

Developing enhanced modified bitumens with waste engine oil products combined with polymers

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HIGHLIGHTS

- Bitumen was partially replaced by waste engine oil or recycled engine oil bottom.
- Different waste and virgin polymers can be used to improve binder performance.
- The new modified binders are very flexible but also stable at high temperatures.
- Low non-recoverable creep compliance values were also obtained with these binders.
- New environmentally friendly solutions were developed for pavement materials.

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ABSTRACT

The reduction in the use of natural and finite resources and the reuse of waste materials are current concerns of different research areas. Therefore, the main aim of this study is to develop enhanced modified bitumens with waste engine oil and recycled engine oil bottoms combined with polymers (waste polyethylene, crumb rubber and styrene-butadienestyrene), in order to minimize the use of bitumen. After a thermochemical characterization, different compositions were studied with penetration, softening point and viscosity tests. The bitumens modified with waste engine oil products and polymers have similar penetration values, and softening point temperatures higher than those of commercially modified binders. A rheological analysis of the most encouraging solutions showed low thermal susceptibility, high values of high temperature PG and low non-recoverable creep compliance values, which could indicate a promising performance using high amounts of waste materials.

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1. Introduction

The road paving industry uses a high amount of natural and finite resources, such as bitumen and aggregates, for construction and conservation of road infrastructures [1]. In fact, in the construction sector, the paving industry is one of the highest consumers of fossil fuel, namely for production of bitumen for asphalt mixtures [2]. Furthermore, asphalt plants are considered significant sources of pollution [3], with a high level of greenhouse gas emissions [2].

Thus, waste or recycled materials could partially substitute the raw materials used in asphalt mixtures with some important

advantages, namely by reducing the landfill volumes and the amount of natural resources consumption and consequently the need for more extraction [4]. The introduction of several waste materials in asphalt mixtures has already been studied in the past years and their properties were compared to the specification limits, which were usually fulfilled. Moreover, their performance can be improved after waste modification [5], with specific advantages of each solution as presented in the following paragraphs.

Plastic and crumb rubber waste materials have been used for bitumen modification to improve its characteristics [6–9]. The incorporation of plastic wastes in bitumen reduces its penetration values and increases its softening point temperature. The stability and durability of the corresponding asphalt mixtures is improved, namely through the increase of permanent deformation and fatigue resistance [10,11]. Furthermore, some plastic wastes are

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available in large amounts at a reduced price [12], which could be used for bitumen modification. Likewise, crumb rubber incorporation in bitumen increases the softening point temperature and viscosity, reducing the penetration and thermal susceptibility [13,14]. Moreover, the asphalt rubber mixtures can significantly improve the permanent deformation resistance and increase the fatigue resistance at low temperatures [15,16], which could increase the pavements durability, although they typically use higher amounts of binder. This waste material is considered a serious environmental problem, as a result of a fast accumulation and difficult elimination [17], and new solutions for its reuse would be certainly well accepted.

Furthermore, several studies have mentioned the use of waste engine oil and recycled engine oil bottoms or re-refined engine oil bottoms (REOB) as bitumen extenders or modifiers [18–20]. The addition of waste motor oil is used to increase penetration and decrease softening point temperatures and viscosity of a bitumen, thus reducing production and compaction temperatures of asphalt mixtures. However, as a result of its incorporation, the elastic recovery and permanent deformation resistance may be compromised [21], which demands for a careful mix design of these materials. On the other hand, the recycled engine oil bottoms is the non-distillable waste from the recycling of waste engine oil by atmospheric distillation [18,22] and it is used as a binder additive in the United States and Canada due to its low cost and increasing availability over the years [23]. The asphalt mixtures with this waste material showed similar or higher resistance to permanent deformation, water susceptibility and fatigue cracking, when compared with conventional mixtures [24]. Nevertheless, the modified binder with recycled engine oil bottoms exhibited excessive aging, which could lead to premature cracking in pavements [25,26].

Both waste engine oil and recycled engine oil bottoms can be used as binder extenders, but their incorporation rates are usually low in order to guarantee an adequate performance of the asphalt mixtures [18,23,27]. However, according to Jia et al. [21] the waste engine oil products could have a higher commercial value for the road paving industry should they be used as a partial substitute of bitumen, especially if the problems resulting from their incorporation could be minimized or eliminated. Taking into account that polymers are used to solve some of those problems, the bitumen modification with waste engine oil products and polymers could be a promising, environmentally friendly and economic solution for paving industry.

Thus, the main aim of this study is to maximize the use of waste engine oil and recycled engine oil bottoms, combined with different polymers, in order to reduce the amount of base bitumen through the addition of waste materials. Furthermore, these new modified binders should maximize the use of waste materials without compromising their performance, i.e., they should present similar or higher properties than a commercial polymer modified bitumen (PMB) in order to assure equivalent rheological performances.

2. Materials and methods

2.1. Materials used in this study

Two waste engine oil products were used in this study to partially substitute bitumen. One of them was a waste engine oil (EO) from heavy and light vehicles, which was not subjected to any kind of treatment and was supplied by a certified waste treatment company (Sogilub, Lda.). The other product is the waste material generated from the recycling process of the EO, known as recycled engine oil bottoms (RB), and was supplied by the same waste treatment company. This material is an oil with higher viscosity because a large part of the light compounds were removed during the recycling process of the EO. Thus, it basically comprises the heavy compounds of the EO.

The base bitumen used as base for this study is a 35/50 penetration grade binder (B35/50), according to EN 12591 standard, supplied by Cepsa Portugal. This bitumen and a commercial PMB (PMB45–80/60, according to EN 14023 standard) were used as references for comparison purposes.

Three different polymers were used in this work to allow higher rates of EO or RB incorporation in final binder. The selected polymers are a high density polyethylene (HDPE) from plastic waste recycling, a crumb rubber (CR) from waste tires and the most commonly used polymer for bitumen modification, i.e., styrene-butadienestyrene (SBS). HDPE and SBS polymers were supplied by Gintegral S.A., while CR was supplied by Recipneu Lda.

2.2. Methods

2.2.1. Characterization of waste engine oil and recycled engine oil bottoms

The waste EO and RB materials were mechanically tested to evaluate their rheological properties. Then, they were thermally characterized in order to assess the loss of volatile compounds when submitted to high temperatures. Finally, they were chemically characterized with the main purpose of identifying their chemical constitution and the presence of heavy metals and other contaminants. These materials were compared to the base 35/50 bitumen, which is the reference material being substituted by EO and RB.

First, dynamic viscosity tests using Brookfield Rotational Viscometer were carried out to characterize the rheology of both EO and RB, according to EN 13302 standard, over a range of temperatures (30–180 °C), with 10 °C increments. The base bitumen (B35/50) was also evaluated in this range of temperatures for comparison purposes, using the same equipment for temperatures above 100 °C, and a dynamic shear rheometer (DSR) equipment for temperatures below 100 °C.

Thermogravimetric analysis (TGA) was also carried out to obtain the mass loss of those materials with the increase of temperature, in order to evaluate the possibility of volatile compound loss at asphalt mixing temperatures. In this test, a sample of 7 mg is placed in a sealed aluminium capsule, which is submitted to a heating rate of 10 °C/min, in a temperature range of 40 °C–750 °C, in a nitrogen atmosphere, which weight is continuously monitored with a high sensitivity balance.

