Mutual changes in bitumen and rubber related to the production of asphalt rubber binders

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Abstract

Asphalt rubber (AR) mixtures are currently a material with an increasing use in road pavements due to their improved performance and environmental benefit of recycling rubber from used tires. AR binders have been widely applied, but the bitumen and rubber interactions remain poorly understood.

The aim of this work is to quantify and correlate the changes in bitumen and rubber during AR binders' production, in order to characterize the interactions between the AR constituent materials, e.g. residual bitumen and recovered rubber. A good correlation between the rheological and physical changes in the properties of rubber, bitumen and AR binder was observed.

Introduction

Healthy economies require an appropriate transportation system, in which roadways are an essential part. The construction and maintenance of road pavements should be long lasting due to their major impact on the economy of a nation. The main reasons for the damaged conditions of roads include the increase in the overall traffic, poor material quality and climatic effects.

Rubber from recycled tires is a material with a highly valuable constituent: vulcanized natural and synthetic rubber. Therefore, beyond the traditional constituents of the bituminous pavement layers, the use of crumb rubber recycled from used tires should be studied as a form of environmental stewardship and as a pavement performance enhancer. The increasing demands concerning the durability of pavements lead to the need of a deeper knowledge of the interaction between the constituents of the AR binders, e.g. bitumen and rubber.

Thus, the main objective of this research paper is to quantify and correlate the mutual changes in the bitumen and rubber during the production of AR binders. A new approach was used to study the AR binders and its components after AR production, consisting in the separation and characterization of the recovered rubber and the residual bitumen (the effective binder in AR). The results of this study could be used to infer the characteristics of residual bitumen and recovered rubber using the properties of the base bitumen. In fact, this work presents important data regarding the properties of recovered rubber and residual bitumen in AR binders, which presently involves demanding, costly and time consuming procedures.

Multiple bitumens ranging from very low (10/20) to very high (150/220) penetration grades of the same origin and batch were used in the production of AR binders. Then, the changes in the properties of the AR binders were assessed and the recovered rubber particles and the residual bitumen were separated by using a modified "basket drainage method". The changes in the rubber particles were studied through swelling and weighing processes, while assessing the changes in the physical and rheological properties of the residual bitumen and AR binder.

Theory about the interaction between asphalt rubber components

Discarded rubber tires have found end-use applications in bitumen binders. Behind the obvious positive impact on the environment, the incorporation of these recycled products in the constitution of flexible bituminous pavements can provide improved characteristics with impact in their performance [1-3]. Compared with unmodified conventional bituminous mixtures on roadways, the service life of asphalt rubber mixtures will be prolonged [4-7].

The obvious benefit of adding rubber to bitumen is that the rubber imparts elasticity to the binders, which helps increase pavement fatigue life, as well as reduces reflective cracking. This elasticity can also improve a pavement's flexibility and resistance to low-temperature cracking [8,9]. It has been reported that rubber also improves the aging resistance and the tensile strength, ductility, toughness, resiliency, tenacity, and thus, the durability to AR binders/mixtures is improved as compared to conventional ones [10-15]. AR binders produced by the wet process method have a higher softening point than unmodified bitumens and can improve the penetration index, flexibility, low-temperature ductility, rutting/deformation resistance, thus enhancing the stability at high temperatures and crack resistance of AR mixtures [16-18]. The improved adhesion characteristic of AR binders with aggregates promotes chip retention when it is used as a chip seal [19,20].

On the one hand, by using asphalt rubber it is possible to reduce the thickness of layers/overlays in flexible pavements [21] due its superior properties [22]. On the other hand, the addition of rubber increases the viscosity of the binder at high temperatures, which can lead to compaction being more difficult during construction. The higher viscosity at compaction temperatures can lead to high/inadequate air void contents and thus, high rates of oxidation which, over time, leads to pavement enbrittlement [19].

When crumb rubber is mixed and heated with bitumen, the modified binder produced has significantly different properties than the original constituents. Property changes are due to physical and compositional changes during the interaction process [23]. Property modification depends on both material and interaction variables [23-25].

Material variables include bitumen properties and crumb rubber properties. Bitumen properties include stiffness and chemical composition, which depends on the amount of the aromatic fraction, temperature, and viscosity [22]. Crumb rubber properties include source, the production method (ambient or cryogenic), size distribution, specific surface area, and chemical composition (e.g., amount of natural rubber). Another material factor affecting the binder properties is the crumb rubber concentration [26].

Interaction process variables include curing temperature and duration and mixing shear energy [4,7,23,27-31]. Statistically significant variations in viscosity of AR binders were found when the same crumb rubbers were mixed with different bitumen sources with similar penetration grades and viscosity [22]. The rubber particles swell in a time and temperature dependent manner during the interaction process, which results in a reduction in the interparticle distance, thereby increasing viscosity [23]. These findings were recently confirmed [2], since a significant change was reported in the viscosity and rutting parameter ($G^*/\sin\,\delta$) of AR binders with different rubber concentrations, which only marginally affected the values of the LMS (large molecular size) of the residual bitumen.

When polymer networks are exposed to low-molecular weight liquids, the liquid molecules diffuse into the networks and are absorbed within the polymer network. The liquid molecules occupy positions among the polymer molecules forcing them to move apart such that the polymer swells. This process continues until an equilibrium in the swelling is reached. Swelling of rubbers by organic liquids may also be considered to be a partial dissolution process in which there is a limited solubility of the un-vulcanized polymer in the solvent [32].

The swelling of the rubber particles due to the absorption of light fractions into the rubber particles, and stiffening of the residual binder phase are the main mechanism of the interaction [1,17]. The measured swelling ratio varies from 200% to 400% and is mainly related to the rubber content and bitumen composition [27]. The extent of rubber swelling in bitumen varies according to the temperature and time of rubber-asphalt contact, chemical composition of bitumen, rubber type, method of grinding, and rubber particle size. The chemical nature of bitumen determines the equilibrium swell value whereas the bitumen viscosity determines the rate of swell [1,23 – 25,28,33,34], which increases as the viscosity of the liquid decreases. The increase in rubber mass through the absorption of the light molecular weight fractions of the binders may be considered independent of the rubber-bitumen ratio provided that sufficient light fractions exist in the bitumen to allow absorption to occur [1,27].

Bitumen composition is a major factor affecting the interactions between bitumen and rubber. It is accepted that light fractions of bitumen swell the rubber particles and some authors introduced the concept of compatibility between the rubber and bitumen as a material variable, suggesting the use of base bitumen containing highly aromatic oily fractions to blend with the rubber [23,27]. The best swelling agents for a given polymer are those whose chemical structure is closely related to that of the polymer [32]. Bitumen components differ in solubility parameters [35], presenting values of 17.5,18.2,19.5 and 22.3$MPa^{1/2}$ respectively for saturates, aromatics, resins and asphaltenes [36]. The solubility parameter for rubber ranges from 17.8 to 20.8$MPa^{1/2}$ [37]. Comparing the solubility parameters of bitumen components and rubber, it may be expected that saturates are the most compatible of the bitumen with rubber.

