



Article Influence of the Naphthenic-Aromatic Content of the Base Binder on the Characteristics of Crumb Rubber Modified Binders and Asphalt Mixtures

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Abstract: The extent of rubber-bitumen interaction in crumb rubber modified (CRM) binders depends on the contact time of rubber-bitumen as well as the temperature and mixing energy. However, this can vary depending on the composition of the base binders as well as the characteristics of the rubber particles (composition, method of grinding, and size). The present study aims to determine the influence of the composition of the base binders and the type of rubber on the properties of the crumb-rubber modified (CRM) binders and the performance of the asphalt mixtures produced with them. To carry out this project, two different base binders were chosen with the same penetration grade but different naphthenic-aromatic content (56.7 versus 46.0%). Additionally, different types of ambient ground rubber powder were evaluated: two different sources (70% of truck tyres +30% of passenger car tyres and 100% of truck tyres) and two different maximum particle sizes (0.8 and 1.25 mm). According to the main results of this study, higher naphthenic-aromatic content of the base binder results in greater modification of the CRM binders. Likewise, asphalt mixtures made with CRM binders from base binder with higher naphthenic-aromatic content appear to offer better performance in terms of water resistance and fatigue life.

Keywords: bitumen; naphthenic-aromatics; crumb rubber modified binders; asphalt mixtures

1. Introduction

Nowadays, the principal nations generate millions of used tyres all over the world. Instead of being sent to landfills, the rubber powder obtained from end-of-life tyres (ELTs) is being used in different applications like rubber modified asphalt materials for road construction and maintenance [1]. The asphalt industry has been developing pavements containing crumb-rubber modified (CRM) binders over the last 40 years and this is likely to increase as it is an excellent way to make use of waste and to provide the asphalt mixtures with an improved mechanical [2–4] compared to conventional mixtures. The service life of asphalt rubber (AR) mixtures is longer when compared to conventional mixtures [4]. These mixtures offer better performance under heavy traffic loads, and higher resistance to rutting at high temperatures and to thermal cracking at low temperatures [5,6]. These facts can be related to the modification of the binder by rubber and comparable with binders modified with Styrene Butadiene Styrene (SBS), as Lo Presti et al. have demonstrated [6]. Wang et al. have reported that CRM binders are more resistant than SBS modified binders in terms of thermal aging [7]. Nevertheless, two detailed studies by Behnood and Olek [8,9] reported different performance (i.e., reduced stiffness and elastic recovery) of the CRM binders due to the fact that CRM does not produce a polymeric network as in the case of SBS modified binders. In deeds, the

measurement of the viscosity of CRM binders requires complex procedures [10] due to the rubber particles in suspension. Furthermore, the evolution of the properties with the storage time demands special studies [11].

The characteristics of CRM binders depend on the source of the bitumen [12]. Regarding the composition of the bitumen, asphaltenes are high molecular weight phenols and heterocyclic compounds. They are the hardest components, giving the bitumen stability, body, and adhesiveness. They are also responsible for some of the rheological properties like their non-Newtonian behaviour. Other components of the bitumen enhance certain properties: resins provide ductility, plasticity, and adhesion while saturates and aromatics are usually related to viscosity [8,9,13–15].

Due to the complexity of the chemical composition of the bitumen, the asphalt industry usually separates its components in accordance with their molecular weight. These components are Asphaltenes, Saturates, Naphthenic-aromatic, and Aromatic-polar compounds, as early proposed by Corbett et al.[10,11], [16]. These fractions are determined by method ASTM D 4124 or the corresponding Spanish method NLT-373 [17].

The cyclic aromatic hydrocarbons are lightweight compounds with higher capacity to react with the crumb rubber [18], especially the non-polar naphthenic-aromatic fraction. The rubber-bitumen modification includes the absorption of light components, decomposition of rubber, and the generation of new compounds [19].

Putman and Amirkhanian [20] established that the variations of properties during the CRM modification might be related to their particle effect; this is the addition of particulate matter to the binder as well as the interaction of rubber particles and the binder. The diffusion of the light fractions during rubber-bitumen interaction was verified with high-pressure gel permeation chromatography (HP-GPC). In the same line, Cong et al. [21] have reported that the high proportion of lightweight fractions enhances the performance of CRM binders. Consequently, due to the composition of the bitumen to be modified with CRM, the properties of the CRM binders and the performance of CRM asphalt mixtures could vary.

Additionally, the type and amount of rubber powder can also influence the result [22]. Some properties of crumb rubber might affect rubber-bitumen interaction. Average particle size and specific surface appear to be predominating factors as well as the grinding method to produce CRM [23].

In this study, two base binders with high and low content of non-polar naphthenic aromatic compounds were selected; ambient grinding was chosen instead of cryogenic grinding, as it is the only one available in the Spanish market. This method processes scrap tyres at room temperature and provides irregularly shaped particles with large surface areas that are able to promote the interaction between the rubber and the bitumen [21,23]. Regarding the source of rubber, two sources were selected for this study: (1) CRM obtained by grinding 70%-30% truck-passenger car tyres and (2) CRM achieved by grinding 100% truck tyres. Also, two maximum particle sizes were taken into account: 0.8 and 1.25 mm.

