

## Effect of base bitumen composition on asphalt rubber binder properties

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**ABSTRACT:** The asphalt rubber blend properties are strongly related to its base components properties. The base bitumen composition is considered as a key factor influencing the final rheological properties of asphalt rubber binder.

This paper describes results from a laboratory investigation of the interaction between crumb rubber and different composition bitumen according to the wet process. The bitumen composition is determined according to the SARA decomposition approach.

The composition's analyses are carried out on both base bitumen and residual bitumen extracted from the final asphalt rubber blend. The extraction process consists of a centrifuging procedure ensuring a reasonable aging and a minimum physical or chemical alteration of the phases.

The evolution of the bitumen composition during the curing process indicates that aromatic fractions of bitumen are the major cause of rubber swelling through a migration phenomenon.

Viscoelastic properties measurements demonstrate that base bitumen composition should be selected carefully to achieve a good compromise between a sufficient rubber swelling and a reasonable viscosity of the final binder.

### 1. Introduction

Asphalt rubber binder use in road materials applications is getting increasing interest from the paving industry since the 60's. Asphalt rubber blends produced according to the wet process, are considered as a good alternative to pure bitumen and were investigated intensively (PIARC, 1999).

The use of recycled rubber particles in bitumen binder applications is an environmentally efficient valorisation of the reclaimed material. Unlike using tire rubber as fuel for cement kilns, asphalt rubber binder take advantage of the exceptional elastic properties of rubber while allowing further recycling of the asphalt mixture at the end of the lifespan.

Asphalt rubber production is assumed to be essentially a physical interaction between bitumen and rubber particles (PIARC, 1999, Rouse, 1997 and Singleton et al, 2000). The main change in the composite system bitumen-rubber is the swelling of the rubber due to the migration of light fractions of bitumen through the cross-linked polymeric network. The swelling of rubber goes hand in hand with an increase in viscosity which is a major concern for satisfactory pumping and mixing conditions.

Heating of asphalt rubber during the curing process induces some breaks in rubber cross-links referenced by some authors as devulcanisation (Billiter et al, 1997). This phenomenon induces a progressive decrease in viscosity which is considered in some papers as the initial degradation of the polymer chains. Both swelling and devulcanisation are present during the asphalt rubber curing, even for the so-called dry process (rubber is introduced as a filler in

the asphalt mixing plant). The predominance of one of the phenomena relies on the processing parameters and essentially on blending temperature and blending duration.

The development of an effective asphalt rubber binder is mainly an experimental iterative process. Assuming a predetermined choice of components, a large number of parameters (contents, temperatures, blending duration) are investigated to select the optimum combination of these factors. Any modification of the previous parameters alters the final product properties and imposes an experimental correction.

Fortunately, many years of practical experiences allowed defining good-practice guidelines for components and processing parameters. These guidelines permitted achieving satisfactory binder properties without understanding the major phenomena and interactions between asphalt and rubber.

The main limitation in studying the composite medium bitumen/rubber is the complexity of a direct investigation of the components or phases at the end of the curing process. Rheological measurements are carried out on the base components as well as on the final blend but rarely on the effective final constituting phases. Some authors tried to separate the bitumen and rubber after the curing process without altering their properties (Singleton et al, 2000). A filtration procedure is proposed with some recommendations to minimise the unwanted interaction between the rubber and the solvent.

An interesting mechanical separation approach was experimented on polymer modified bitumen in (Hadrzynski and Such 1998). A centrifuging process is implemented at high temperature to separate the constituting phases without alteration. This technique is widely used in biology for DNA and blood analyses and was applied to modified bitumen. The present research investigates the efficiency of the centrifuging process to assess the physical properties of the binary system bitumen/rubber.

## 2. Experimental description

### 2.1 Experiment design

The description of the experimental approach is given succinctly in this paper. Detailed explanations could be found in (Ould Henia *et al*, 2006, Ould Henia, 2005).