The increase of the effective volume of rubber particles due to the absorption of maltenes leaves the AR binder with a higher content of asphaltenes [23]. Other authors [36] found that the lighter nonpolar fractions, especially the *n*-alkylbenzenes and *n*-alkanes, possess the highest propensity to penetrate into rubber particles. The traditional oxidation of bitumen at high temperatures also occurs during AR production and, consequently, the residual bitumen is richer in higher molecular weight components [34].

Other processes occur as the AR binder is subjected to different combinations of time and temperature [23], i.e., once the rubber has swelled, if the temperature is maintained too high or for too long, the rubber begins to disintegrate into the bitumen by partial depolymerization [23]. Swelling accounts for a partial degeneration of the polymer properties [38]. By blending under conditions of high temperature and high shear, the rubber particles can be devulcanized and depolymerized in the bitumen, especially when bitumens are rich in aromatics [39]. If the rubber is not partially devulcanized, it produces a heterogeneous binder with the rubber acting mainly as flexible filler [35]. When rubber particles significantly depolymerize, the liquid phase of a binder made with fine material will be stiffer than that of a binder made with a coarse material.

Materials and methods

3.1. Materials

Bitumens

In order to minimize any variability in the characteristics of the materials due to their source and processing, bitumens were collected from the same batch of the *La* Rábida Refinery of CEPSA in Huelva, Spain. Asphalt rubber binder properties are very dependent on the used bitumen. In this work several grades of bitumens were initially chosen in order to evaluate their influence on the AR binder characteristics. Due to the complexity of supplying other bitumens than the commercial line ones (10/20,40/50,60/70 and 150/200), these commercial bitumens were combined in varying proportions in order to obtain eight base bitumen samples (Table 1).

Crumb rubber

The crumb rubber used in this work was produced by the cryogenic process and, according to the supplier, was obtained by the grinding of 30% of truck tires and 70% of car tires. The range of crumb rubber sizes used was 0.18 – 0.60 mm (ASTM sieve sizes of #30 to #80), as these are the typical sizes used for AR mixtures produced/applied in Portuguese roads. The supplied crumb rubber was sieved again in the laboratory, thus rejecting all particles with dimensions less than 0.18 mm (sieve ASTM #30), so that the separation ("basket drainage") process could be successfully carried out later.

Methods

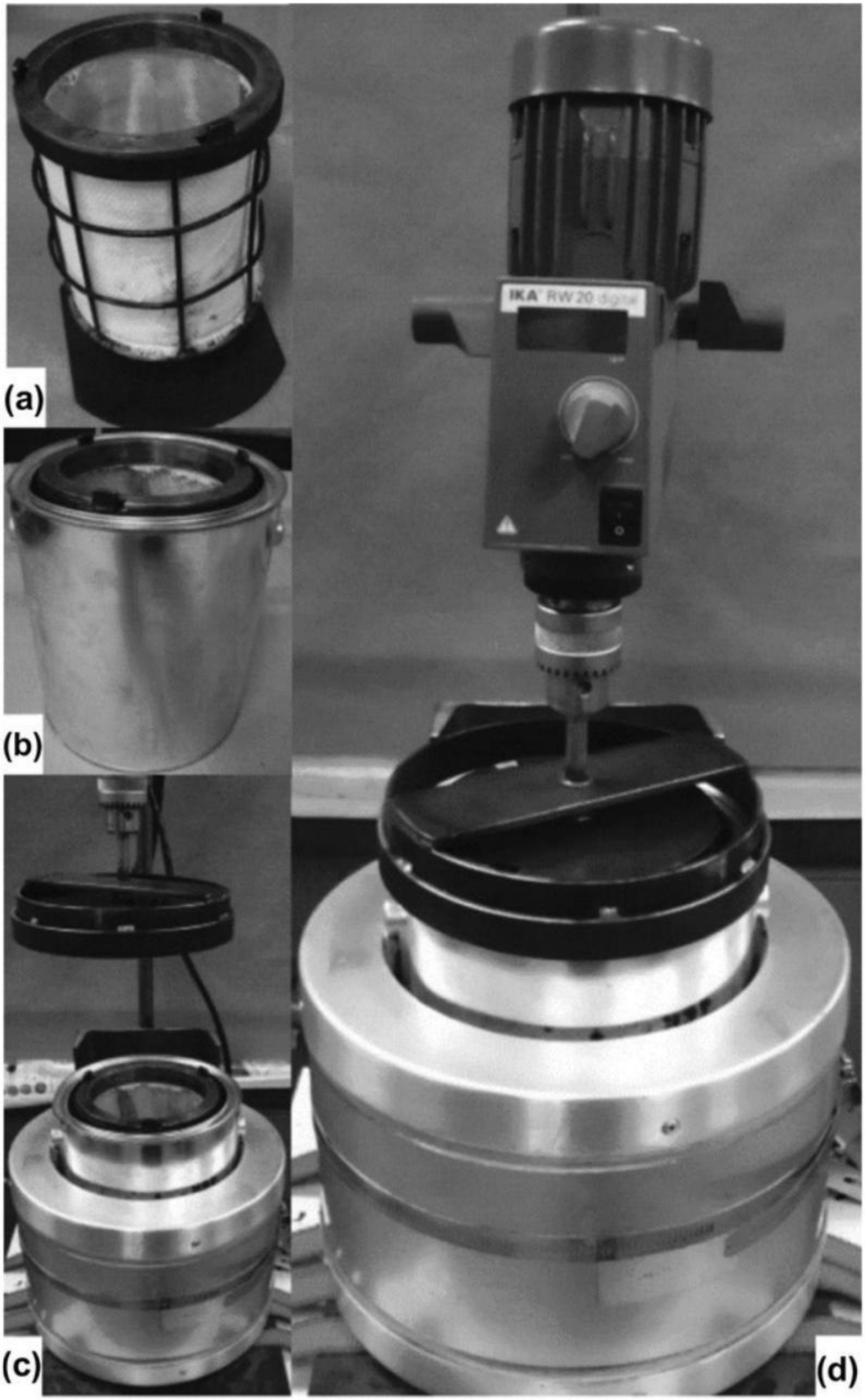
Production and separation of the asphalt rubber binder

The method used to produce and collect the desired samples of AR binder, of recovered swelled rubber and of residual bitumen was a modified "basket drainage method" [26,34]. The asphalt rubber production facility is formed by a wire basket placed inside an aluminum cylindrical container, where the AR binder will be produced, a heating blanket and an agitation helix. This equipment is assembled in a laboratory ventilation chamber. The wire basket used in the AR binder production facility was manufactured with a wire mesh with an opening dimension of 0.160 mm . This reduced dimension to 0.180 mm was selected in order to retain all the recovered swelled rubber of the AR binder during the separation process.