To determine the influence of all these factors regarding the binder modification, several tests were performed including softening point, penetration, and viscosity. Furthermore, in order to relate the bitumen composition and the characteristics of the rubber powder to the performance of the CRM asphalt mixtures, the volumetric properties, the resistance to water attack, and the fatigue life of the mixtures were studied.

2. Materials and Methods

This investigation has followed an empirical method based on laboratory tests. Over the following sections, the methodology and stages of the process are described.

2.1. Description of the Laboratory Tests

The laboratory process can be structured in two stages: (1) On the basis of the materials detailed in Section 3, several combinations of rubber and bitumen types were used to produce CRM binders; then the modified binders were tested by dynamic viscosity, penetration, and softening point to evaluate their modification degree. (2) A selection of the CRM binders produced in the first stage was then used to produce gap-graded asphalt mixtures to be tested by volumetric properties, water sensitivity, and resistance to fatigue. Figure 1 shows the flow diagram of the work done and the main conclusions drawn from the results.

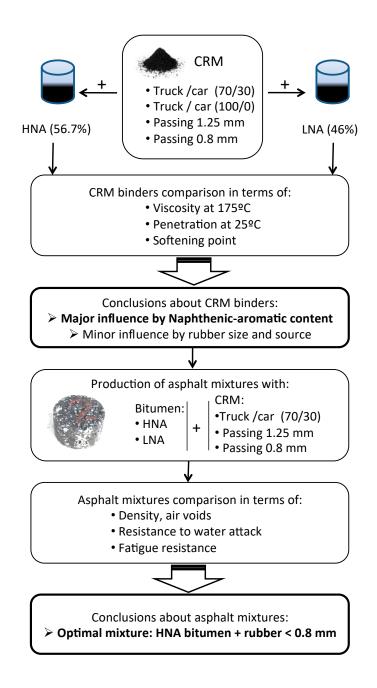


Figure 1. Flow chart of the investigation.

2.2. Laboratory Procedures

To characterize the rubber, the size of the particles was evaluated by sieving, according to EN-933-1 (Determination of particle size distribution. Sieving method). The sieves used were 1.25, 0.8, 0.5, 0.25, and 0.063 mm. Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fractions by monitoring the weight change that occurs as a sample is heated at a constant rate. TGA offers a quantitative evaluation of the compounds present in the sample: Volatile, Rubber, Carbon black, and Ash. To complete the characterization, the content of natural rubber was obtained by the 14C technique, which is a reliable and precise method for determining the biomass content of rubber from end-of-life tyres [24].

All the binders included in the investigation–base binders as well as CRM binders were characterized through penetration at 25 °C, softening point, and viscosity at 175 °C. The penetration test establishes the consistency of the bitumen at 25 °C by means of an indentation test in accordance with EN 1426 [25]. The softening point test establishes the temperature at which the bitumen softens according to EN 1427 [26]. Regarding viscosity, the binders were tested with a Brookfield rotational viscometer at 175 °C following standard EN 13,302 [27]. In all cases, the tests were performed on two different replicates of the CRM binders to calculate the average and standard deviation of the reported properties.

The properties studied for the CRM asphalt mixtures were: density, air void content, water sensitivity, and fatigue life. The maximum density was determined according to EN 12697-5 [28]. Combined with the bulk density, the maximum density is essential to calculate the void percentage of an asphalt mixture. The bulk density was determined according to EN 12697-6 [29]. The water sensitivity was evaluated through the immersion-compression test NLT-162 [30], which is a Spanish Standard that evaluates the effect of water on the cohesion of compacted bituminous mixtures. The test consists of the manufacture of cylindrical specimens (101.6 mm in diameter and 100 mm in height) by static compaction (17 tons for 2 min). Four specimens are conditioned in a water bath at 49 °C for four days. Another four specimens are held in the air at 20 °C during the same period. Finally, these specimens are tested on comprehensive strength at 20 °C and a speed of 5 mm/min. The average compressive strength is obtained for each group of specimens: S_w for the samples submerged and S_d for the airconditioned samples. The retained strength is the ratio S_d/S_w ×100.

The fatigue cracking resistance was determined by the Spanish Standard NLT-350 [31]. This is a three- point dynamic flexural test performed under strain-controlled conditions. A minimum of nine specimens was tested for each mixture under study.

2.3. Bitumens

The original binders used in this study were two different 35/50 penetration grade binders. The first bitumen, referred to hereafter as HNA, has a high naphthenic-aromatic content (56.7%). The second bitumen, referred to hereafter as LNA, has a lower naphthenic-aromatic content (46.0%). Table 1 summarizes the basic properties and composition of the two base binders by the Spanish standard NLT-373 [32].

	bitumens.			
			HNA	LNA
Properties	Standard	Unit	Test R	esults
Penetration (25 °C)	EN-1426	0.1 mm	48	44
Softening point	EN-1427	°C	49.2	52.8
Viscosity (175 °C)	EN 13302	cP	170	179
Composition	Standard	Unit	Test R	esults
Asphaltenes		(%)	10.2	17.7
Saturates	NH T 272	(%)	17.3	18.0
Naphthenic-aromatic	NLT-373	(%)	56.7	46.0
Aromatic-polar		(%)	15.8	18.3
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 Table 1. Characteristics of the high napthenic-aromatic (HNA) and low naphthenic-aromatic (LNA)

 bitumens

2.4. Crumb Rubber

All crumb rubber used in this study was produced by the ambient grinding process (scrap tyres are ground at or above room temperature), as this method of grinding increases the swelling rate when compared with cryogenically ground rubber [21]. The first rubber powder studied was obtained by the grinding of 70% truck tyres and 30% passenger car tyres (referred to hereafter as 70-30) and the second rubber powder was obtained by the grinding of 100% truck tyres (referred to hereafter as 100-0). These combinations of passenger car-truck tyres were selected as they are common in the Spanish CRM factories. Their composition can be seen in Table 2.