The chemical analysis was carried out through Fourier Transform Infrared Spectroscopy (FTIR) to identify the different compounds and functional groups of the tested materials. Before testing, the EO and RB were placed in a vacuum oven in order to eliminate possible water from the samples. Then, the samples were dropped onto potassium bromide plates and analysed in a FTIR Jasco equipment, in wavenumbers ranging from 4000 to 440 cm^{−1}, with 32 scans. The base bitumen was dissolved in chloroform with 10 wt% concentration, and later dropped onto the same plates previously mentioned.

Finally, the analysis of heavy metals and other contaminants in the RB, the EO and the base bitumen was carried out by Inductively Coupled Plasma spectroscopy (ICP), according to D5185–09 standard, in an accredited external laboratory from Canada (AGAT laboratories). This test allowed quantifying the heavy metals and other contaminants present in those materials.

2.2.2. Characterization of polymers

The characterization of the polymers used in this study was made regarding their dimension and thermal behaviour by differential scanning calorimetry (DSC) tests and thermogravimetric analysis (TGA).

The differential scanning calorimetry test identifies melting and/or glass transition temperatures [28]. In this test, a sample of 10–20 mg is placed in a sealed aluminium capsule, which is submitted to a heating rate of 10 °C/min, in a temperature range of −60 °C–160 °C, over two heating and cooling cycles. The thermogravimetric analysis was used to determine the mass loss of the polymers at bitumen mixing temperatures.

2.2.3. Production of modified binders

In a first phase of the study, the partial substitutes (EO and RB) were blended with the base bitumen (B35/50) using a low shear mixer, during 20 min, at the production temperature of the base bitumen (150 °C). Samples were taken at this stage for further characterization. The initial contents of EO and RB used in this phase were 10% each, which is higher than the common contents used for rejuvenating or as extenders. However, higher amounts of these materials were later used together with polymer modification to maximize the use of these waste materials as partial substitutes of bitumen.

After that, the binders with EO or RB were modified with polymers using a high shear mixer, during 20 min, at a temperature of 180 °C. This new mixer was used to obtain a better dispersion of the polymers in the binder. The polymer contents depend on the type of polymer used, bearing in mind the goal of maximizing the use of waste materials. According to the suggestion of different authors [14,29,30], a rate of 20% of crumb rubber incorporation was selected. The most usual contents of the other types of polymers used for binder modification are 5–6% [31]. Thus, the contents of SBS and HDPE used in this study were 5 and 6%, respectively. The amount of EO and RB used in this phase were defined in order to achieve a polymer modified binder with properties similar to those of the control PMB45–80/60 binder, maximizing the use of waste materials.

2.2.4. Characterization of modified binders

Initially, all the binders were characterized regarding their basic properties, namely penetration at 25 °C (EN 1426 standard), softening point temperature (EN 1427 standard) and dynamic viscosity (EN 13302 standard). Then, the most promising binders were also characterized through the rolling thin-film oven test (RTFOT), according to EN 12607-1 standard, in order to evaluate the aging resistance based on their mass loss, before carrying out the rheological characterization.

Rheological properties were only evaluated for the selected polymer modified and commercial binders. The two main rheological parameters obtained from this analysis are the complex modulus and phase angle. The rheology tests were carried out according to EN 14770 standard, in a Dynamic Shear Rheometer (DSR), at temperatures of 30, 45, 60, 70 and 80 °C, for a range of frequencies between 0.1 and 20 Hz, using the equipment AR-G2.

The elastic and non-elastic response of the polymer modified and commercial binders under different stress levels were obtained by Multiple Stress Creep Recovery (MSCR) tests, performed according to AASHTO TP 70-11 standard. The stress levels selected were 25, 50, 100, 200, 400, 800, 1600, 3200 Pa [32]. In this test, a sample with 1 mm thickness is placed on a 22 mm diameter plate, and the sample is subjected to a loading time of 1 s, followed by a recovery time of 9 s (this cycle is performed 10 times for each stress level). The test is carried out at the higher performance grade temperature specified for the Portuguese conditions (64 °C).

3. Results and discussion

3.1. Properties of waste engine oil and recycled engine oil bottoms

3.1.1. Thermal properties

The effect of temperature on the dynamic viscosity properties of EO, RB and base 35/50 bitumen is presented in Fig. 1.

Both EO and RB showed viscosity values lower than the base bitumen over the range of temperatures studied, which justifies their use as rejuvenators or binder extenders. Furthermore, the RB presented a viscosity higher than that of EO for temperatures below 150 °C. This higher viscosity at service temperatures could promote the use of higher contents of RB, as partial substitute of bitumen, in comparison to EO.

It should be pointed out that both RB and EO show lower viscosities than the recommended viscosity for mixtures production (0.3 Pa.s). Thus, their addition to bitumen will certainly reduce its final viscosity and facilitate the mixing production process. In addition, those materials would reduce the stiffness of the binder over the normal of service temperature range, resulting in a reduction of the asphalt mixture stiffness modulus and rutting resistance.

Thermogravimetric analysis was carried out to evaluate the loss in mass of volatile compounds present in the EO and RB, in comparison with the base bitumen (Fig. 2). A previous work from Bredin et al. [33] stated that EOs usually exhibit four phases of mass loss. The first is related to the presence of water or with the loss of highly volatiles compounds (for temperatures below 200 °C). The second occurs in the range of temperatures between 200 °C and 700 °C. The third and fourth phases are related to the loss of non-volatile but oxidizable compounds and with ashes resulting from this process (after switching to an oxidizing atmosphere).

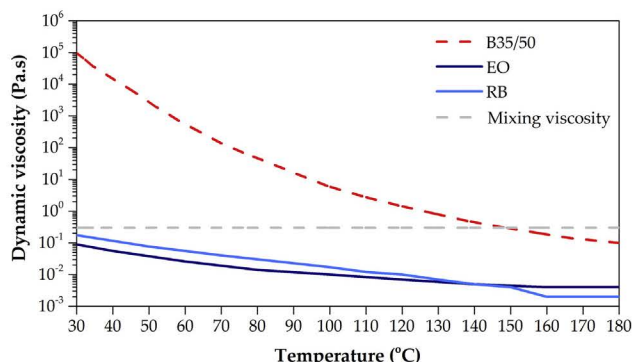


Fig. 1. Dynamic viscosity results of the base bitumen, EO and RB.

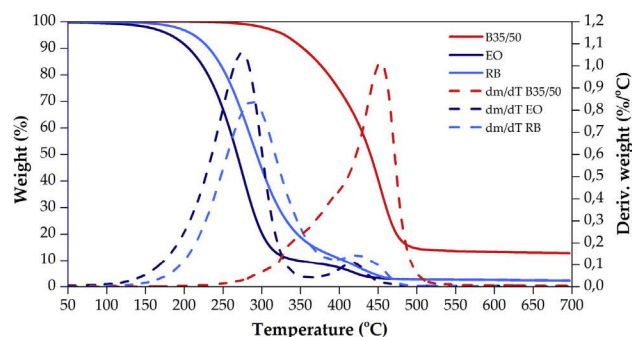


Fig. 2. Thermogravimetric analysis of the base 35/50 bitumen, EO and RB.