The process used to produce and collect the several samples of AR binder, of recovered swelled rubber and of residual bitumen consisted of heating of 1 kg of each base bitumen (Bb) at 180°C (collecting a sample). Then, 17.35%(w/w) of crumb rubber was added to the bitumen, and the resulting AR binder was continuously heated at 180°C for 60 min (reaction time), while stirring the binder at 230rot/min, and a sample of the produced asphalt rubber (AR) binder was taken for posterior analysis and testing. After the AR binder production, the remaining AR binder was separated by quickly centrifuging the AR binder in the fine wire mesh basket (that was put in a cylindrical centrifuge cage), thus draining out the residual bitumen into an aluminum container. This method, the "Binder Accelerated Separation" method - BAS (Fig. 1), was developed to separate, collect and weigh the two phases of the AR binder, namely, the residual bitumen (Res) and the recovered swelled rubber.

Recovery and analysis of the swelled rubber particles in the AR binder

The weight of the recovered rubber was determined at the end of its interaction with all studied base bitumens, after using the BAS method to separate the residual bitumen of the AR through a high centrifuge speed. The final weight of the swelled rubber was compared with the initial weight of crumb rubber introduced in the AR,


(a)
(b)
(c)
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(d)

Fig. 1. "Binder accelerated separation" method - BAS: (a) Wire basket; (b) wire basket in the aluminum container; (c) heating system and top of the centrifuging device; (d) centrifuge device attached to the stirrer.
in order to quantify the rubber mass change after interaction with each one of the studied bitumens. This method is simple and very effective due to the success and good reproducibility of the separation process used in the BAS method. However, the recovered and swelled rubber particles obtained in the BAS method are still coated by a very thin layer of bitumen that should be subtracted to the final weight of the swelled rubber in order to increase the accuracy of the measurement. Thus, crushed glass particles (inert material that is not able to interact with bitumen) with the same dimensions of the recovered rubber, and with clearly known weight, were used to quantify the weight of the thin layer of residual bitumens involving the rubber. The crushed glass was mixed with the base bitumens and then separated using exactly the same procedures previously explained for the AR binders in order to obtain an equivalent quantity of residual bitumen around the glass. The difference between the final and initial weight of the glass can be considered as the equivalent weight of the thin layer of bitumen surrounding the swelled rubber. This quantity was deducted from the final weight of the swelled rubber samples in order to determine the change of mass of rubber.

Analytical determinations

The laboratory characterization of several asphalt binder samples was carried out in order to evaluate empirical properties, namely the penetration at 25°C (EN 1426), ring and ball softening point (EN 1427), apparent viscosity (EN 13302),

Table 1
Proportions of commercial bitumens used to obtain eight base bitumen samples.

Bitumen sample labeling		A	B	E	I	J	M	O	P
Commercial bitumen	10/20	1.00	0.75	-	-	0.25	-	-	-
	40/50	-	0.25	1.00	-	-	-	-	-
	60/70	-	-	-	1.00	0.75	-	0.50	0.75
	150/200	-	-	-	-	-	1.00	0.50	0.25

Table 2
Analytical determinations carried out in this work.

Analytical determinations	Pen	R&B	AV	ER	DSR
Type of materials studied	All (Bb; AR; Res)	All (Bb; AR; Res)	All (Bb; AR; Res)	Only AR	Only bitumens (Bb; Res)

and elastic recovery (ASTM 5329), as well as rheological properties, according to EN 14770, using a dynamic shear rheometer (DSR) to determine the relaxation times of the binder samples.

Table 2 summarizes the research and analytical determinations carried out in this work with the base bitumens (Bb), asphalt rubber binders (AR) and residual bitumens (Res) collected during the production and separation phases. Specifically, the materials' characteristics, the penetration at 25°C (Pen), the ring and ball softening point (R&B), the apparent viscosity (AV), the elastic recovery (ER) and the rheological properties (DSR), are summarized in Table 2.

DSR of AR binder should not be performed due to the small gap of the shearing geometry in comparison with the rubber particle size. However, the AV determination was possible because the gap between the cylinder and the cup is much larger than the rubber particles. The ER was only assessed for AR binders because the ER of the base and residual bitumens is nearly zero.
3.2.4. Rheological characterization

The rheological properties were assessed using a stress controlled rotational rheometer (Stresstech-HR, Reologica) equipped with 40 mm parallel plates and a gap of 1 mm . Small amplitude oscillatory shear (SAOS) tests were performed at multiple temperatures (25,35,50 and 80°C). In a preliminary set of experiments, stress sweep tests were performed at 1 Hz to determine the linear regime for each temperature and sample. As a result of these tests, frequency sweep tests recorded with stresses of about 1000 Pa for tests at 25 and 35°C, 200 and 40 Pa for temperatures of 50 and 80°C, respectively, allowed obtaining the mechanical spectra of each sample at the corresponding temperatures. Before recording the mechanical spectra, time sweep tests were applied using a frequency of 1 Hz and the stresses mentioned above in order to check that samples reached both thermal and structural equilibrium conditions. The experimental procedures for the rheological characterization of the base and residual bitumens were based on the European standard EN 14770, as previously referred.

Results and discussion

Construction of master curves and determination of relaxation times

The procedure of superimposing curves at different times/frequencies and temperatures is known as the time-temperature superposition theory (TTS) and the resulting master curves cover large time or frequency domains well beyond the frequency range experimentally accessed by the rheometer. An important criterion for the use of the method of reduced variables is that the shapes of the original curves at different temperatures must overlap over a substantial range of frequencies or times. An equally important criterion to evaluate the applicability of the method of reduced variables is the requirement that the same values of the horizontal shifting factor must superimpose all viscoelastic functions [40].

The master curves of the several base and residual bitumen samples at medium and high service temperatures ($25-80^{\circ}\mathrm{C}$) were constructed using the IRIS software (Innovative Rheological Interface Software v9.0) of Rheo-Hub Innovative Rheology Information Systems, IRIS Development, LLC. In a previous work [41], it was observed that the mechanical spectra obtained at temperatures below $80^{\circ}\mathrm{C}$ could not be superimposed on the mechanical spectra recorded at higher temperatures. This indicates that bitumens are not thermorheologically simple over the entire range of temperatures spanning from in-service to production/application temperatures (above $80^{\circ}\mathrm{C}$), since that in this range of temperatures bitumen behaves as a Newtonian fluid. However, master curves could be constructed for temperatures below that transition temperature, as illustrated in Fig. 2 for the bitumen most commonly used in Portugal (referred in this work as base or residual bitumen I).

The master curves obtained at service temperatures ($25 \leqslant T(^{\circ}\mathrm{C}) \leqslant 80$) reached high frequency elastic plateau values at $25^{\circ}\mathrm{C}$, both for base bitumen (4.127 GPa) and residual bitumen (4.872 GPa). This behavior and the corresponding values for the elastic modulus are in agreement with the values reported in the literature, which point towards the formation of a glassy plateau between 1 GPa [42,43] and 5 GPa [44].

A characteristic relaxation time (τ) corresponding to the inverse of the frequency where $\tan\ \delta=1$ can be extracted from the master curve for both base and residual bitumens [41]. The frequencies corresponding to the relaxation times are indicated with vertical arrows in Fig. 2 as τ_{Res} and τ_{Base} for residual and base bitumen, respectively.