TGA	70% Truck-30% Passenger Car	100% Truck
Volatile (%)	4.7	4.8
Rubber (%)	57.2	57.0
Carbon black (%)	32.0	31.6
Ash (%)	6.3	6.8
Natural rubber (%)	42.0	47.0

Table 2. Thermogravimetric analysis of crumb rubber.

Although the composition is similar in both cases, it may be noted that the content of natural rubber is higher in the rubber powder 100-0 compared to the 70-30. This result is interesting, since natural rubber interacts with bitumen easier than synthetic rubber [12]. Two gradations for both sources of crumb were used during the study (Table 3).

Table 3. Gradation for both 70% truck-30% passenger car and 100% truck crumb rubber.

Passing (%)						
Sieve (mm) EN 933-2	Maximum Size 0.8 mm	Maximum Size 1.25 mm				
1.25	100	100				
0.8	100	37.0				
0.5	56.0	19.0				
0.25	25.0	6.0				
0.063	2.1	0.5				

It is worth mentioning that the price of crumb rubber decreases as the maximum size increases. The price of the 0.8 mm maximum size crumb rubber is about twice that of the 1.25 mm maximum size due to grinding costs. However, there is usually no price difference between the HNA and LNA binders.

2.5. CRM Binders

For the preparation of the modified binders, the following tooling was used: an oil bath with a maximum temperature of 225 °C, a mixer with a maximum velocity of 10,000 rpm fitted with a propeller agitator, and a one-litre metal container for mixing. To produce the CRM binders, on the basis of previous studies [19] as well as the Spanish experience with CRM binders, a fixed proportion of 80/20 bitumen/rubber in weight and a working temperature of 185 °C were selected. The temperature of the binder can be controlled with a precision of ± 1 °C. A bitumen sample of 500 g was heated in the oven at 180 °C and then placed in the oil bath. Then 125 g of rubber powder was added. The blend was subsequently mixed for 5 min at 4000 rpm, ensuring that the rubber was properly soaked. The blend was then stirred for another 90 min at 900 rpm at a constant temperature of 185 °C. Special attention was then paid to storage conditions of the test samples before testing (1 h at 25 °C \pm 0.5 °C) to avoid any differences during the storage period.

This procedure was carried out for 7 different CRM binders. Two replicates per type of binder were produced to obtain average values and standard deviations. Table 4 presents the modified binders under study and the nomenclature used.

		Table 4. Diffuers le	sieu.	
Binder	Base Bitumen	Bitumen/Rubber (%)	Rubber Maximum Size (mm)	Truck-Passenger Car Tyre (%)
HNA/0.8/70-30	I ligh generation	80/20	0.8	70-30
HNA/1.25/70-30	High naphthenic- aromatic content (HNA)	80/20	1.25	70-30
HNA/0.8/100-0		80/20	0.8	100-0
HNA/1.25/100-0		80/20	1.25	100-0
LNA/0.8/70-30	T	80/20	0.8	70-30
LNA/1.25/70-30	Low naphthenic- aromatic content (LNA)	80/20	1.25	70-30
LNA/0.8/100-0		80/20	0.8	100-0
LNA/1.25/100-0		80/20	1.25	100-0

2.6. Production of Crumb Rubber Modified (CRM) Asphalt Mixtures

The aggregates used to produce the AR mixtures were porphyry, limestone, and Portland cement as filler in the proportions shown in Table 5. The resulting gap-graded curve is displayed in Figure 2.

Table 5. Proportioning of the aggregates fractions.

Aggregate	Size (mm)	%
Porphyry	6/12	84
Limestone	0/4	14
Portland cement	0.063/0	2

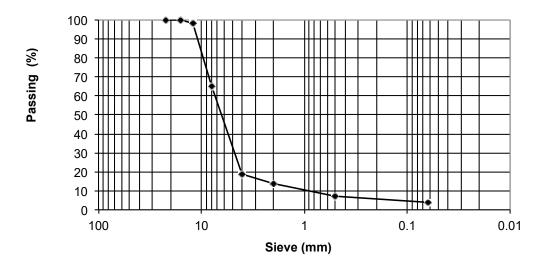


Figure 2. Gradation curve for the asphalt mixtures.

In all cases, the CRM binder content was 8.4% over the weight of the mixture. This elevated binder content is usual for anti-cracking CRM asphalt mixtures [4]. This combination of CRM binder and the gap-graded curve for the mixtures results in air void contents around 7%. The production temperature was 175 °C and the compaction temperature was 165 °C in all cases.

3. Results and discussion

In the following paragraphs, the laboratory results for the aforementioned tests are shown and discussed.