According to literature guidelines, the most significant parameters affecting the properties of asphalt rubber blends (PIARC, 1999, Epps, 1994, Billiter et al, 1997) were enumerated hereafter:

1. Rubber Powder properties:
  - a. content,
  - b. chemical composition,
  - c. size distribution,
  - d. micro-morphology of particles
2. Curing temperature and duration
3. Mixing shear energy
4. Base bitumen composition

Three parameters are retained for the present study: rubber content, size distribution and base bitumen type. The other parameters are either known influencing the speed of the curing process (shear energy, temperature) or parameters for which literature recommends good-practice values.

For each parameter of the study, two levels are investigated (Table 1) and a total of 8 blends are prepared and tested.

**Table 1:** Laboratory experiments program

Rubber mass content (%)	Rubber particle size distribution (mm)	Bitumen type
10	0 / 1	Low aromatic bitumen (A)
20	0 / 0.5	Highly aromatic bitumen (B)

## 2.2 Materials properties

Bitumen composition is a major factor affecting the interactions between bitumen and rubber. It is admitted that light fractions of bitumen swell the rubber particles and some authors introduced the concept of compatibility between rubber and bitumen and recommended the use of base bitumen containing highly aromatic oily fractions (Eckmann et al, 1983).

Bitumen is separated into its generic fractions according to the method of Thin Layer Chromatography coupled with a Flame Ionisation Detector (TLC-FID). Bitumen major groups, by order of increasing polarity, are Saturates, Aromatics, Resins and Asphaltenes (SARA groups). The separation process is achieved in two steps: the determination of asphaltene content by precipitation with n-Heptane (based on ASTM 3279) followed by the Iatroscan analyses of the maltenes (the three phases are separated with respectively pentane and toluene/chloroform).

Two 70/100 grade straight forward bitumen are selected for this study regarding their aromatic oil contents. The selected bitumen have different properties but are considered commercially as equivalent products. Bitumen properties are shown in Table 2.

**Table 2:** Bitumen properties

Binder	Bitumen A	Bitumen B
Density [g/cm <sup>3</sup> ]	1.024	1.012
Penetration at 25°C [1/10 mm]	76	86
Ring & Ball temperature [°C]	50.3	44.9
Penetration index	-0.1	-1.3
SARA groups		
Saturates [%]	4	0
Aromatics [%]	70	86
Resins [%]	8	12
Asphaltenes [%]	18	2
Colloidal instability index	0.28	0.02

Rubber is obtained thru scrap tires grinding. The combination of truck and light vehicles tires ensures an equivalent content of natural and synthetic rubber in the delivered product. The rubber powder has a 0-1 mm size distribution as shown in Figure 1. A finer powder is obtained by using the 0.5 mm sieve.