Properties of the base bitumen, AR binder and residual bitumen samples

Table 3 summarizes the absolute results of the characterization tests carried out with the three bituminous materials (base and residual bitumens and AR binders) studied in this work, for the eight different types of bitumen used.

The different types of bitumen presented in Table 3 are sorted decreasingly by their stiffness (or increasingly by their penetration), i.e., the hardest bitumen is labeled A , and the softest is labeled M. Is was observed that the base bitumens have a great influence on the performance of the AR binder produced and residual bitumen obtained, because the stiffness sequence by which the base bitumens are organized is generally maintained after analyzing the final properties of the corresponding residual bitumens and AR binders.

In comparison with the base bitumens, the range of the values of the evaluated properties is narrower and shifted to values that indicate stiffer materials for the residual bitumens, and especially for AR binders. However, the penetration test results are the exception for this rule, since the residual bitumens presented lower penetration values than the AR binders. This is due to the fact that rubber particles behave as filler, thus affecting the flow behavior that commands R&B and AV tests. However, penetration test do not depend on flow but on the relative stiffness of each material. Since rubber swells by the diffusion of the lighter molecules of asphalt, AR binder can be softer than the residual asphalt, presenting less resistance to penetration.

The 40/50 and 60/70 pen grade bitumens are those typically used both for AR binder/mixture and conventional asphalt concrete mixture production. Nevertheless, by using those penetration grade bitumens to produce AR binders, it was observed that the penetration for the resulting residual bitumens and AR binders range, respectively, between $20-25$dmm and $23-30$dmm. In addition, all other properties (AV, R&B and τ) confirm the higher stiffness of the residual bitumens and AR binders that are traditionally obtained. Thus, considering that the residual bitumen is the effective binder in AR mixtures, it appears more suitable to use softer base bitumens to produce more flexible AR binders/ mixtures.

Relationship between the residual bitumen and rubber changes during the AR production

After assessing the initial and final properties of each component of the AR binder (bitumen and rubber), one of the main objectives of this work is to understand if there is a good relationship

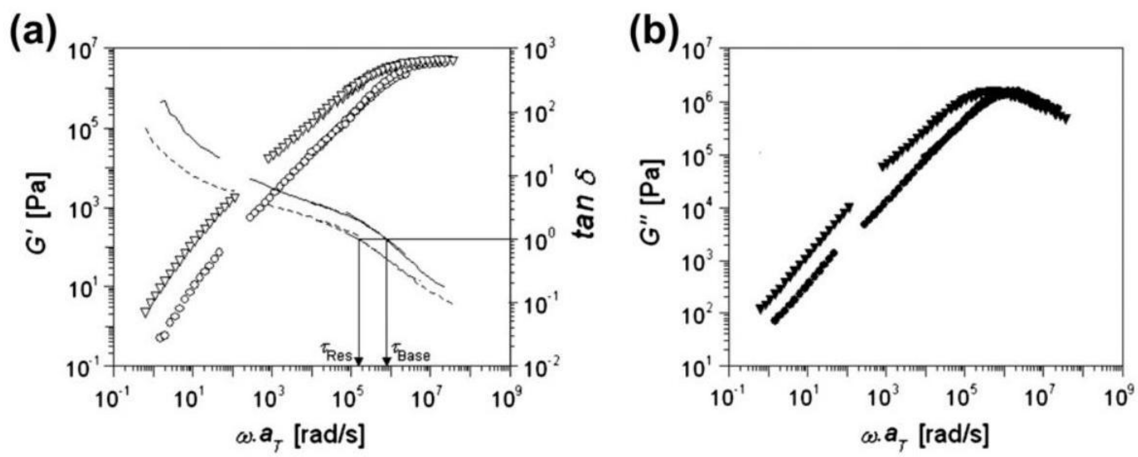

Fig. 2. Master curves ($T_{\text{ref.}}=80^{\circ}\mathrm{C}$) of (a) elastic modulus, tan δ and (b) loss modulus for base (circles) and residual (triangles) bitumen I.

Table 3
Physical and rheological properties of the base and residual bitumens and AR binders.

Type of binder	Tests	Binder sample labeling							
		A	B	E	J	I	P	O	M
Base bitumen	Pen (dmm)	1.34E + 1	2.25E + 1	4.58E + 1	4.89E + 1	5.86E + 1	7.88E + 1	9.93E + 1	1.43E + 2
	AV (cP)	2.50E + 2	2.00E + 2	1.25E + 2	1.34E + 2	9.58E + 1	8.75E + 1	7.50E + 1	5.00E + 1
	R&B (°C)	6.53E + 1	6.10E + 1	5.60E + 1	5.60E + 1	5.23E + 1	5.00E + 1	4.69E + 1	4.43E + 1

	τ(s)	3.19 E-4	3.13E − 5	2.34E − 5	9.42E − 6	8.29E − 6	7.02E − 6	5.72E − 6	3.14E − 6
Residual bitumen	Pen (dmm)	8.70E + 0	1.47E + 1	2.07E + 1	2.22E + 1	2.46E + 1	3.34E + 1	3.91E + 1	4.54E + 1
	AV (cP)	4.63E + 2	4.75E + 2	3.00E + 2	2.96E + 2	2.32E + 2	2.13E + 2	2.38E + 2	2.13E + 2
	R&B (°C)	7.34E + 1	6.92E + 1	6.57E + 1	6.57E + 1	6.17E + 1	6.25E + 1	6.08E + 1	5.94E + 1
	τ(s)	1.06E − 3	1.39E − 4	1.09E − 4	4.88E − 5	4.70 E-5	4.48E − 5	4.05 E-5	2.53E − 5
Asphalt rubber binder	Pen (dmm)	1.17E + 1	1.54E + 1	2.30E + 1	2.46E + 1	3.05E + 1	3.39E + 1	3.67E + 1	4.21E + 1
	AV (cP)	3.70E + 3	4.17E + 3	3.25E + 3	2.67E + 3	3.52E + 3	4.65E + 3	3.11E + 3	3.95E + 3
	R&B (°C)	8.28E + 1	8.05E + 1	8.01E + 1	8.01E + 1	7.42E + 1	7.33E + 1	7.14E + 1	7.37E + 1
	ER (%)	4.18E + 1	4.77E +1	4.85E + 1	4.90E + 1	5.00E + 1	4.90E +1	5.30E + 1	5.60E + 1

between the changes in the bitumen properties and in the mass of rubber, caused by the AR binder production. Thus, it should be possible to examine the existence of mutual modifications between these two materials.

The changes in bitumen and rubber during the AR binder production were evaluated through the calculation of indexes (ratios) of their properties before and after interaction. The only calculation made for the rubber was the mass index (mass of recovered swelled rubber/initial mass of crumb rubber, as explained previously), but the following indexes were determined for the bitumen properties:

- Pen index = Pen of base bitumen/Pen of residual bitumen.
- AV index = AV of residual bitumen/ AV of base bitumen.
- R&B index = R&B of residual bitumen/R&B of base bitumen; and - τ index = τ of residual bitumen /τ of base bitumen.

Fig. 3 shows the relationship between the rubber changes (mass index) and the bitumen changes (Pen, AV, R&B and τ indexes) measured for the eight different base bitumens studied.