3.1. Viscosity

The results of viscosity at 175 °C can be seen in Table 6 and Figure 3. The first result focuses on the effect of CRM on viscosity. The rubber dramatically increases the viscosity of the CRM binder regardless of the base binder. As for the influence of the Naphthenic Aromatic content, HNA bitumen yields higher viscosity values; about twice those of the LNA modified binders. Nevertheless, the type of CRM (composition and particle size) appears to have little or no influence on the viscosity of the modified binders, as displayed on Figure 3. The enhancement of the CRM binders with HNA base binder is in line with the findings of Cong et al. [21]. Nevertheless, the general lack of influence of the rubber particle size is not in accordance with the work of Shen et al. [23], and should be revised in further investigations.

To confirm these comments, an analysis of variance (ANOVA) was elaborated for two factors with two replicates/group. This statistical technique allows us to analyze the influence of two factors on the variable response (i.e., viscosity). In this study case, as there are three variables (binder source, CRM source and CRM size) it is necessary to establish the value of one of them before analyzing the influence of the other variables. For instance, by establishing the binder source as HNA, the influence of CRM size and CRM source can be analyzed. Accordingly, the interpretation of the ANOVA results should be (carried out or calculated) for every value of the established variable.

Binder	Sample	Viscosity (cP)	Average (cP)	Coefficient of Variation (%)
HNA	#1	179	170	7.65
	#2	161	170	7.85
LNA	#1	171	179	6.15
LINA	#2	207	179	0.15
HNA/0.8/70-30	#1	3901	4063	5.64
111NA/0.0/70-30	#2	4225	4003	5.04
LINIA /1 25/70 20	#1	4290	4133	5.37
HNA/1.25/70-30	#2	3976	4155	5.57
HNA/0.8/100-0	#1	4635	4764	4.24
	#2	4893	4704	4.24
HNA/1.25/100-0	#1	4962	4810	4.49
111 11 ,25/100-0	#2	4657	4010	4.42
LNA/0.8/70-30	#1	2604	2492	6.34
LINA/0.0/70-30	#2	2380	2492	0.34
LNA/1.25/70-30	#1	2214	2419	11.99
LINA/1.23/70-30	#2	2624	2419	11.99
LNA/0.8/100-0	#1	2382	2476	5.37
LINA/0.0/100-0	#2	2570	2470	5.57
I NIA /1 25/100 0	#1	2864	2728	7.04
LNA/1.25/100-0	#2	2592	2120	7.04

Table 6. Viscosity at 175 °C.

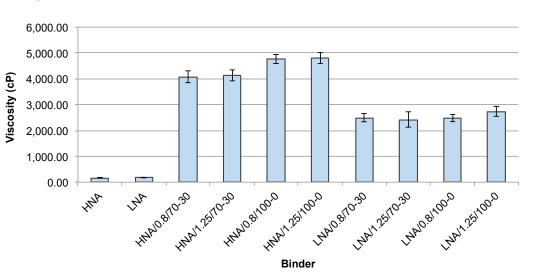


Figure 3. Viscosity for base binders and Crumb Rubber Modified (CRM) binders (at 175 °C).

According to the ANOVA results for the viscosity values (Table 7), the CRM source is a significant variable for the HNA binder and more reactive than the LNA binder. For both, the 70-30 and the 100-0 rubber powders, the use of HNA or LNA results in statistically different viscosity. This means that the use of the HNA binder really yielded CRM binders with higher viscosity. These conclusions are in accordance with Thodesen et al. [12] that found that the factors with major influence on viscosity were: base bitumen, rubber content, and source of CRM.

Established Factor	Variable Factors	F Value	F Critical (α = 0.05)	Statistical Significance
HNA	CRM size	0.1469	7.7086	-
ΠΝΑ	CRM source	20.8999	7.7086	YES
LNA	CRM size	0.3912	7.7086	-
	CRM source	1.0482	7.7086	-
70.20	CRM size	0.0362	7.7086	-
70-30	HNA/LNA	108.5477	7.7086	YES
100-0	CRM size	1.3165	7.7086	-
	HNA/LNA	283.9914	7.7086	YES

Table 7. Viscosity. Analysis of variance.

3.2. Penetration

The penetration test results can be seen in Table 8 and Figure 4. CRM binders show a lower penetration when compared with the original HNA and LNA binders. The interaction of the light fractions with the rubber particles appears to result in harder binders. Additionally, the 0.8 mm maximum size apparently results in lower penetration values.