Two phases of mass loss were identified in EO and RB materials, with visible peaks in their derived thermogravimetric (DTG) curves, both related to the loss of volatile compounds. In the case of the EO, these two phases represent losses of respectively 91% (between around 100 °C and 350 °C) and 7% (between around 350 °C and 450 °C), while these values are 89% (between around 130 °C and 380 °C) and 9% (between around 380 °C and 480 °C) for the RB.

Base bitumen presents three mass loss phases, as stated in Fang et al. [34] work: i) volatilization of light compounds (between 220 and 370 °C); ii) decomposition of asphaltene and resin (between 380 and 500 °C) and, iii) thermal decomposition of asphaltene (approximately at 550 °C). As can be seen in Fig. 2, the base bitumen DTG curve only presented two mass loss phases of 14 and 72%, related to the two first loss phases previously mentioned. The third phase is barely visible at 550 °C, but the remaining mass (14%) could be considered as asphaltenes.

Additionally, the beginning of the loss in mass of the EO and RB occurred at temperatures around 90 and 150 °C, respectively, while that happened at around 260 °C for the base bitumen. As expected, the base bitumen is thermally more stable than the RB and EO, because the material decomposition starts at a higher temperature.

3.1.2. Chemical properties

The Fourier Transform Infrared Spectroscopy (FTIR) is a very useful tool used to analyse the materials macromolecules, because it allows to identify the different chemical organic compounds [21,35]. The characteristic wavenumbers of the compounds typically present in bitumen and EO materials could be seen in Table 1.

Taking into account the values presented in Table 1 and the FTIR spectra of Fig. 3, it is possible to identify the main compounds and functional groups corresponding to the peaks of FTIR spectra of base bitumen, EO and RB.

All materials presented the main peaks between 2850 and 3000 cm^{-1} bands, corresponding to C–H stretching in saturated hydrocarbons compounds and in the wavenumbers 1461 cm^{-1} and 1377 cm^{-1} related to CH_2 and CH_3 deforming in aromatic hydrocarbons.

Table 1

Compounds and functional groups identified from FTIR wavenumbers (adapted from Refs. [21,35]).

Wavenumbers (cm^{-1})	Compounds name	Functional groups
2850–3000	Saturated hydrocarbons	C–H
1700	Carbonyl	C=O
1600	Aromatics	C=C
1460	Aromatic hydrocarbons	C–H de (CH_2) _n
1375		C–H de (CH_3)
1030	Sulfoxide	S=O
650–910	Alkanes	C–H

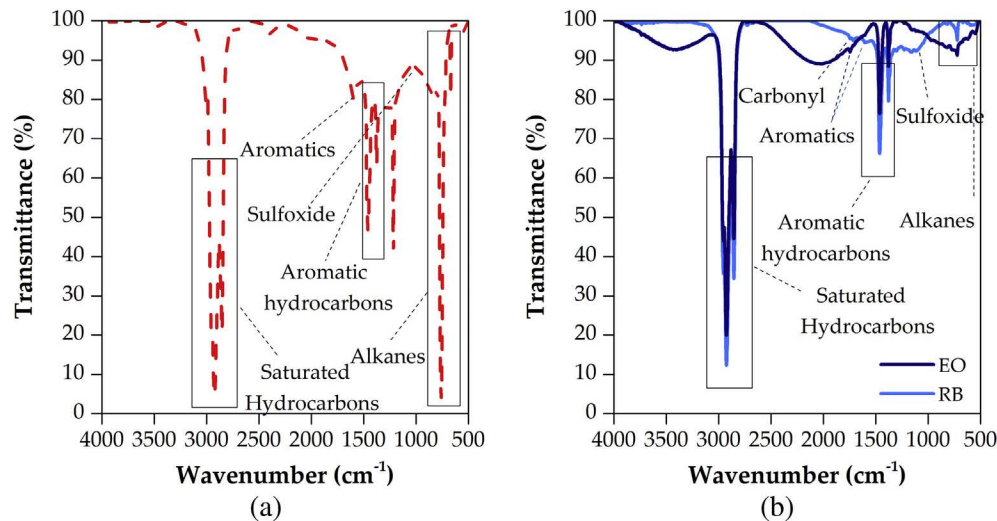


Fig. 3. FTIR analysis of (a) base bitumen and (b) EO and RB.

Additionally, all materials showed several peaks in the wavenumber range of 650–910 cm^{-1} , related to C–H deforming in alkanes compounds. Moreover, additional peaks were also identified in the wavenumber 1601 cm^{-1} , corresponding to C=C functional groups (aromatics).

DeDene and You [35] mentioned in their study that sulfoxide (S=O) and carbonyl (C=O) peaks identified in FTIR spectra can be used to evaluate the bitumen aging, including for bitumens incorporating EO. In this work, on the one hand the RB spectrum showed peaks in wavenumbers 1030 and 1711 cm^{-1} , corresponding to the presence of carbonyl and sulfoxide compounds, respectively. On the other hand, only the peak related to the presence of sulfoxide is visible for the base 35/50 pen bitumen, while the EO only presented a peak related to the presence of carbonyl. Therefore, it was concluded that the RB presents a similar chemical composition to the EO and the base bitumen, but it can be considered further aged due to the presence of both compounds, namely, carbonyl and sulfoxide.

3.1.3. Analysis of heavy metals and other contaminants

As mentioned above, inductively coupled plasma spectroscopy can be used to identify and quantify the presence of heavy metals and other contaminants in the studied materials. As can be seen in Table 2, several heavy metals and other contaminants were found in the base bitumen, EO and RB.

The base bitumen showed the lower concentration in contaminants for most of elements evaluated, in comparison to the other materials, except for As, Ni, Se, Si and Sn. Besides, for the great majority of contaminants the RB presented concentrations higher than the EO. The high concentration of iron (Fe) in the EO and RB could be related to their direct contact with several steel lubricated parts present in engines. The high level of K and Na could be associated to the presence of coolant additives, dust and dirt contamination. According to Rauckyte et al. [36], the waste motor oil used for energy recovery should have a regulatory limit of 5 ppm for As, 2 ppm for Cd, 10 ppm for Cr and 100 ppm for Pb. As can be observed, all materials showed contaminant concentration values lower than the previously mentioned limits. The same authors mentioned previous studies where the presence of heavy metals and other contaminants was analysed and their concentration values can be considered similar to those obtained in the present study for EO and RB [36].

However, it should be highlighted that even though the contaminants concentration showed similarities with results from

Table 2

Analysis of heavy metals and other contaminants in the base bitumen, EO and RB.

Contaminant	Units	B35/50	EO	RB
Ag	ppm	0	0	0
Al	ppm	9	15	37
As	ppm	2	0	0
B	ppm	0	76	40
Ba	ppm	4	8	10
Be	ppm	0	0	0
Ca	ppm	120	1850	4410
Cd	ppm	0	0	0
Co	ppm	1	1	1
Cr	ppm	2	3	7
Cu	ppm	1	24	25
Fe	ppm	60	120	317
Hg	ppm	0	0	0
K	ppm	8	69	203
Mg	ppm	16	67	207
Mn	ppm	1	4	9
Mo	ppm	0	21	28
Na	ppm	58	70	254
Ni	ppm	120	2	2
P	ppm	20	887	2000
Pb	ppm	4	10	11
Sb	ppm	1	2	1
Se	ppm	9	0	0
Si	ppm	52	47	38
Sn	ppm	7	2	4
Ti	ppm	1	1	1
V	ppm	2	1	2
Zn	ppm	35	960	995
Zr	ppm	0	0	0

previous works, and fulfilled the limits for energy recovery, EO and RB should not be landfilled because they could contaminate the groundwater. These are hazardous materials and should be managed by competent authorities.