The correlation obtained between the residual bitumen indexes and the rubber mass indexes follow a proportional rational trend line, i.e., Pen $_{\text{Base / Res}} = 1/(1.62 - 0.45^{*}$ Mass $_{\text{RR / CR}})$, AV $_{\text{Res / Base}} = 1/(1.07 - 0.26^{*}$ Mass $_{\text{RR/CR}})$, $\tau_{\text{Res/Base}} = 1/(0.77 - 0.23^{*}$ Mass

$_{\text{RR/CR}}$), except for the R&B indexes relationship with the rubber mass index that follows an exponential trend line, i.e., $R\&B_{\text{Res / Base}} = 0.936 * e^{(10* \text{ Mass } R/ \text{ CR})} + 1.12$. A good relationship between the rubber mass index and the indexes of the properties of residual bitumen was noticed, except at higher temperatures for the AV index. Generally, these results demonstrate the influence of the mutual changes induced in these materials by the AR production process, and this is especially noticed at service temperatures. The indexes that better reflect the referred relationship are those determined with R&B and τ properties (R^2 is 0.69,0.73 and 0.77 respectively for Pen, R&B and τ test results). The low R^2 obtained for AV index (0.46) show that the changes in rubber do not explain the properties of the residual bitumen at very high temperatures (the correlation between these variables is very low or does not exist), when the performance is mainly controlled by the binder and less by the rubber.

It must also be referred that all the previous relationships are only valid when the indexes are obtained for base bitumens with penetration values lower than 100 dmm (thus excluding base bitumen M). This observation may be explained by the concomitant occurrence of three phenomena influencing the properties of rubber and residual bitumen, as the authors have previously shown [26]:

- When softer bitumens are used to produce AR binders, the rubber particles reach their saturation point and split, thus an irreversible degradation (depolymerization and devulcanization) of the rubber particles occurs and a reduction on the rubber mass index.
- Meanwhile, the degradation and splitting of the rubber particles increase the volume fraction of rubber in the AR binder. In the presence of high temperatures (AR production), this can induce a process of revulcanization or repolymerization that entraps the lighter molecules of the bitumen, thus increasing the physical and rheological indexes of the residual bitumen.
- Additionally, during AR binder production bitumen ages/hardens due to the high production times and temperatures. This phenomenon is more evident in softer bitumens [41], i.e., base bitumen M , thus increasing the changes in the residual bitumen M .

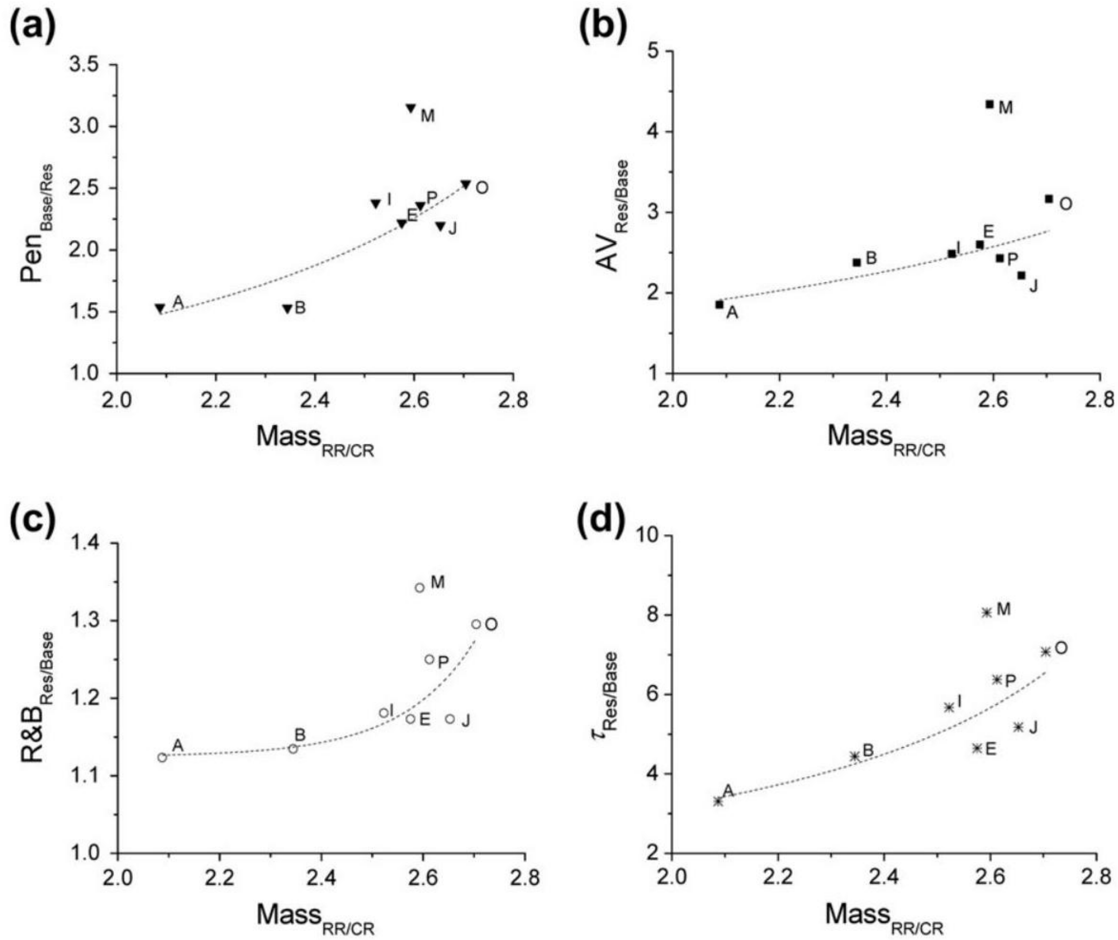

Fig. 3. Relationship between the rubber mass index and the indexes of the properties of residual bitumen, including (a) Pen index, (b) AV index, (c) R&B index and (d) τ index (the dash lines are the fits to the experimental data).

The use of indexes to identify and quantify the changes that occur in the rubber and in the residual bitumen are very effective, as previously observed [41]. This is illustrated by the rubber mass index (presenting values from 2.1 to 2.7), and by the physical indexes of the residual bitumen (always higher than 1.5). However, the changes in the residual bitumen were most effectively identified with the rheological τ index, since it shows the largest range of variation (between 3 and 8).

Relationship between the AR binder and rubber changes during the AR production

In order to understand the influence of the rubber mass changes in the properties of the final product (AR binder), the following indexes of the physical properties of the AR binder were plotted against the rubber mass indexes, as shown in Fig. 4:

- Pen index = Pen of base bitumen/Pen of AR binder.
- AV index = AV of AR binder/AV of base bitumen; and

- R&B index = R&B of AR binder/R&B of base bitumen.

Additionally, a graphic with the evolution of the elastic recovery values of the AR binder in function of the rubber mass index was also plotted in Fig. 4 as the ER is one of the most important characteristics of AR binders. This graphic was plotted with the absolute ER values of AR binders, and not with the ER indexes, because the ER of the base bitumens is nearly zero (thus being impossible to determine the ER indexes).