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Table 8. Penetration at 25 °C.						
Binder	Sample	Penetration (10 ⁻¹ mm)	Average (10 ⁻¹ mm)	Coefficient of Variation (%)		
HNA	#1 #2	47 48	47.5	1.49		
LNA	#1 #2	44 44	44.5	0.00		
HNA/0.8/70-30	#1 #2	20 23	21.5	9.86		
HNA/1.25/70-30	#1	29	30	4.70		

	#2	31		
HNA/0.8/100-0	#1	20	21	6.71
111NA/0.0/100-0	#2	22	21	0.71
HNA/1.25/100-0	#1	29	27.5	7.71
111NA/1.23/100-0	#2	29	27.5	7.71
INIA /0.0/70.20	#1	25	26	5.42
LNA/0.8/70-30	#2	27		5.42
	#1	31	33	8.58
LNA/1.25/70-30	#2	35		0.30
INA /0.8/100.0	#1	25	26	5.42
LNA/0.8/100-0	#2	27		0.42
	#1	32	34	8.32
LNA/1.25/100-0	#2	36	34	0.32

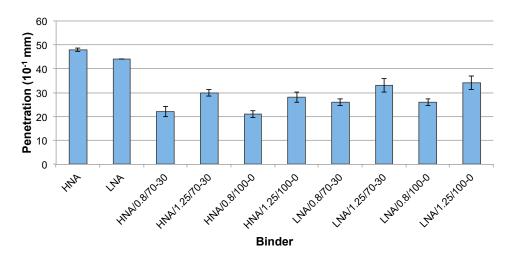


Figure 4. Penetration for base bitumens and Crumb Rubber Modified (CRM) binders.

According to the ANOVA for the penetration results (Table 9), it appears that the CRM source affects the penetration results. Additionally, for both sources of rubber (70-30 and 100-0) the CRM size influence has statistical significance, with F values above the 7.7086 critical value. The 1.25 mm maximum size rubber CRM binders yielded CRM binders with higher values of penetration. Nevertheless, these CRM binders are not stable during storage; they decant so that in the upper part of the penetration sample where the needle penetrates and therefore only the smallest particles of rubber remain. The coarse particles settled, especially in the case of the 1.25 mm maximum particle size. The upper portion of the sample does not represent the entire sample because it contains only a portion of fine rubber particles. For this reason, every conclusion based on the penetration values may not be reliable. It is necessary to emphasize that the settling problem does not affect the viscosity test because it is an in-motion test, neither the softening point because of the reduced size of the sample that allows faster cooling compared to larger penetration samples and prevents the settling of the rubber particles.

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Established Factor	Variable Factors	F value	F Critical (α = 0.05)	Statistical Significance
HNA	CRM size	0.5294	7.7086	-
TINA	CRM source	64.0588	7.7086	Yes
LNA	CRM size	0.1000	7.7086	-
	CRM source	22.5000	7.7086	Yes
70.20	CRM size	29.1212	7.7086	Yes
70-30	HNA/LNA	6.8201	7.7086	-
100-0	CRM size	45.000	7.7086	Yes
	HNA/LNA	24.2000	7.7086	Yes

Table 9. Penetration. Analysis of variance.

3.3. Softening Point

Table 10 and Figure 5 show that the addition of CRM increases the softening point of the CRM modified binders. The influence of the presence of rubber can be attributed to the absorption of the light non-polar fractions of the bitumen by the rubber. It is in line with the results of viscosity and penetration displayed above. This result is also in line with the findings of Sienkiewicz et al. [33].

Figure 5 shows that the softening point values for the HNA modified binders are higher than those for the LNA binders. As for the influence of size and source of the CRM, it appears that there is no noteworthy trend. The softening point values are very similar in all cases. So, the composition of the base bitumen appears to be the main factor influencing the softening point of the CRM binders.

Binder	Sample	Softening Point (°C)	Average (°C)	Coefficient of Variation (%)	
	#1	48.4			
HNA	#2	49.2	48.8	1.17	
LNA	#1	52.8	53.0	0.53	
LINA	#2	53.2	53.0	0.53	
HNA/0.8/70-30	#1	84.6	85.8	1.98	
111NA/0.0/70-30	#2	87.0	05.0	1.98	
HNA/1.25/70-30	#1	87.6	89.4	2.85	
111177/1.25/70-50	#2	91.2	07.4	2.85	
HNA/0.8/100-0	#1	86.8	87.8	1.61	
111110.0/100 0	#2	88.8	07.0	1.01	
HNA/1.25/100-0	#1	98.2	94.6	5.38	
111 (11, 1.20, 100 0	#2	91.0	71.0	0.00	
LNA/0.8/70-30	#1	69.2	69.0	0.41	
2111,010,7000	#2	68.8	0710	0.11	
LNA/1.25/70-30	#1	72.0	71.3	1.39	
. , ,	#2	70.6			
LNA/0.8/100-0	#1	72.0	72.2	0.39	
	#2	72.4			
LNA/1.25/100-0	#1	73.2	75.1	3.58	
21 11 1, 1.20, 100 0	#2	77.0			

Table 10. Softening point.

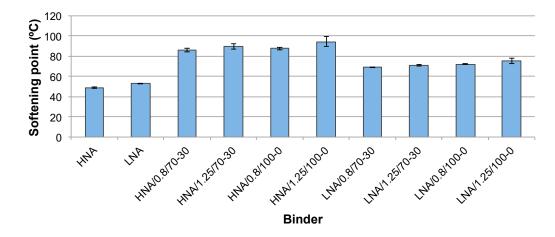


Figure 5. Softening point for base bitumens and Crumb Rubber Modified (CRM) binders.

The ANOVA for the softening point values shows (Table 11) that for both 70-30 and the 100-0 rubber sources, the use of HNA or LNA base bitumen makes differences with statistical significance. The HNA bitumen yielded CRM binders with higher softening point values.

