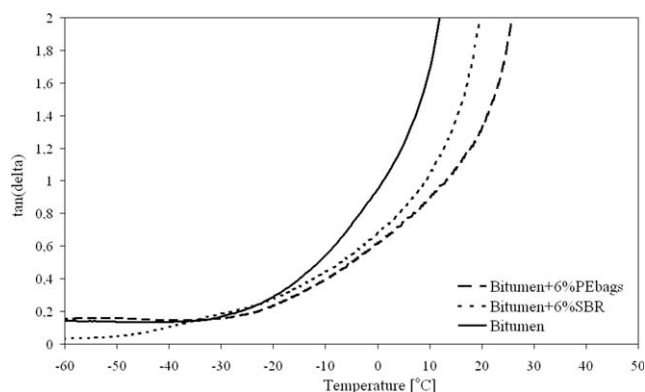
Diagram 9 $\tan \delta = f(T)$ curves of bitumen/PE_{bags} and bitumen/SBR blends with total polymer content in bitumen 6 wt %.

Bitumen/SBR blends displayed relatively lower changes in viscoelastic behavior at higher temperatures (Diagram 9).

The results from the rheological and optical measurements previously discussed undoubtedly suggest that they are strongly interrelated. The polymer addition disturbs the colloidal state of bitumen building new network structures on the basis of its ability to interact with the bitumen matrix. Hence, the PE_{bags} addition forms morphological structures characterized with swollen spherical particles, whereas fibrillar structures are obtained with SBR. Although the state of dispersion dictates the rheological behavior of the polymer-modified blends (see Figs. 1–7 and Diagrams 1–9), the rheological function of temperature is primarily determined by the shape of the created morphology. At high temperatures, better results with respect to the stiffness and viscoelasticity of bitumen were obtained with PE_{bags} modifier, whereas at lower temperatures, flexibility was greatly improved with SBR. These findings show that the state of dispersion (morphological structure) can be a useful tool to study and to assess the quality of the process of modification. To have the state of dispersion as a valid criterion, it needs to be more precisely defined as it is influenced by many factors: polymer structure and content, processing conditions (temperature, time, and rotational speed of mixing), and bitumen constitution.

Conventional tests

Samples of neat and modified bitumen were also characterized using conventional test methods with respect to the softening point, penetration, and Fraas breaking point related to the ability of the binder to resist rutting and thermal cracking. The results are given in Tables IV and V. The PE_{bags} modifier reduces the penetration and rises the softening points of bitumen significantly as the content increases, but no influence on the Fraas breaking point is noticed (Table IV). Thus, PE_{bags} noticeably improves the workability of bitumen at high temperatures by increasing its softening point from 52°C up to 73°C. On the contrary, with SBR, better effects are achieved at low temperatures where big positive changes on Fraas breaking points are obtained (a decrease from −10°C to −20°C). The penetration of bitumen/SBR blends remains almost constant (Table V).

Bitumen/polymer mixture (SBR + PE_{bags})

Also, modification of bitumen was performed using a mixture of SBR and PE_{bags} with three different ratios 25/75, 50/50, 75/25, whereas the total polymer content in bitumen, as previously, was 4, 6, and 8 wt %. Some of the results from latest conventional measurements carried out on these samples are presented in Table VI. Based on the values of Fraas breaking points and softening temperatures, it is found that the workability of bitumen is improved in the whole temperature range from −31 to 69°C which means that the presence of the second

TABLE V
Conventional Properties of Bitumen/SBR Blends

Polymer content (wt %)	Penetration (dmm)	Softening point (°C)	Fraas breaking point (°C)
0	44	52	−10
4	40	62	−15
6	44	64	−18
8	42	67	−20

TABLE IV
Conventional Properties of Bitumen/PE_{bags} Blends

Polymer content (wt %)	Penetration (dmm)	Softening point (°C)	Fraas breaking point (°C)
0	44	52	−10
4	28	59	−11
6	20	66	−10
8	14	73	−8.0

TABLE VI
Conventional Properties of Bitumen Modified with SBR/PE_{bags}[a] Mixtures

	Softening point (°C)	Fraas breaking point (°C)	Ductibility (%)
Neat bitumen	52	−10	0
SBR/PE_{bags} 25/75	69	−20	70
SBR/PE_{bags} 50/50	67	−31	70
SBR/PE_{bags} 75/25	66	−30	75

[a] The total polymer content in bitumen is 6 wt %.