3.2. Properties of the polymers

The dimensions and the thermal behaviour of the polymers were the properties evaluated in this work. Regarding the polymer dimensions, SBS was provided with a maximum dimension of 4 mm, while crumb rubber (CR) showed dimensions between 0.18 and 0.6 mm. HDPE was provided with bigger dimensions, and thus it was submitted to a milling process in order to reduce its maxi-

imum dimension to about 4 mm in order to obtain a material comparable to SBS.

The thermal behaviour analysis of different polymers was carried out to gather important information for the bitumen modification process, i.e. the melting/glass transition temperatures or degradation temperatures of the polymers. First, Differential Scanning Calorimetry (DSC) tests were carried out to measure energy variations subjecting the polymer samples to an increase in temperature at constant rate.

According to Fig. 4, it is possible to observe that HDPE showed a melting temperature (T_m) of 131 °C, corresponding to the peak in the HDPE curve. This melting temperature is close to the characteristic melting temperature of the HDPE [37]. It was not possible to determine the glass transition temperature of HDPE, usually around –85 °C, due to a limitation in the equipment used (the minimum temperature is limited to –60 °C).

Regarding the DSC curve of SBS, it is possible to observe an inflexion at a temperature of 77 °C, in the temperatures range of 60–80 °C, related to the glass transition temperature of the styrene block [38]. As mentioned above, it was not possible to define the glass transition temperature of the butadiene block, which should be around –90 °C.

Even though Thodesen et al. [39] stated that the glass transition temperatures of natural (around –70 °C) and/or synthetic (around

–108 °C) rubber can be determined in a sample of crumb rubber, through DSC analysis it was not possible to confirm this in the present work due to the abovementioned equipment limitation.

Taking the DSC results into account, it is possible to conclude that only HDPE would be melted at the usual binder production temperatures (between 150 and 180 °C). Thus, HDPE would be easier to disperse in bitumen than the other two polymers, which would need higher production temperatures.

The thermogravimetric behaviour of the different polymers used in this study is presented Fig. 5.

HDPE showed only one phase of mass loss (related to the peak in DTG curve) of 97.9%, beginning at a temperature of 367 °C, representative of this kind of polymer [40,41]. This temperature is clearly higher than the binder production temperatures, indicating that the polymer will not show signs of decomposition or oxidation during that process.

The thermal degradation of the SBS usually occurs in two stages: i) butadiene block degradation at a temperature of approximately 232 °C; and ii) styrene block degradation at a temperature of around 437 °C [42,43]. In fact, in this work the TGA and DTG curves of SBS (Fig. 5) showed a small loss in mass that began at a temperature of 322 °C, related to the butadiene block (10% of loss) and a bigger mass loss (89%) at a temperature of 400 °C from the styrene block, similar to what is mentioned in the literature. Again,

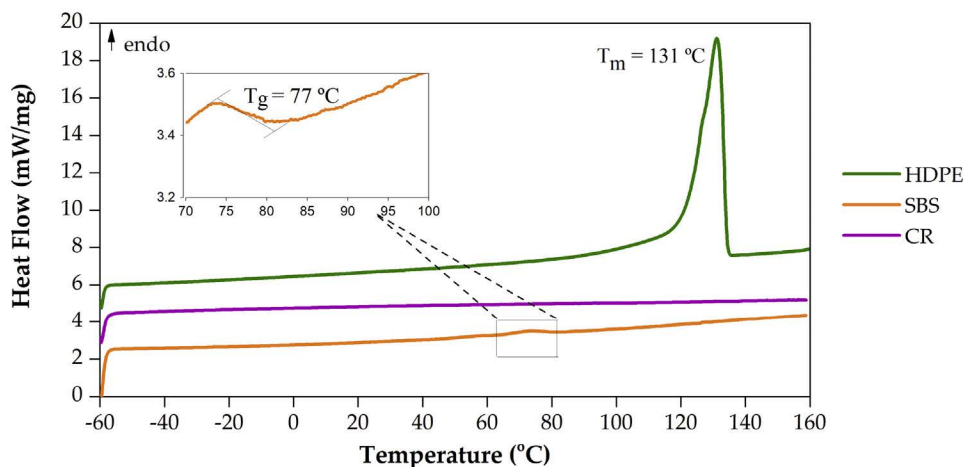


Fig. 4. Differential scanning calorimetry analysis of HDPE, SBS and CR polymers.

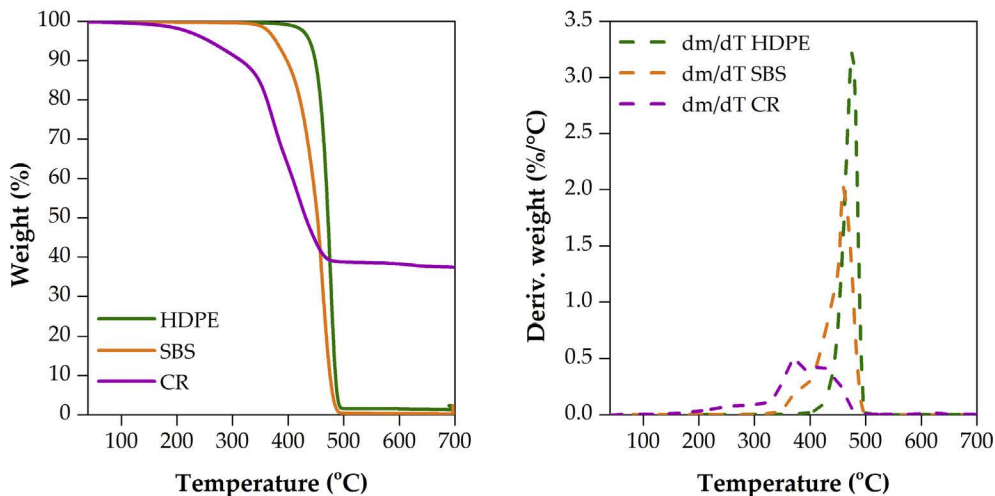


Fig. 5. Thermogravimetric analysis of the HDPE, SBS and CR polymers.

SBS is not expected to show any degradation or mass loss during binder production.

According to Chen and Qian [44], CR presents three different phases of mass loss. The first occurs at temperatures below 300 °C, during which the oils, volatile compounds and additives are lost. The second mass loss occurs between 300 and 500 °C and can be seen in this work by the presence of two consecutive peaks in the DTG curve. These two peaks could be related to the presence of natural and synthetic rubber, respectively. In the last phase, occurring at temperatures above 500 °C, it is possible to find inorganic filler, soot and ashes, whose reaction/loss is triggered by the presence of oxygen [45]. The CR used in this study showed the first two mass loss phases previously mentioned. A mass loss of 10% was observed due to the loss of volatile compounds and oils (beginning at a temperature of 115 °C). Then, two consecutive peaks in DTG curve were observed between 300 and 500 °C, related to two mass losses of natural and synthetic rubbers (around 26% each).