Established Factor	Variable Factors	F Value	F Critical (α = 0.05)	Statistical Significance
HNA	CRM size	5.8025	7.7086	-
ΠΝΑ	CRM source	2.7811	7.7086	-
LNA	CRM size	1.0144	7.7086	-
LINA	CRM source	1.0134	7.7086	-
70.00	CRM size	6.6814	7.7086	-
70-30	HNA/LNA	233.7831	7.7086	Yes
100-0	CRM size	4.2655	7.7086	-
100-0	HNA/LNA	63.3543	7.7086	Yes

Table 11. Softening point. Analysis of variance.

3.4. Volumetric Properties

At the beginning of the work with CRM asphalt mixtures, it was decided to reduce the study ignoring the rubber source variable. The influence of this variable on the properties of the CRM binders was not evident. The only source considered was 70-30 rubber. Nevertheless, the maximum particle size of the rubber powder continued to be studied. In the Spanish market, it is not easy to find crumb rubber suppliers that guarantee the source of rubber (proportion of truck/passenger car tyres ground to produce the CRM). Nevertheless, it is possible to order products with different maximum sizes. For this reason, it was decided to thoroughly study the influence of the maximum particle size on the performances of the CRM asphalt mixtures.

The specimens (100 mm in diameter and 100 mm in height) were mixed at 175 °C, and then compacted at 165 °C by static pressure, 17 tons during 2 min. The results of density, as well as the results for the air void content, can be observed in Table 12. The maximum density had a value of 2.345 g/cm³ in all cases.

The main result from Table 12 is that the density of mixture LNA/1.25/70-30 is the lowest. This is probably due to coarse rubber particles remaining in the CRM binder and making compaction difficult. The coarse particle size of 1.25 mm causes difficulties during compaction. On the other hand, it seems plausible that the CRM asphalt mixtures made with HNA binders (viscosities above 4000 cP at 175 °C) would lead to mixtures with lower densities. However, mixtures made with LNA bitumens, despite having viscosities of about 2500 cP due to lesser reactivity with the rubber, present more rubber particles in suspension that can hinder compaction, counteracting the advantage of lower viscosity. For this reason, CRM asphalt mixtures with LNA binders present lower densities

when using 1.25 mm maximum size rubber. This problem was not unexpected. Navarro et al. [34] recommended a maximum size of 0.35 mm to avoid problems in compaction. It is probable that this particle size is not practical because it is difficult to find in the market and it is expensive, but maximum sizes above 0.8 mm could be problematic.

	_	Bulk Density	Air Void Content		
Mixture	Average (g/cm ³)	Coefficient of Variation (%)	Average (%)	Coefficient of Variation (%)	
HNA/0.8/70-30	2.163	0.51	7.75	5.81	
HNA/1.25/70-30	2.158	0.60	7.97	6.78	
LNA/0.8/70-30	2.165	0.46	7.68	5.86	
LNA/1.25/70-30	2.131	1.36	9.13	13.58	

Table 12. Volumetric properties (values from 8 specimens/mixture).

3.5. Immersion-Compression Test

The results of the immersion–compression test can be observed in Table 13. As for the strength of the dry conditioned specimens, it may be observed that the highest value is obtained for the HNA-0.8/70-30 mixture. A similar effect is observed in the results of retained strength. On the other hand, the lower reactivity of the LNA-binders and the larger maximum rubber size 1.25 mm and compaction difficulties yielded a mixture with less resistance to the effect of water: the lower level of naphthenic-aromatics, as well as the coarser rubber particles, resulted in a weaker mixture in terms of resistance to water attack.

Table 13. Resistance to water action	Table 13.	Resistance	to	water	action.
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Mixture	Compressive Strength Sd (MPa)	Compressive Strength Sw (MPa)	Retained Strength (%) Average Sw/Average S₀
HNA/0.8/70-30	3.58 ± 0.12	2.81 ± 0.12	78.4
HNA/1.25/70-30	3.4 ± 0.08	2.53 ± 0.10	74.3
LNA/0.8/70-30	3.29 ± 0.11	2.37 ± 0.14	72.1
LNA/1.25/70-30	3.32 ± 0.10	2.31 ± 0.16	69.6

3.6. Fatigue Life

The fatigue laws were obtained in prismatic specimens subjected to a flexural three-point bending test (NLT-350). The results are shown in Figure 6. The slope of the graphs is lower for the mixtures with HNA binders. This results in a more favorable performance in terms of fatigue life when compared with the mixtures produced with LNA binders. This fact can be attributed to the higher degree of modification of the HNA modified binders, as demonstrated above, in the sections regarding the viscosity and the softening point of the CRM binders.

Furthermore, the HNA/1.25/70-30 asphalt mixture shows better performance (higher fatigue graph) than the HNA/0.8/70-30 asphalt mixture. Although this fact would recommend the use of the 1.25 mm maximum size rubber with HNA base binder, from the point of view of the compactability of the mixture and the resistance to water attack, it may be slightly advantageous to select the 0.8 mm maximum size rubber.

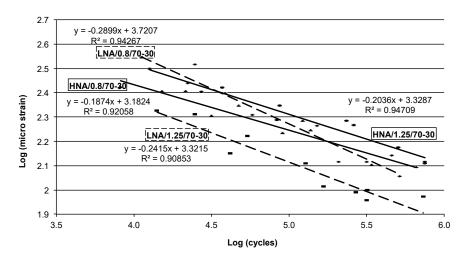


Figure 6. Fatigue performance of the Crumb Rubber Modified (CRM) asphalt mixtures.