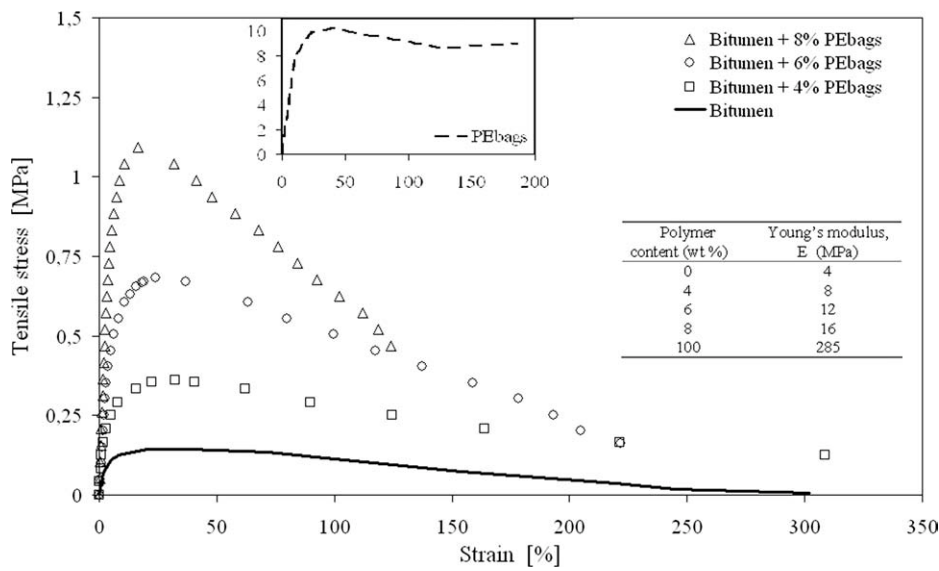| Polymer content (wt %)	Young's modulus, E (MPa)
0	4
4	8
6	12
8	16
100	285

Diagram 10 Tensile strain–stress curves of bitumen/PE$_{bags}$ blends at different PE$_{bags}$ content.

polymer in bitumen does not prevent the beneficial effects of the first one. Each of the polymer components in bitumen retains its integrity and acts separately as it is confirmed with photomicrographs presented in Figures 8–10 (see the section State of dispersion).

Conventional parameters were checked after several months of storage of bitumen blends at room temperature. In all cases, almost the same results were obtained which implies that there is no segregation of the polymer modifier.

Tensile properties

As the modification process was performed to broaden workability of bitumen without worsening, its physico-mechanical properties, tensile tests were conducted as well. Both, the obtained strain–stress curves of neat and bitumen modified with PE$_{bags}$ and SBR, as well as evaluated values of Young's modulus, are presented in Diagrams 10–12.

Materials with higher Young's modulus and tensile strength are obtained when bitumen is modified with PE$_{bags}$ or SBR (Diagrams 10 and 11) indicating that modified blends have greater stiffness than the bitumen itself. Both the tensile strength and Young's modulus are higher when modification is performed with PE$_{bags}$, whereas improved ductility is achieved when bitumen is modified with SBR (Diagram 12).