As can be observed from the previous thermogravimetric analysis, HDPE and SBS polymers shall remain thermally stable during binder production, maintaining their initial properties. The same can be said regarding CR, despite a slight mass loss of this material observed at binder production temperatures.

3.3. Properties of the modified bitumens with waste engine oil or recycled engine oil bottoms

Initially, the base bitumen (B35/50) was partially replaced by the waste engine oil (EO) or recycled engine oil bottoms (RB) in a proportion of 10% by weight. These binders modified with EO or RB shall be compared to the commercial base bitumen used in their modification and with a commercial modified bitumen (PMB45-80/60) in order to evaluate the effect of EO and RB incorporation.

The basic properties of the binders evaluated in this phase of the study are presented in Figs. 6 and 7. The new modified binders (EO10 and RB10) showed increased penetration values and lower softening point temperatures than both commercial bitumens. In addition, among the modified binders, the RB10 presented the lowest penetration value and the highest softening point temperature, which could be explained by the higher viscosity of RB when compared to EO. This could indicate that a higher amount of RB can be

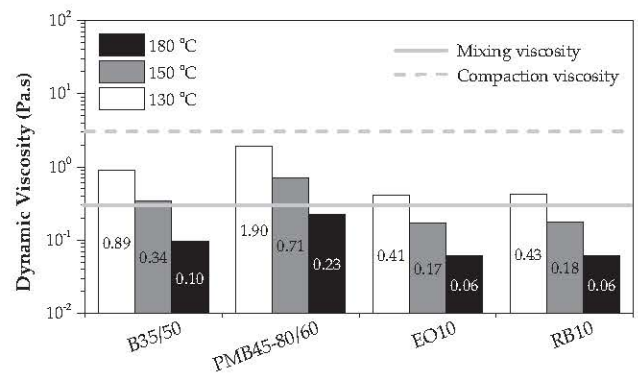


Fig. 7. Dynamic viscosity of the binders modified with 10% EO and RB.

used in order to obtain a similar binder using a lower amount of EO.

In comparison to the commercial bitumens, EO10 and RB10 binders presented lower viscosity values in the temperature range evaluated. Again, the dynamic viscosity of RB10 is slightly higher than that of EO10. The incorporation of both EO and RB decreased the binder production temperature, as can be easily observed when comparing the dynamic viscosity values at 150 °C to the reference mixing viscosity.

Although the incorporation of EO or RB in bitumen can be used with some advantages already presented, the corresponding binders may not present the necessary properties to be directly used in asphalt mixtures, particularly at high service temperatures, due to their low viscosity and softening point temperatures, which could result in high permanent deformations. Thus, this type of binders should be combined with polymers, which are known as materials that improve the permanent deformation resistance and thermal susceptibility of bitumen. In the next section of this work, the combined effect of polymers and EO or RB on the bitumen properties are discussed and evaluated.

3.4. Properties of the polymer modified binders with waste engine oil or recycled engine oil bottoms

Three different polymers were used for binder modification in this part of the study, namely SBS and HDPE and CR wastes. These

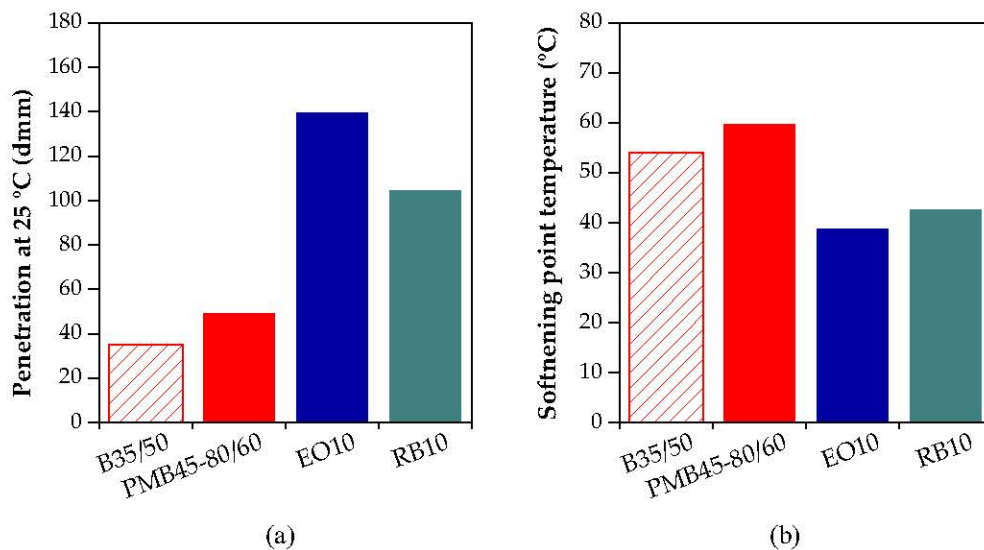


Fig. 6. Basic properties of binders modified with 10% EO and RB: (a) penetration; (b) softening point temperature.

polymer modified binders were evaluated through their basic properties (penetration, softening point temperature and dynamic viscosity) and rheological properties (stiffness, phase angle and non-recoverable creep compliance). The notation used to classify each modified binder followed the structure “aXbY”, where: “a” stands for EO or RB, depending on the waste motor oil product used; “X” is the percentage of the waste motor oil product incorporated; “b” stands for H (HDPE), S (SBS) or R (CR), depending on the type of polymer used; and “Y” is the percentage of polymer content.

3.4.1. Basic properties

The basic properties of the HDPE modified binder are presented in Figs. 8 and 9, for two amounts (10 and 15%) of EO and RB incorporation.

The increase in the content of EO or RB increased the penetration values of the binders for the same content of HDPE. Additionally, the increase in the penetration values of the polymer modified binders with EO was more significant than that observed in the binders with RB. The softening point temperatures increased with the increase of EO or RB incorporation, with similar values among them. This apparently unexpected increase may be a result of the high amount of HDPE used, which may need a higher proportion of liquid phase (maltenes) to be adequately dispersed. The higher amount of EO or RB may be acting positively to achieve that objective. Nonetheless, different results may be obtained for binders produced with lower amounts of HDPE. It is important to highlight that the softening point temperatures of all binders were higher than those of the commercial PMB.

In an attempt to obtain polymer modified binders with penetration values similar to that of the commercial PMB (50×10^{-1} mm), the best possible combinations with HDPE were the incorporation of 10% EO and 6% HDPE (EO10H6) or 15% RB and 6% HDPE (RB15H6).

Regarding the dynamic viscosity results, the binders modified with RB and HDPE showed higher viscosity than the other binders. In addition, all the new polymer modified binders, both with EO or RB, presented high mixing temperatures (around 180 °C or higher), due to the high HDPE content used. Based on the results, the compaction temperatures of mixtures produced with those binders should be around 135 °C or slightly higher.

A similar testing protocol was followed for the other two polymers studied in this work. Therefore, the basic properties of the

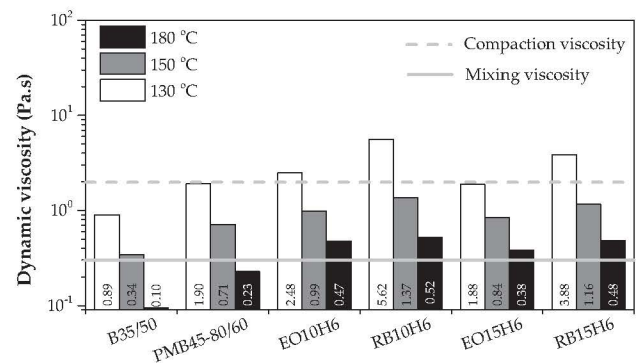


Fig. 9. Dynamic viscosity of the binders modified with EO and RB and 6% HDPE.