4. Conclusions

From the results obtained in this paper the following conclusions can be drawn:

- The HNA base binder with a higher content of non-polar naphthenic-aromatic compounds yielded crumb rubber modified (CRM) binders with higher values for viscosity and softening point than those produced from the LNA base binder with lower content of naphthenic-aromatics
- This fact can be related to the higher reactivity of the non-polar naphthenic-aromatic compounds with the rubber particles
- No evident trends were obtained regarding the influence of rubber source and maximum size on the properties of the CRM binders, except for the rubber obtained from truck tyres, with a higher content of natural rubber when combined with HNA base binder.
- Regarding the influence of rubber size on the CRM asphalt mixture, the only conclusion that can be drawn is that the coarser gradation (1.25 mm versus 0.8 mm maximum size) might cause difficulties during compaction of the CRM asphalt mixture, especially when combined with low reactivity LNA base binder.
- In terms of asphalt mixture performance, the CRM asphalt mixture with HNA base binder showed higher resistance to water attack and longer fatigue life

As a final result, it can be stated that among the material studied, the use of base binder with a high content of naphthenic-aromatic compounds and rubber with particle maximum size of 0.8 mm seems to be the optimal option to produce crumb rubber modified binders and asphalt rubber mixtures.

The results obtained in this investigation can be extended to other crumb rubber products and procedures. In this regard, the influence of cryogenically ground crumb rubber could be studied. Since its specific surface area is lower than that of the ambient ground crumb rubber, its reactivity to the binder could be different, as well as compactability of CRM asphalt mixtures. Additionally, as European countries will adopt the performance base specifications for binders in the near future, it would be interesting to replicate this investigation with rheology studies.

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References

- 1. Lo Presti, D. Recycled Tyre Rubber Modified Bitumens for road asphalt mixtures: A literature review. *Constr. Build. Mater.* **2013**, *49*, 863–881, doi:10.1016/j.conbuildmat.2013.09.007.
- 2. Moreno, F.; Sol, M.; Martín, J.; Pérez, M.; Rubio, M.C. The effect of crumb rubber modifier on the resistance of asphalt mixes to plastic deformation. *Mater. Des.* **2013**, *47*, 274–280, doi:10.1016/j.matdes.2012.12.022.
- 3. Paje, S.E.; Luong, J.; Vázquez, V.F.; Bueno, M.; Miró, R. Road pavement rehabilitation using a binder with a high content of crumb rubber: Influence on noise reduction. *Constr. Build. Mater.* **2013**, *47*, 789–798, doi:10.1016/j.conbuildmat.2013.05.008.
- 4. Kaloush, K.E. Asphalt rubber: Performance tests and pavement design issues. *Constr. Build. Mater.* **2014**, *67*, 258–264, doi:10.1016/j.conbuildmat.2014.03.020.
- 5. Huang, B.; Mohammad, L.N.; Graves, P.S.; Abadie, C. Louisiana experience with crumb rubber-modified hot-mix asphalt pavement. *Transp. Res. Rec. J. Transp. Res. Board* **2002**, *1789*, 1–13, doi:10.3141/1789-01.
- 6. Lo Presti, D.; Memon, N.; Airey, G.; Grenfell, J. Comparison between bitumen modified with crumb tire rubber and styrene butadiene styrene. In Proceedings of the International Conference on Maintenance and Rehabilitation of Pavements and Technological Control (MAIREPAV6), Turin, Italy, 8–10 July 2009.
- 7. Wang, Q.; Li, S.; Wu, X.; Wang, S.; Ouyang, C. Weather aging resistance of different rubber modified asphalts. *Constr. Build. Mater.* **2016**, *106*, 443–448, doi:10.1016/j.conbuildmat.2015.12.138.
- Behnood, A.; Olek, J. Rheological properties of asphalt binders modified with styrene-butadiene-styrene (SBS), ground tire rubber (GTR), or polyphosphoric acid (PPA). *Constr. Build. Mater.* 2017, 151, 464–478, doi:10.1016/j.conbuildmat.2017.06.115.
- 9. Behnood, A.; Olek, J. Stress-dependent behavior and rutting resistance of modified asphalt binders: An MSCR approach. *Constr. Build. Mater.* **2017**, *157*, 635–646, doi:10.1016/j.conbuildmat.2017.09.138.
- 10. Lo Presti, D.; Fecarotti, C.; Clare, A.T.; Airey, G. Toward more realistic viscosity measurements of tyre rubber–bitumen blends. *Constr. Build. Mater.* **2014**, *67*, 270–278, doi:10.1016/j.conbuildmat.2014.03.038.
- 11. Pais, J.; Lo Presti D.; Santos, C.; Thives, L; Pereira, P. The effect of prolonged storage time on asphalt rubber binder properties. *Constr. Build. Mater.* **2019**, *210*, *242–255*, doi:10.1016/j.conbuildmat.2019.03.155.
- Thodesen, C.; Shatanawi, K.; Amirkhanian, S. Effect of crumb rubber characteristics on crumb rubber modified (CRM) binder viscosity. *Constr. Build. Mater.* 2009, 23, 295–303, doi:10.1016/j.conbuildmat.2007.12.007.
- 13. Oyekunle, L.O. Influence of Chemical Composition on the Physical Characteristics of Paving Asphalts. *Petrol. Sci. Technol.* **2007**, *25*, 1401–1414, doi:10.1080/10916460500528854.
- 14. Lesueur, D. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Adv. Colloid Interface Sci.* **2009**, *145*, 42–82, doi:10.1016/j.cis.2008.08.011.
- 15. Asphalt Institute and Eurobitume. *The Bitumen Industry—The Global Perspective*, 2nd ed.; Asphalt Institute and Eurobitume: Lexington, KY, USA, 2011.
- 16. Corbett, L.W. Composition of Asphalt Based on Generic Fractionation using Solvent Deasphaltening Elution-Adsorption Chromatography and Densimetric Characterization. *Anal. Chem.* **1969**, *41*, 576–579, doi:10.1021/ac60273a004.
- 17. CEDEX. NLT-373/94 Fraccionamiento de los Betunes Asfálticos; CEDEX: Madrid, Spain, 1994.
- 18. Chehovits, J.G. Binder design procedures. In *Crum Rubber Modifier Workshop Notes;* Report no. FHWA-SA-93-011; U.S. Department of Transportation: Washington, DC, USA, 1993.
- 19. Li, P.; Ding, Z.; Zou, P.; Sun, A. Analysis of physico-chemical properties for crumb rubber in process of asphalt modification. *Constr. Build. Mater.* **2017**, *138*, 418–426, doi:10.1016/j.conbuildmat.2017.01.107 2017.
- 20. Putman, B.J.; Amirkhanian, S.N. Characterization of the Interaction Effect of Crumb Rubber Modified Binders Using HP-GPC. *J. Mater. Civ. Eng.* **2010**, *22*, 153–159, doi:10.1061/(ASCE)0899-1561(2010)22:2(153).
- 21. Cong, P.; Xun, P.; Xing, M.; Chen, S. Investigation of asphalt binder containing various crumb rubbers and asphalts. *Constr. Build. Mater.* **2013**, *40*, 632–641, doi:10.1016/j.conbuildmat.2012.11.063.
- Peralta, J.; Silva, H.M.R.D.; Machado, A.V.; Pais, J.; Pereira, P.A.A.; Sousa, J.B. Changes in Rubber Due to its Interaction with Bitumen when Producing Asphalt Rubber. *Road Mater. Pavement Des.* 2010, *11*, 1009– 1031, doi:10.3166/RMPD.11.1009-1031.