The three graphics that relate the indexes of the physical properties of AR binder with the rubber mass index have approximately the same tendency previously observed for the residual bitumen indexes. Thus, the Pen and AV indexes follow a proportionally rational trend, i.e., $\mathrm{Pen}_{\mathrm{AR/Base}} = 1/\left(2.56 - 0.80^{*}\mathrm{Mass}_{\mathrm{RR/CR}}\right)$, with $R^2 = 0.88$, and $\mathrm{AV}_{\mathrm{AR/Base}} = 1/(0.16 - 0.05^{*}\ \mathrm{Mass}\ _{\mathrm{RR/CR}})$, with $R^2 = 0.22$, while the R&B indexes have an exponential trend line relationship with the rubber mass indexes ($\mathrm{RB}_{\mathrm{AR/\ Base}} = 1.72\mathrm{E} - 3^{*}\mathrm{e}^{\mathrm{Mass\ RR/CR//0.51}}$, with $R^2 = 0.82$). A good relationship between the rubber mass index and the Pen and R&B indexes of AR binder was noticed, with R^2 values higher than those previously observed for the residual bitumen. In fact, it was expected that the rubber particles are more influent in the AR binder that in the residual binder obtained after separation of those particles. Meanwhile, it was observed that a clear correlation between the rubber mass index and the AV index of AR binder does not exist, because the correlation coefficient $R^2(0.22)$ is extremely low. Although this has already been observed for the AV index of the residual bitumens, the AR binder presents a higher scattering of results due to the heterogeneity of AR binder at higher temperatures used in the AV test (175°C). In fact, at these temperatures the AR binder behaves as a suspension of the rubber particles (filler) in the residual bitumen (Newtonian fluid). Moreover, the AR binder produced with the very soft base bitumen M does not follow the general tendency of the other base bitumens, as previously reported and justified for the residual bitumen.

Finally, the dependence of the ER values of the AR binder on the rubber mass index show a linear direct relationship ($\mathrm{ER}_{\mathrm{AR/\ Base}} = 12.79 + 14.26^{*}\mathrm{MasS}_{\mathrm{RR/CR}}$, with $R^2 = 0.79$), again with only one exception of the AR binder produced with base bitumen M. As the ER property of AR binders is mainly controlled by the presence of rubber, it was expected that an increase in the rubber mass should cause an increase in the ER value. The increase of the ER of the AR binder produced with base bitumen M , although the rubber mass index has decreased, can be justified by: (i) the formation of new bonds between the rubber particles (repolymerization) with a global increase in the elasticity of rubber; (ii) the high connectivity between rubber and bitumen matrix (interface); (iii) increase in the specific surface of the highly irregular particles [45].

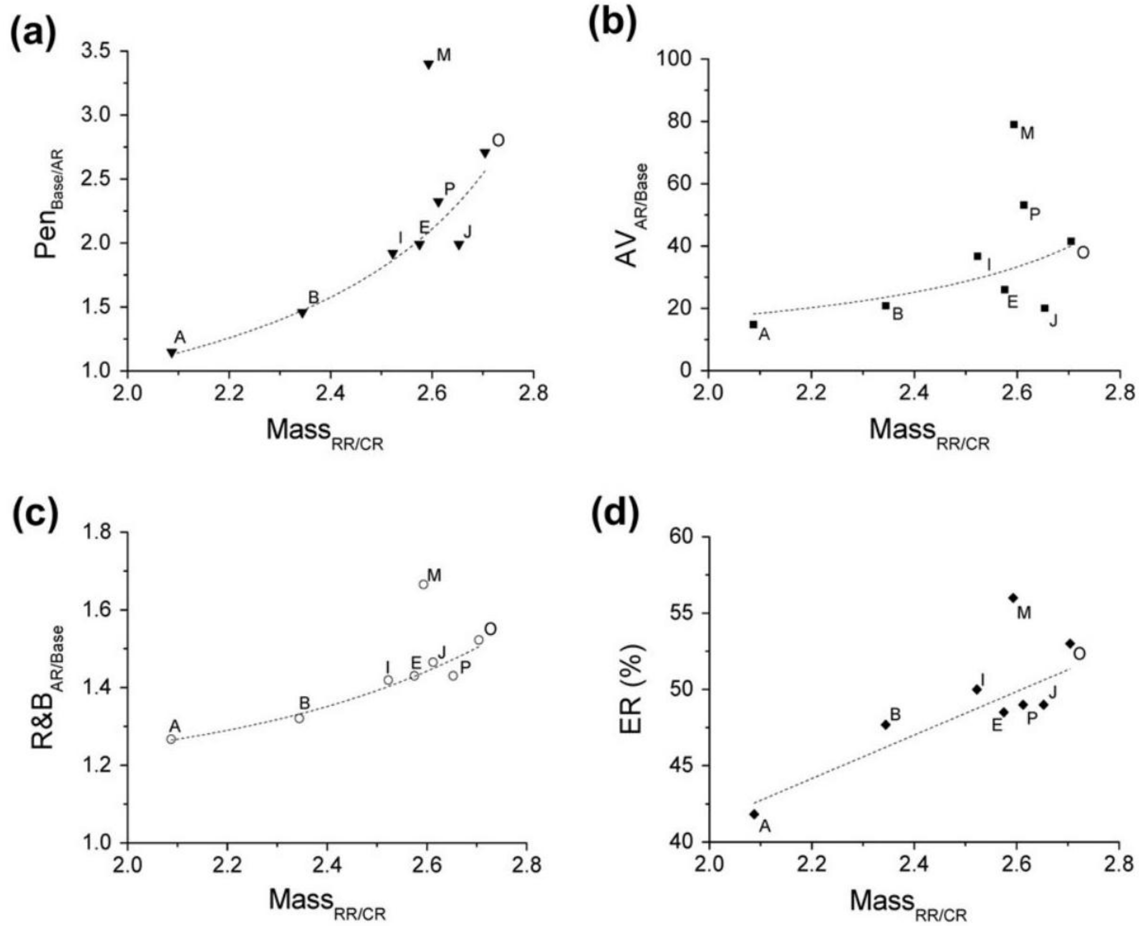

Fig. 4. Relationship between the rubber mass index and the indexes of the physical properties of AR binder, including (a) Pen index, (b) AV index, (c) R&B index and (d) ER values (the dash lines are the fits to the experimental data).