SBS modified binder are presented in Figs. 10 and 11, for three amounts of EO or RB incorporation (10, 12.5 and 15%).

Again, the increase in the content of EO or RB increased the penetration values of the binders modified with 5% SBS. However, in this case the rate of penetration is increasingly higher than that of the binders modified with HDPE, probably due to the lower amount of SBS used for binder modification. Furthermore, the penetration values of the SBS modified binders incorporating EO are typically higher than those incorporating RB (for similar amounts of EO and RB). Thus, higher amounts of RB can be used to produce SBS modified binders complying with the limits of a PMB 45-80/60.

The softening point temperatures of the SBS modified binders were higher than those of the commercial PMB, which could indicate a good permanent deformation behaviour of asphalt mixtures incorporating these binders. The influence of EO or RB content in the softening point temperatures was limited, with a maximum variation of 9 °C between all SBS modified binders. When comparing SBS (5%) and HDPE (6%) modified binders, it appears that this property is mainly influenced by the polymer type and content.

Again, the polymer modified binders with SBS were selected to obtain properties similar to those of the commercial PMB (penetration and softening point values) used for comparison purposes, while maximizing the percentage of waste materials used. Thus, the binders selected in this phase were those with: 10% EO and 5% SBS (EO10S5); and 12.5% RB and 5% SBS (RB12.5S5).

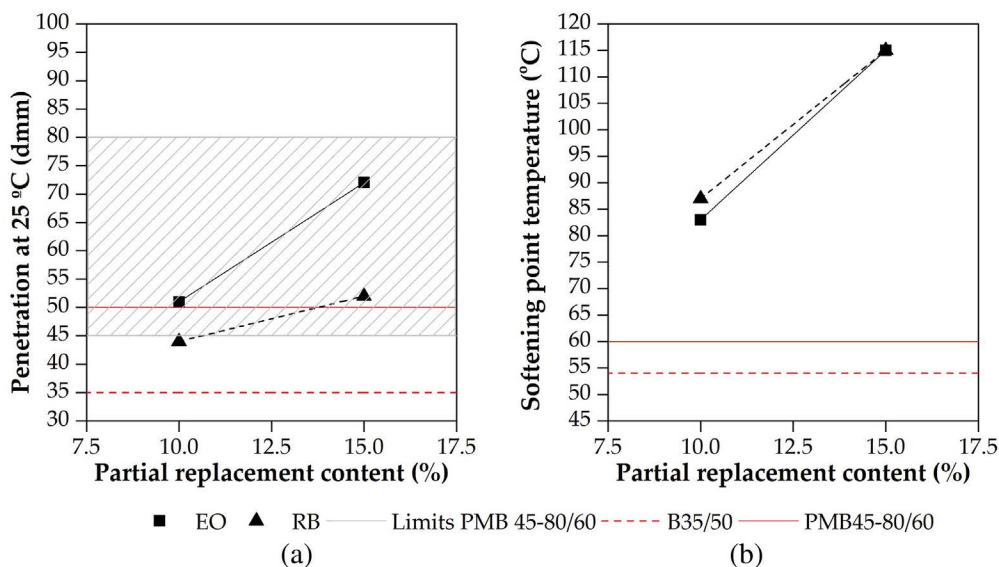


Fig. 8. Basic properties of binders modified with EO and RB and 6% HDPE: (a) penetration; (b) softening point temperature.

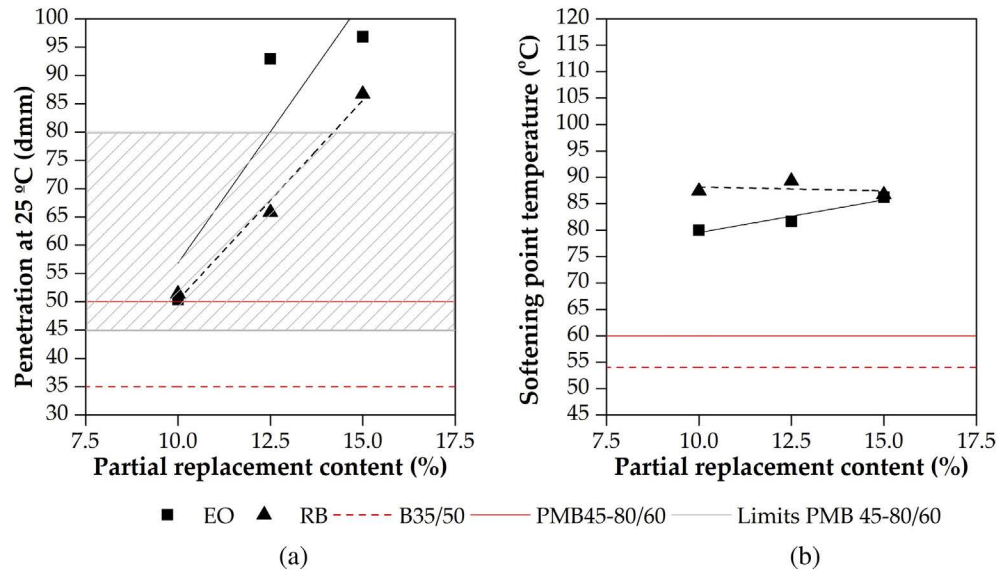


Fig. 10. Basic properties of binders modified with EO and RB and 5% SBS: (a) penetration; (b) softening point temperature.

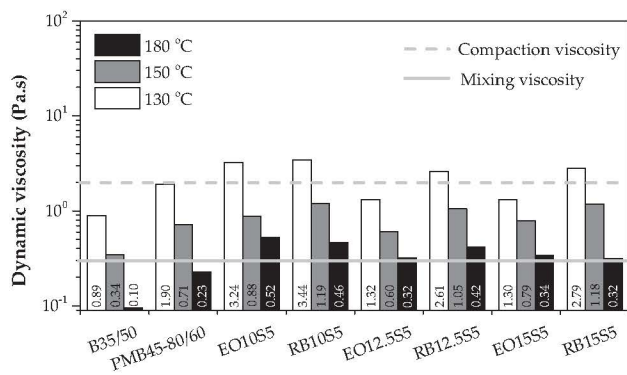


Fig. 11. Dynamic viscosity of the binders modified with EO and RB and 5% SBS.

The dynamic viscosity results of the SBS modified binders with RB were higher than those with EO. Moreover, the SBS modified binders were slightly less viscous than the corresponding binders with HDPE, probably due to the lower amount of polymer used. However, these binders showed similar mixing (around 180 °C or higher) and compaction (around 135 °C) temperatures.

As previously mentioned, it is viable and common to use higher contents of crumb rubber (20% in this work) when compared with the other polymers studied, i.e. HDPE or SBS, thus increasing the recycling rate of this specific solution. Following the same testing protocol previously mentioned, the basic properties of the CR modified binders are presented in Figs. 12 and 13, for three amounts of EO or RB incorporation (7.5, 10 and 15%).