These results as well as those from conventional measurements are in consistency with those obtained from DMT analysis.
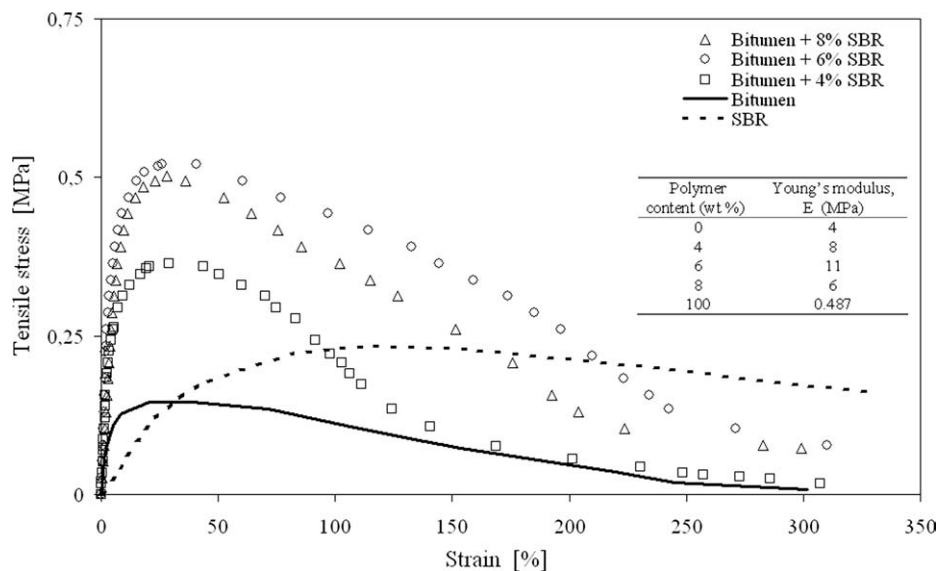

Polymer content (wt %)	Young's modulus, E (MPa)
0	4
4	8
6	11
8	6
100	0.487

Diagram 11 Tensile strain–stress curves of bitumen/SBR blends at different SBR content.
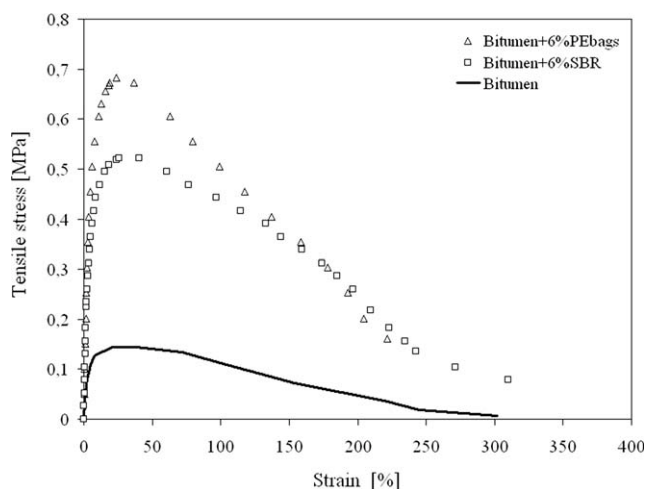
Diagram 12 Tensile strain–stress curves of bitumen/PE$_{bags}$ and bitumen/SBR blends with total polymer content in bitumen 6 wt %.

CONCLUSIONS

The aim of this investigation, to extend the service temperature of neat bitumen beyond its two extremes (−14°C and +52°C) by increasing the flexibility at lower temperatures and stiffness and viscoelasticity at higher temperatures, modifying bitumen with SBR or PE$_{bags}$, was entirely accomplished. Both polymer modifiers cause very important changes in deformation characteristics of the base bitumen without harming its physico-mechanical properties. Enhanced resistance to cracking at temperatures up to −34°C and improved resistance to rutting at temperatures up to 73°C were obtained with SBR and PE$_{bags}$, respectively. These entirely different improvements of rheological properties at low and high temperatures are due to the entirely different morphological structures of bitumen/SBR and bitumen/PE$_{bags}$ blends; the first ones with fibrillar structures and the others with spherical polymer particles. Another important observation of this investigation is that the state of dispersion plays dominant role on the rheological behavior and consequently on ultimate properties of modified blends. Thus, it can serve as a useful tool for quality assessment of the modification process.

Beneficial effects in both temperature regions, crucial for the applicability of bitumen in road pavements, were noticed with modified bitumen blends with a mix of spherical and fibrillar structures. This is the case when bitumen was modified using a mixture of PE$_{bags}$ and SBR.

Finally, it is important to note that the use of waste polymers as modifying agents additionally contributes to both cost and ecological effects.

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