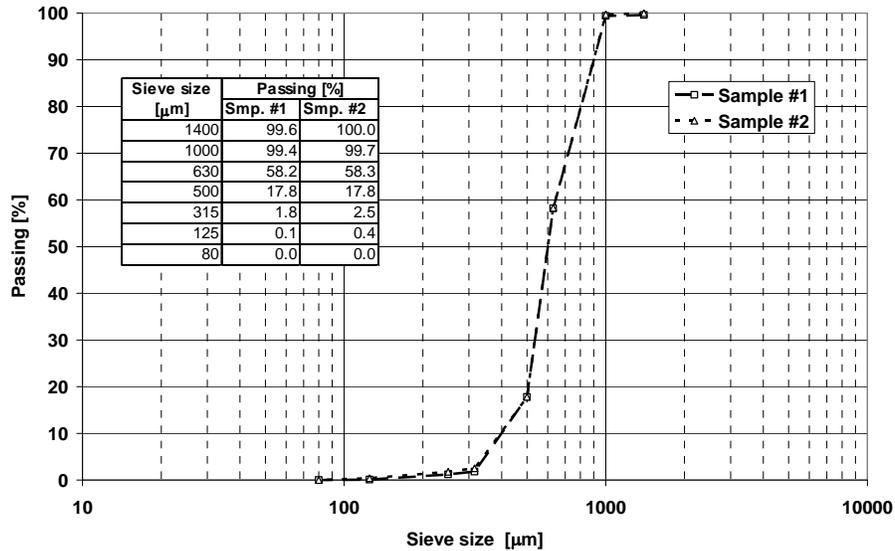


Figure1: Size distribution of the rubber powder

### 2.3 Asphalt rubber production protocol

Production of asphalt rubber samples is achieved thanks to a rigorous protocol.

The mixing process is achieved at a controlled temperature of 170 °C inside an oven coupled with a low shear blender. The mixing blade has a diameter of 50 mm and is placed at 5 mm from the bottom of the test-can which is 110 mm in diameter and contains approximately 200 g of binder.

The blend is homogenised at a revolution speed of 1000 rpm during 3 hours (see Ould Henia, 2005). Temperature inside the sample is maintained around 170°C by reducing the oven air temperature from 175°C at the start of the process to 172°C after the first hour.

Test samples are prepared immediately after the curing process.

### 2.4 Centrifuging process

The physical separation of the final phases of asphalt rubber blends is difficult due to the close densities of the two components. Heating the binder increases the mobility of rubber particles with the disadvantage of generating an excessive aging of bitumen if applied for a long period. The centrifuging process overcomes the previous limitations by increasing the acceleration and thus the speed of decantation of rubber particles (Hadrzynski, 1995).

The centrifuging process consists of applying 7000 G acceleration at 170 °C on 10 g samples during 1 hour. The samples are cooled at the end of the process and stored at 5 °C.

The effect of the centrifuging process on bitumen aging was not investigated in this study. One way to do this is the application of the described heating history (3 hours of binder curing and 1 hour of centrifuging) on pure base bitumen. However, we assume that this approach

will overestimate the alteration of the bitumen properties when it is associated with rubber. Indeed, the presence of anti-oxidant compounds within tire rubber composition can reduce considerably the oxidation of bitumen.

The two phases are easily distinguished and are weighed after their separation.

## 2.5 Rheological measurements

Viscoelastic characterisation of bituminous binders within the linear domain is carried out using an oscillatory shear loading rheometer (RHEOMETRICS ARES-RDA). A rotational shear strain is applied to samples placed between the parallel plates of the rheometer. The device allows sweeping temperatures from -20 to 60 °C and frequencies from 1 to 100 rad/s (0.16 to 16 Hz).

For each blend, complex shear modulus ( $G^*$ ) is measured on base bitumen, asphalt rubber, base rubber and centrifuged bitumen and rubber phases. A measurement protocol is established on the basis of a preliminary investigation of the linear viscoelastic zone of the tested binders.

For low temperatures (-20 to 40 °C), test conditions are:

- Samples of 8 mm in diameter and 2 mm in thickness
- Frequency: 1, 3.16, 10, 31.6, 100 rad/s
- Loading: 0.3% strain control

For medium temperatures (30 to 60 °C), we fix on the following conditions:

- Samples of 25 mm in diameter and 2 mm in thickness
- Frequency: 1, 3.16, 10, 31.6, 100 rad/s
- Loading: 1% strain control

Results are presented on the Black's space which is the plot of phase angle versus the decimal logarithm of the shear modulus norm. Each plotted value is the average of three repetitions. The transition between the two geometries (8 and 25 mm diameters) is appreciated visually at all frequencies and is found to be around 20 °C for bitumen and 40 °C for asphalt rubber and rubber phase.