The penetration and softening point temperature results of these CR modified binders are clearly more influenced by the type of oil used (EO or RB) than the previous polymers, as can be observed from Fig. 12. Due to the high penetration value of the binder with 10% EO, a lower amount (7.5%) of EO (and RB, for comparison purposes) was tested in order to obtain a penetration value closer to that of a commercially available PMB45-80. In fact, the penetration limits specified for a PMB45-80 are generally fulfilled for EO contents between 7.5% and 10%, even though higher contents of RB, between 10% and 15%, can be used for the same purpose.

Regarding the softening point temperatures, the results obtained for CR are lower than those obtained for the HDPE and SBS polymers, because there is a lower interaction between crumb rubber and bitumen. For that reason, the softening point temperatures of the CR modified binders slightly reduce with the increase of EO or RB contents. Nevertheless, all binders modified with CR and RB showed softening point temperatures higher than those of the commercial PMB.

Taking these results into account, it is possible to define the best possible combinations with CR in order to obtain polymer modified binders with penetration and softening point values similar to those of the commercial PMB, while maximizing the use waste materials. The EO content was mainly limited by the softening point temperature, while the RB content was limited by the penetration value. Consequently, the binders selected were those with 7.5% EO and 20% CR (EO7.5R20) or 15% RB and 20% CR (RB15R20).

The binders modified with RB showed higher dynamic viscosity values than those modified with EO, as can be seen in Fig. 13. Furthermore, these CR modified binders presented the highest viscosity values among all PMBs evaluated in this work due to the use of high CR content (20%). Therefore, this influenced the selection of the target mixing (higher than 180 °C) and compaction (around 150 °C or slightly higher) temperatures of this type of mixtures.

According to the EN 14023 standard specification, a modified bitumen classified as PMB45/80-60 should not have a mass loss higher than 0.5% in the RTFOT test, in order to guarantee an adequate resistance to hardening/aging. Thus, the selected modified binders, as well as the base bitumen and the commercial PMB, were tested to obtain their mass loss values, which were compared with the specification limit. All the tested binders fulfilled those requirements, and therefore the incorporation of EO or RB combined with polymers is not expected to result in excessive hardening of the corresponding binders. Moreover, it was observed that binders produced with EO showed higher mass loss values (between 0.38% and 0.49%) than the binders produced with RB (between 0.09% and 0.18%). Among these values, the lowest ones were obtained for the incorporation of rubber, and the highest ones were obtained for the incorporation of HDPE, as a consequence of different swelling capabilities of the polymers. For comparison purposes, the base bitumen (35/50 pen) and the commercial PMB presented, respectively, mass loss values of 0.04% and 0.35%, con-

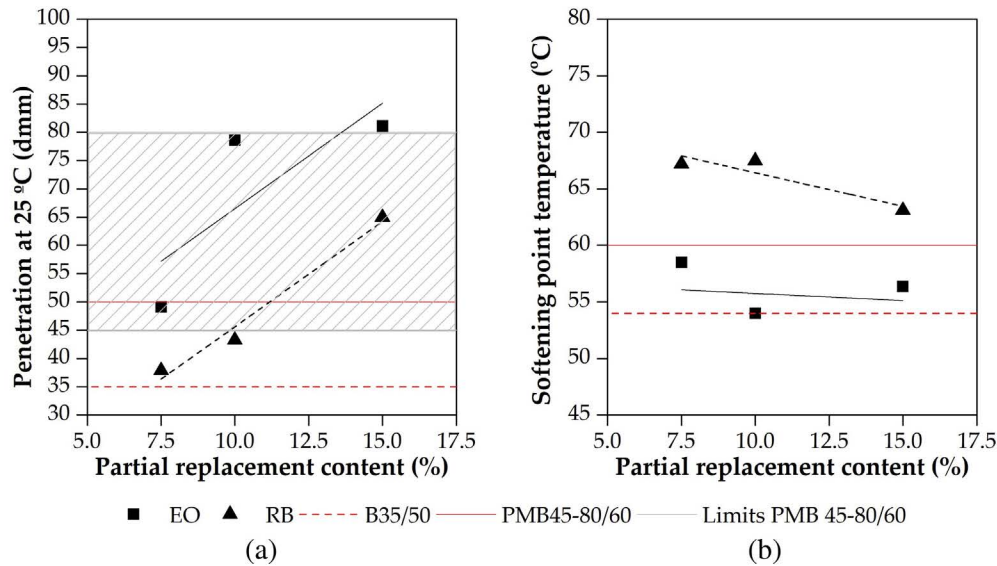


Fig. 12. Basic properties of binders modified with EO and RB and 20% CR: (a) penetration; (b) softening point temperature.

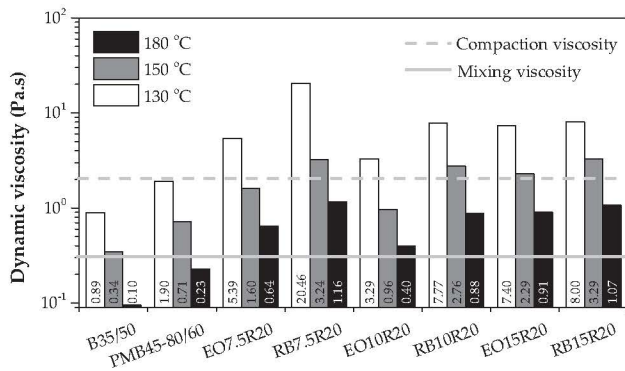


Fig. 13. Dynamic viscosity of the binders modified with EO and RB and 20% CR.

firming that the developed binders have a performance similar to that of the commercial PMB.

After selecting the best combinations for the new polymer modified binders with EO or RB, taking into account their basic proper-

ties, a further rheological analysis was carried out to compare the performance of the selected binders with that of the commercial alternatives, as presented in the next section.

3.4.2. Rheological properties

Two of the main rheological properties of bitumen binders used to characterize their performance under different temperature and loading time conditions are the complex modulus (G^*) and phase angle (δ), generally presented under the form of master curves [27,30,46]. The complex modulus represents the stiffness of the binder while the phase angle is related to its viscoelastic response [47]. These two properties can also be used together (i.e. using the ratio $|G^*|/\sin\delta$) to determine the high temperature performance grade (PG) of the binder [48]. The complex modulus and phase angle master curves of all studied binders are presented in Fig. 14.