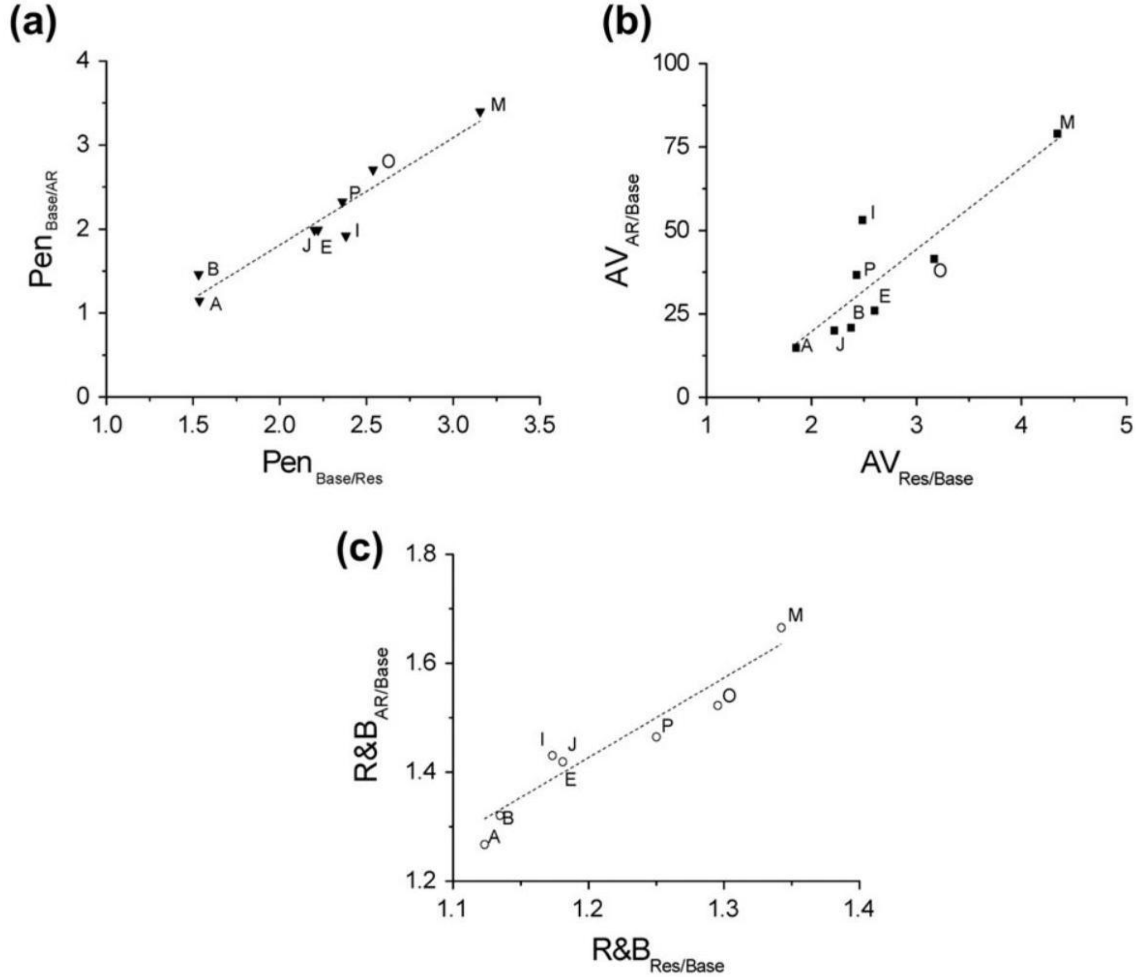

Fig. 5. Relationship between the indexes of the (a) Pen, (b) AV and (c) R&B physical properties of the AR binders and the corresponding residual bitumens (the dash lines are the fits to the experimental data).

Relationship between the AR binder and residual bitumen changes related with the AR production

Similarities can be observed between some graphics of Figs. 3 and 4, suggesting that the evolution of AR binder properties is very dependent on the changes of the residual bitumen caused by the AR production, in addition to the changes observed in the rubber.

Fig. 5 illustrates the dependence of the changes determined for the AR binder on the changes observed for the corresponding residual bitumen, i.e., the relationship between the physical indexes (Pen, AV and R&B) of the AR binders and respective residual bitumens.

Two observations are evident when analyzing the three graphics presented in Fig. 5:

- The good linear relationship between the indexes of the AR binder and the residual bitumen ($R^2 = 0.90, 0.74$ and 0.88 respectively for Pen, AV and R&B); and

- The inclusion of all studied materials, namely the very soft base bitumen M , in the overall trend lines that relate the properties of the AR binder and residual bitumen.

Despite the changes in the rubber mass are influenced by the use of different base bitumens and influence the final properties of the AR binder, the previous observations lead to the conclusion that, during the AR production, the final properties of the AR binder are clearly influenced by the changes evaluated on the residual bitumens.

The slope of the trend lines of the graphics presented in Fig. 5 is quite diverse, increasing with the test temperature as a consequence of the higher influence of the rubber particles in the results of the tests carried out at higher temperatures.

Conclusions

The main conclusions that can be drawn from this original study on the mutual changes of bitumen and rubber during the AR production are the following:

- All physical and rheological properties (Pen, AV, R&B and τ) indicate the stiffening of the AR binders and residual bitumens when compared with the base bitumen.
- The correlation between the residual bitumen indexes and the rubber mass indexes follow a proportional rational trend line, $y = 1/(a + b * x)$, except for the R&B indexes that relate with the rubber mass index by an exponential trending line, $y = a * e^{(-x/b)} + y0$.
- The mutual changes between the bitumen and rubber during AR production are evident, as observed in tests carried out at in service temperatures (Pen, R&B, τ and ER tests).
- There is no correlation between the changes of rubber and bitumen in the AV tests carried out at very high temperatures, because the influence of rubber particles in the performance of the binder is almost null at these temperatures.
- The good correlation between the bitumen and rubber changes are only valid for base bitumens with penetration values lower than 100 dmm .
- The changes in the residual bitumen were most effectively identified with the rheological τ index.
- The linear and good correlation between the AR binder and residual bitumen indexes show that the final properties of the AR binders are more dependent on the residual bitumen changes than on rubber changes.