## 3. Results

### 3.1 Swelling extent of rubber particles

The swelling extent of rubber particles ( $s$ ) is calculated from centrifuging process data.

$$s = \frac{V^R}{V_0^R} = \frac{\rho^R M^R}{\rho_0^R M_0^R} \quad (1)$$

Where:

$V^R$ ,  $\rho^R$ ,  $M^R$  are respectively the volume, the density and the weight of rubber after swelling,

$V_0^R$ ,  $\rho_0^R$ ,  $M_0^R$  are respectively the volume, the density and the weight of rubber before swelling.

Assuming that rubber and rubber phase densities are close enough, swelling extent ratio is given by the simplified expression:

$$s = \frac{M^R}{M_0^R} = \frac{M^R}{cM^T} \quad (2)$$

$M^T$  is the total weight of the asphalt rubber sample and  $c$  is the rubber content by mass.

The extent of swelling is measured for each blend on 4 samples. The results are summarised in Table 3.

**Table 3:** Rubber swelling extent ratios

Blend (rubber content, bitumen type, max. rubber size)	Mean	Standard deviation	Coefficient of variation
10%, Bitumen A, 1 mm	3.48	0.09	2.5%
10%, Bitumen B, 1 mm	3.81	0.07	1.8%
20%, Bitumen A, 1 mm	2.11	0.09	4.3%
20%, Bitumen B, 1 mm	2.61	0.01	0.5%
10%, Bitumen A, 0.5 mm	3.23	0.03	0.9%
10%, Bitumen B, 0.5 mm	4.01	0.07	1.8%
20%, Bitumen A, 0.5 mm	1.74	0.01	0.8%
20%, Bitumen B, 0.5 mm	2.76	0.05	1.9%

We can notice that rubber content is the major parameter affecting rubber swelling. The swelling ratio depends thus on the volumetric repartition of the phases. This is not the case for a classical polymer/solvent swelling experiment where the solvent is large enough in the composite to obtain a swelling ratio which is independent from the introduced polymer quantity.

Base bitumen type has also a significant effect on the swelling extent. It appears clearly that the high aromatic content binder (bitumen B) produces higher swelling ratios.

### 3.2 Bitumen composition evolution

Bitumen phases obtained with the centrifuging process are separated into their generic fractions according to the (TLC-FID) method. The results for all the blends are represented in Table 4. Ascending or descending arrows indicate the evolution of the fraction content compared to the base bitumen level.

Rubber particles' swelling induces a decrease in aromatics content and an increase in both resins and asphaltenes. This is a clear confirmation of the fact that aromatic fractions of bitumen are the major oils migrating into rubber network (Hadrzynski and Such, 1998, Singleton, Airey et al 2000).

**Table 4:** Evolution of bitumen SARA groups after curing

Blend (rubber content, bitumen type, max. rubber size)	Sat. (%)	Arom. (%)	Res. (%)	Asph. (%)
Base bitumen A	4	70	8	18
10%, Bitumen A, 1 mm	3 ↓	61 ↓	12 ↑	24 ↑
10%, Bitumen A, 0.5 mm	7 ↑	57 ↓	12 ↑	24 ↑
20%, Bitumen A, 1 mm	1 ↓	52 ↓	15 ↑	32 ↑
20%, Bitumen A, 0.5 mm	1 ↓	57 ↓	12 ↑	30 ↑
Base bitumen B	0	86	12	2
10%, Bitumen B, 1 mm	0	78 ↓	17 ↑	5 ↑
10%, Bitumen B, 0.5 mm	3 ↑	76 ↓	18 ↑	3 ↑
20%, Bitumen B, 1 mm	2 ↑	64 ↓	24 ↑	10 ↑
20%, Bitumen B, 0.5 mm	3 ↑	70 ↓	21 ↑	6 ↑