The global shape of complex modulus master curves of all studied binders is similar, showing that the rheological behaviour of the selected binders modified with EO or RB is comparable to that of the commercial bitumens. However, the binders modified with EO or RB presented higher stiffness modulus values than the com-

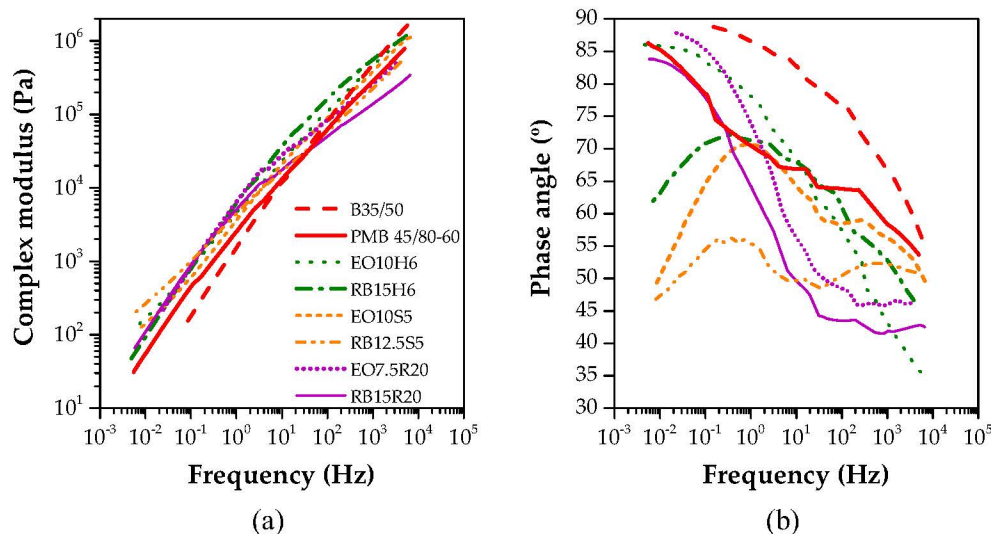


Fig. 14. Master curves of the studied binders ($T_{ref} = 60$ °C): (a) complex modulus and (b) phase angle.

mercial modified bitumen (PMB45-80/60), except for RB15R20 and RB12.5S5 binders at very high frequencies and/or low temperatures. The modified binders developed in this work showed a lower thermal susceptibility because they present high stiffness values at high temperatures (low frequencies) and similar or lower stiffness values at low temperatures (high frequencies). This behaviour may represent an advantage of the use of this type of binders, because they will perform better for a wider range of service temperatures, being more rut resistant at high temperatures and more flexible at low temperatures. Regarding the phase angle master curves of the binders modified with EO and RB, the polymer that presents a significantly different behaviour is SBS, which presented the lowest phase angle values in the whole range of temperatures/frequencies. This is a consequence of the elastomeric nature of SBS that visibly reduces the viscous nature of the binder. Nevertheless, all binders developed in this work have phase angle values lower than those of base bitumen, and similar or lower than those of the commercial PMB. Thus, it is evident that this combination of EO/RB and polymers results in binders with improved rheological performance. The high temperature performance grade of all binders was determined according to the procedure previously mentioned, and is presented in Table 3.

It is possible to observe that all modified binders developed in this work have higher values of high temperature performance grade in comparison to the commercial binders (B35/50 and PMB45-80/60). Indeed, the best performing binder was that obtained by incorporating 12.5% RB and 5% SBS. Taking into account that this high temperature PG is mainly related with the expected rut resistance of the corresponding asphalt mixtures, an excellent performance could be anticipated for mixtures produced with these binders when applied in mild to hot climate areas.

The rheological characterization of bitumen binders can also be made using the Multiple Stress Creep Recovery test. This test is used to determine the elastic and non-recoverable response of a binder under different stress levels, at a selected test temperature

(64 °C in Portugal). According to the AASHTO TP 70-11 standard, the non-recoverable creep compliance parameter (J_{nr}) is an indicator of the permanent deformation/rut resistance under repeated loads. Its value should be as small as possible in order to indicate the best rut resistance performance. These results are presented in Fig. 15.

The binder modified with 12.5% RB and 5% SBS (RB12.5S5) showed the best rut resistance performance due to the clearly lower non-recoverable creep compliance values. Nevertheless, all developed modified binders presented J_{nr} values lower than those of the commercial binders, except for the binder modified with EO and HDPE (EO10H6), which are higher than those of the commercial PMB, for stress levels higher than 0.4 kPa. It should also be highlighted that the binders modified with RB performed better than those modified with EO, since the J_{nr} values obtained for the former were lower than those of the latter. This results is in accordance with the higher softening point temperatures of these binders modified with RB.

4. Conclusions

The present study deals with the development of new modified binders using high amounts of waste materials, namely EO or RB (as partial substitutes of bitumen) and polymers (waste HDPE, waste CR and SBS). New alternative binders were developed in this work with a performance similar or better than that of a commercially available binder. Several conclusions can be drawn from the results of this study, which are presented below:

- The base bitumen can be partially replaced by EO or RB combined with polymers;
- Six of the studied binders presented the most promising basic properties (penetration values and softening point temperatures), namely those modified with 6% HDPE and 10% EO or 15% RB, those modified with 5% SBS and 10% EO or 12.5% RB, and lastly those modified with 20% CR and 7.5% EO or 15% RB;
- The selected binders modified with EO and RB presented a thermal susceptibility lower than that of the commercial binder, being more rut resistant at high temperatures and more flexible at low temperatures;
- Regarding RTFOT results, all the tested binders fulfilled the specification limits, and therefore the incorporation of EO or RB combined with polymers is not expected to result in excessive hardening of the corresponding binders;
- Binders modified with EO and RB also showed higher values of high temperature PG grade and lower values of non-recoverable

Table 3
High temperature performance grade of the studied binders.

Binder	High temperature Performance Grade
B35/50	64
PMB 45-80/60	70
EO10H6	76
RB15H6	76
EO10S5	76
RB12.5S5	82
EO7.5R20	76
RB15B20	76

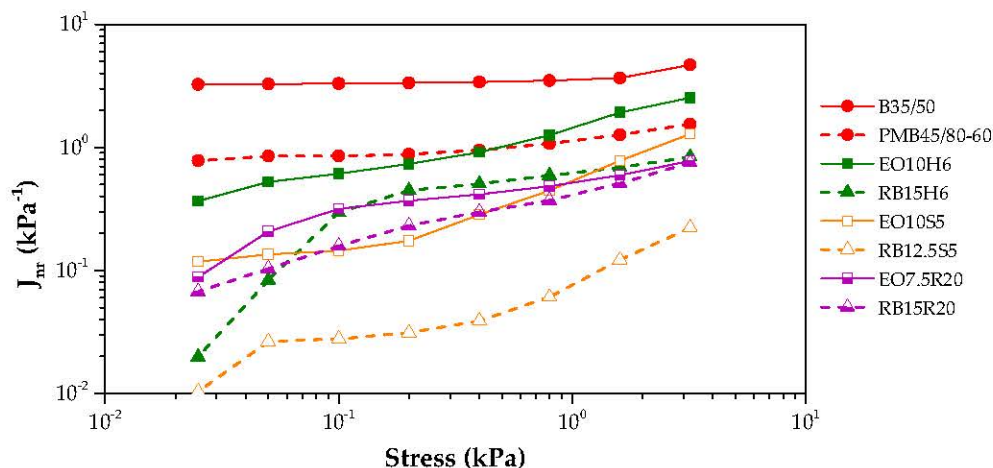


Fig. 15. Non-recoverable creep compliance of the studied binders at different stress levels.

creep compliance, when compared to the commercial binders, which confirms their excellent rut resistance;

- When comparing EO to RB modified binders, it was concluded that RB can replace a higher amount of bitumen without compromising the expected binder properties, which results from its higher viscosity;
- The solution with RB becomes very interesting for the paving industry, namely because it is a waste material without valuable alternative uses and with heavy metals and other contaminant concentrations similar to those of the base bitumen;
- Even though all polymers used for binder modification presented good results, SBS arose as the best performing alternative;
- The very good performance of the modified binders developed in this study highlights the potential of these economic and environmental friendly solutions for road paving applications, namely after in situ performance validation of these solutions.

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