- Saiz-Rodriguez, L.; Maria Bermejo-Munoz, J.; Rodriguez-Diaz, A.; Fernandez-Torres, A.; Rubinos-Perez A. Comparative Analysis of C-14 and Tga Techniques for the Quantification of the Biomass Content of End-Of-Life Tires. *Rubber Chem. Technol.* 2014, *87*, 664–678, doi:10.5254/rct.14.85993.
- 25. CEN. EN 1426. Bitumen and Bituminous Binders-Determination of Needle Penetration; CEN: Brussels, Belgium, 2003.
- 26. CEN. EN 1427:2007. Bitumen and Bituminous Binders—Determination of the Softening Point—Ring and Ball Method; CEN: Brussels, Belgium, 2007.
- 27. CEN. EN 13302:2010. Bitumen and Bituminous Binders—Determination of Dynamic Viscosity of Bituminous Binder Using A Rotating Spindle Apparatus; CEN: Brussels, Belgium, 2010.
- 28. CEN. EN 12697-5:2010/AC:2012. Bituminous Mixtures—Test Methods for Hot Mix Asphalt—Part 5: Determination of the Maximum Density; CEN: Brussels, Belgium, 2012.
- 29. CEN. EN 12697-6:2012. Bituminous Mixtures Test Methods for Hot Mix Asphalt Part 6: Determination of Bulk Density of Bituminous Specimens; CEN: Brussels, Belgium, 2012.
- 30. CEDEX. NLT-162/00 Efecto del Agua Sobre la Cohesión de las Mezclas Bituminosas Compactadas. (Ensayo de Inmersión-Compresión); CEDEX: Madrid, Spain, 2000.
- CEDEX. NLT-350/90 Ensayo de Fatiga en Flexotracción Dinámica de Mezclas Bituminosas; CEDEX: Madrid, Spain, 1990.
- CEDEX. Normas NLT. I, Ensayos de Carreteras. NLT 373/94, Fraccionamiento de Los Betunes Asfálticos; CEDEX: Madrid, Spain, 1999.
- Sienkiewicz, M.; Borzedowska-Labuda, K.; Zalewski, S.; Janik, H. The effect of tyre rubber grinding method on the rubber-asphalt binder properties. *Constr. Build. Mater.* 2017, 154, 144–154, doi:10.1016/j.conbuildmat.2017.07.170.
- 34. Navarro, F.; Partal, P.; Mart nez-Boza, F.; Gallegos, C. Thermo-rheological behaviour and storage stability of ground tire rubber-modified bitumens. *Fuel* **2004**, *83*, 2041–2049, doi:10.1016/j.fuel.2004.04.003.



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