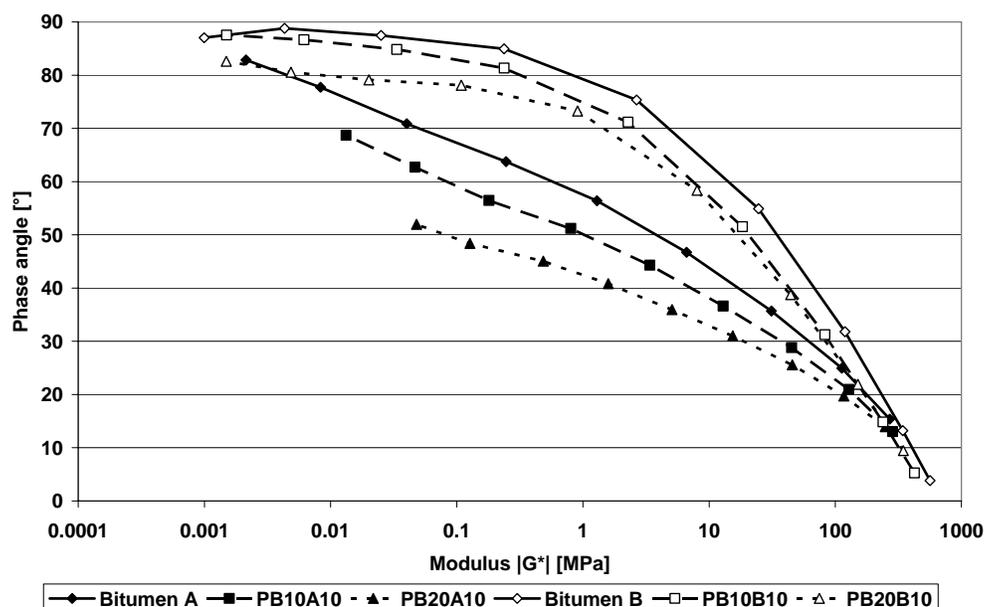
The increase of resins and asphaltenes contents in residual bitumen is mainly due to the loss of aromatics. However, a significant part of this change could be attributed to bitumen aging. Indeed, some authors affirm that thermal aging of bitumen is accompanied with the transformation of some amounts of aromatics into resins, and some amounts of resins into asphaltenes (Boutevin, Pietrasanta et al., 1989; Gailliard, 2003). These changes are concerning only unsaturated molecules.

Moreover, one can keep in mind that for higher viscosity binders (blends based on bitumen A), the asphaltenes content is overestimated due to the presence of a little amount of rubber particles inside the residual bitumen phase.

### 3.2 Viscoelastic properties evolution

Hereafter, temperature labels are not presented beside measurement points to improve the clearness of the charts. The reader can easily deduce this information knowing that temperature ranges from -20 °C to 60 °C with 10 °C increments when moving from the right to the left of the Black's curve (decreasing modulus).

Viscoelastic properties of bitumen A and B, as well as recovered bitumen phases, are presented in Figure 2. The label "PBxxyz" designates a recovered bitumen phase from an asphalt rubber blend produced with bitumen y, with xx% of rubber content, and zz 1/10 mm maximum rubber particles size.



**Figure2:** Evolution of the viscoelastic properties of bitumen after curing at 10 rad/s

Bitumen phases corresponding to the blends produced with finer rubber powder are not presented in Figure 2 because the effect of rubber particles size was found to be very small compared to rubber content and bitumen type.