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References

[1] Airey GD, Rahman MM, Collop AC. Absorption of Bitumen into crumb rubber using the basket drainage method. Int J Pavement Eng 2003;4(2):105-19.
[2] Jeong KD, Lee SJ, Amirkhanian SN, Kim KW. Interaction effects of crumb rubber modified asphalt binders. Constr Build Mater 2010;24(5):824-31.
[3] Shatnawi S. Performance of asphalt rubber mixes in California. Int J Pavement Eng 2001;2(1):1-16.
[4] Xiang L, Cheng J, Que GH. Microstructure and performance of crumb rubber modified asphalt. Constr Build Mater 2009;23(12):3586-90.
[5] Lee SJ, Akisetty CK, Amirkhanian SN. The effect of crumb rubber modifier (CRM) on the performance properties of rubberized binders in HMA pavements. Constr Build Mater 2008;22(7):1368-76.
[6] Chiu CT, Lu LC. A laboratory study on stone matrix asphalt using ground tire rubber. Constr Build Mater 2007;21(5):1027-33.
[7] Navarro FJ, Partal P, Martinez-Boza F, Gallegos C. Thermo-rheological behaviour and storage stability of ground tire rubber-modified bitumens. Fuel 2004;83(14-15):2041-9.
[8] Zborowski A, Kaloush KE. Predictive equations to evaluate thermal fracture of asphalt rubber mixtures. Road Mater Pavement 2007;8(4):819-33.
[9] Gallego J, Castro M, Prieto JN, Vassallo JM. Thermal sensitivity and fatigue life of gap-graded asphalt mixes incorporating crumb rubber from tire waste. Trans Res Rec 2007;1998:132-9.
[10] Pasquini E, Canestrari F, Cardone F, Santagata FA. Performance evaluation of gap graded asphalt rubber mixtures. Constr Build Mater 2011;25(4):2014-22.
[11] Pasquini E, Canestrari F, Santagata FA. Durability assessment of asphalt rubber mixtures. Int J Pavement Res Technol 2012;5(2):69-74.
[12] Partl MN, Pasquini E, Canestrari F, Virgili A. Analysis of water and thermal sensitivity of open graded asphalt rubber mixtures. Constr Build Mater 2010;24(3):283-91.
[13] Wang H, You Z, Mills-Beale J, Hao P. Laboratory evaluation on high temperature viscosity and low temperature stiffness of asphalt binder with high percent scrap tire rubber. Constr Build Mater 2012;26(1):583-90.
[14] Shen J, Amirkhanian S, Lee S-J. The effects of rejuvenating agents on recycled aged CRM binders. Int J Pavement Eng 2005;6(4):273-9.
[15] Xiao F, Amirkhanian SN. Laboratory investigation of moisture damage in rubberised asphalt mixtures containing reclaimed asphalt pavement. Int J Pavement Eng 2009;10(5):319-28.
[16] Fontes LPTL, Trichês G, Pais JC, Pereira PAA. Evaluating permanent deformation in asphalt rubber mixtures. Constr Build Mater 2010;24(7):1193-200.
[17] Shen J, Amirkhanian S. The influence of crumb rubber modifier (CRM) microstructures on the high temperature properties of CRM binders. Int J Pavement Eng 2005;6(4):265-71.
[18] Wong CC, Wong W-g. Effect of crumb rubber modifiers on high temperature susceptibility of wearing course mixtures. Constr Build Mater 2007;21(8): 1741-5.
[19] Billiter TC, Davison RR, Clover CJ, Bullin JA. Physical properties of asphaltrubber binder. Pet Sci Technol 1997;15(3-4):205-36.
[20] Suresha SN, Varghese G, Shankar AUR. A comparative study on properties of porous friction course mixes with neat bitumen and modified binders. Constr Build Mater 2009;23(3):1211-7.
[21] Amirkhanian SN. Establishment of an asphalt-rubber technology service (ARTS). In: Sousa JB, editor. Asphalt rubber 2003 conference. Brasilia, Brazil: Consulpav; 2003. p. 577-88.

[22] Thodesen C, Shatanawi K, Amirkhanian S. Effect of crumb rubber characteristics on crumb rubber modified (CRM) binder viscosity. Constr Build Mater 2009;23(1):295-303.
[23] Jensen W, Abdelrahman M. Use of crumb rubber in performance graded binder. In: Nebraska DoR, editor. Lincoln, NE: University of Nebraska; 2006. p. 157.
[24] Shen J, Serji A, Xiao FP, Tang BM. Influence of surface area and size of crumb rubber on high temperature properties of crumb rubber modified binders. Constr Build Mater 2009;23(1):304-10.
[25] Shen JN, Amirkhanian S, Xiao FP, Tang BM. Surface area of crumb rubber modifier and its influence on high-temperature viscosity of CRM binders. Int J Pavement Eng 2009;10(5):375-81.
[26] Peralta J, Silva HMRD, Machado AV, Pais J, Pereira PAA, Sousa JB. Changes in rubber due to its interaction with bitumen when producing asphalt rubber. Road Mater Pavement 2010;11(4):1009-31.
[27] Ould-Henia M, Dumont A-G. Assessment of the rheological properties of asphalt rubber binder and its residual phases. In: Sousa JB, editor. Asphalt rubber 2006 conference. Palm Springs, CA: Consulpav; 2006. p. 931-48.
[28] Putman B, Amirkhanian S. Crumb rubber modification of binders: interaction and particle effects. In: Sousa JB, editor. Asphalt rubber 2006 conference. Palm Springs, CA: Consulpav; 2006. p. 655-77.
[29] Lee S-J, Akisetty CK, Amirkhanian SN. Recycling of laboratory-prepared longterm aged binders containing crumb rubber modifier. Constr Build Mater 2008;22(9):1906-13.
[30] Lee S-J, Hu J, Kim H, Amirkhanian SN, Jeong K-D. Aging analysis of rubberized asphalt binders and mixes using gel permeation chromatography. Constr Build Mater 2011;25(3):1485-90.
[31] Liu S, Cao W, Fang J, Shang S. Variance analysis and performance evaluation of different crumb rubber modified (CRM) asphalt. Constr Build Mater 2009;23(7):2701-8.
[32] Artamendi I, Khalid HA. Diffusion kinetics of bitumen into waste tyre rubber. J Assoc Asphalt Paving Technol 2006;75:133-64.
[33] Stroup-Gardiner M, Newcomb DE, Tanquist B. Asphalt-rubber interactions. Trans Res Rec 1993;1417:99-108.
[34] Rahman MM. Characterisation of dry process crumb rubber modified asphalt mixtures. PhD thesis. Nottingham University of Nottingham; 2004.
[35] Yen TF, Chilingarian GV. Asphaltenes and asphalts, vol. 1. Amsterdam: Elsevier; 1994.
[36] Gawel I, Stepkowski R, Czechowski F. Molecular interactions between rubber and asphalt. Ind Eng Chem Res 2006;45(9):3044-9.
[37] Hansen CM, Smith AL. Using Hansen solubility parameters to correlate solubility of C-60 fullerene in organic solvents and in polymers. Carbon 2004;42(8-9):1591-7.
[38] Lougheed TJ, Papagiannakis AT. Viscosity characteristics of rubber-modified asphalts. J Mater Civil Eng 1996;8(3):153-6.
[39] Billiter TC, Chun JS, Davison RR, Glover CJ, Bullin JA. Investigation of the curing variables of asphalt-rubber binder. Pet Sci Technol 1997;15(5-6): 445-69.
[40] Polacco G, Vacin OJ, Biondi D, Stastna J, Zanzotto L. Dynamic master curves of polymer modified asphalt from three different geometries. Appl Rheol 2003;13(3).
[41] Peralta J, Hilliou L, Silva HMRD, Machado AV, Pais JC, Oliveira JRM. Rheological Quantification of Bitumen Aging: Definition of a New Sensitive Parameter. Appl Rheol 2010;20(6).
[42] Lesueur D. The colloidal structure of bitumen: consequences on the rheology and on the mechanisms of bitumen modification. Adv Colloid Interface 2009;145(1-2):42-82.
[43] Christensen DW, Anderson DA. Interpretation of dynamic mechanical test data for paving grade asphalt cements. J Assoc Asphalt Paving Technol 1992;61:67-116.

[44] Martinez-Boza F, Partal P, Navarro FJ, Gallegos C. Rheology and microstructure of asphalt binders. Rheol Acta 2001;40(2):135-41.
[45] Peralta J. Study of the interaction between bitumen and rubber. MSc thesis. Guimaraes: University of Minho; 2009.

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