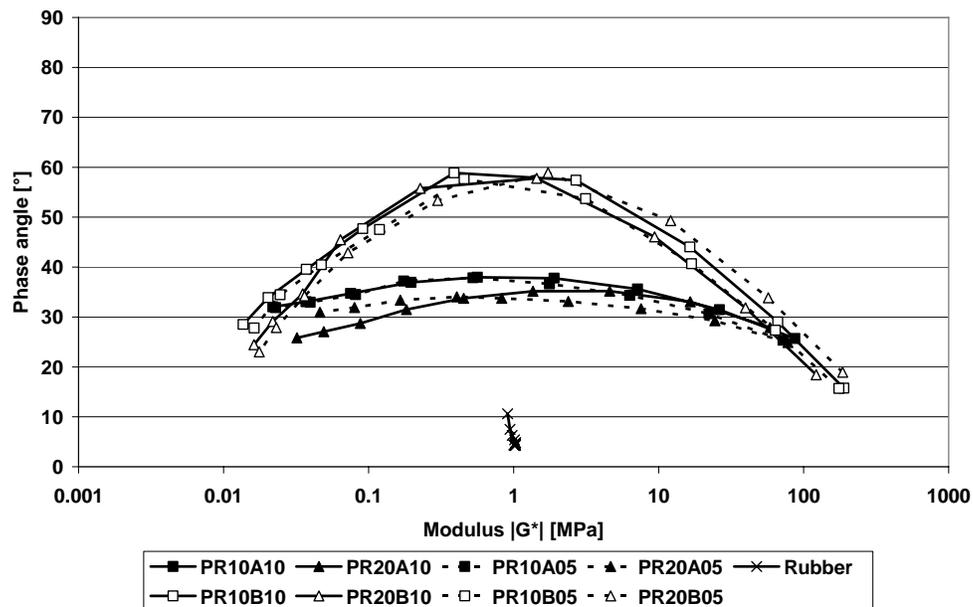
The comparison between base bitumen curves shows that bitumen B (high aromatic content) is more sensitive to temperature than bitumen A. Indeed, bitumen B modulus range is larger than bitumen A for a changing temperature. Bitumen B phase angle shows also a quick change versus temperature compared to bitumen A.

The introduction of rubber powder has a large effect on rheological properties of bitumen A. The higher is the rubber content the lower is the thermal sensitivity of the recovered bitumen. Residual bitumen B is less sensitive to the interaction with the rubber powder.

The loss of aromatic oils in residual bitumen A increases dramatically the viscosity of the binder. This is not the case for bitumen with sufficient aromatic fraction reserve (bitumen B).

As rubber particles' swelling ratio varies from 200% to 400%, absorbed bitumen constitutes the major part of the rubber phase in the final asphalt rubber blend.

Viscoelastic measurements are carried out on base rubber and on the rubber phase which is obtained from the centrifuging process (Figure 3). The label "PRxyzz" designates a recovered rubber phase from an asphalt rubber blend produced with bitumen y, with xx% of rubber content, and zz 1/10 mm maximum rubber particles size.



**Figure3:** Viscoelastic properties of rubber phase after curing at 10 rad/s

The rubber viscoelastic properties measured inside the viscoelastic linear domain are not sensitive to temperature. The shear modulus is around 1 MPa which is a common value for tires rubber with a small pre-strain of the test sample.

The absorption of bitumen modifies significantly the viscoelastic properties of the rubber phase. The modulus range of rubber phase covers more than 4 decades whereas base rubber modulus is very stable around 1 MPa.

Bitumen type is the major factor affecting viscoelastic properties of final rubber phase. It is interesting to notice that neither the rubber content, nor the rubber particles size have an influence on the rheological properties of the rubber phase.

#### 4. Discussions and Conclusions

The centrifuging of asphalt rubber binder or any composite material is an interesting and original process for separating the effective constituting phases without an excessive alteration of their physical or chemical properties. The method permitted a good estimation of the volumetric distribution of the matrix and the inclusion in the final material which is a precious information for a good micromechanical modelling of the composite.

Base bitumen type has a significant effect on the evolution of the bitumen phase properties in the asphalt rubber blend. Bitumen with a low content of aromatics or a high content of asphaltenes produces a high viscosity binder. In fact, aromatic oils act as a lubricant for asphaltenes conglomerates allowing their mobility.

Bitumen composition has to be selected carefully to obtain optimised viscoelastic properties for the final product. The amount of aromatics should be sufficient for swelling rubber without increasing excessively the viscosity. Understanding the bitumen fractions kinetics provides some helpful elements for producing a binder with a good repetitiveness of physical properties.

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