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Faculty of Engineering – Department of Civil Engineering

Nottingham Engineering Transportation Centre

DESIGN AND CHARACTERISATION OF RECLAIMED ASPHALT MIXTURES WITH BIOBINDERS

Thesis submitted to the University of Nottingham for the degree of Doctor of Philosophy in Civil Engineering

by

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August 2017

Abstract

Most pavements around the world are built with asphalt mixtures. Traditional asphalt mixtures are composed of aggregates and bitumen. Current concern about environmental issues and scarcity of these raw materials has motivated the search for different recycled and renewable resources to be used in pavement engineering. Regarding recycling, the use of Reclaimed Asphalt (RA) materials is nowadays a common and valued practice. However, there still exist some concern about its performance when used in high amounts (>30%) due to its aged state. In terms of renewable resources, the relatively new concept of biobinders (binders manufactured from biomass), as suitable asphalt binder alternatives, is gaining force in pavement engineering. To date, biobinders have shown great potential not only to reduce bitumen demand, but also exhibiting good performance in terms of resisting the main distresses affecting pavements. However, biobinders need in-depth and detailed characterisation in terms of engineering properties before they can be used in practice. The combination of RA and biobinders can be considered as an innovative technique to reduce the consumption of aggregates and bitumen.

Within this framework, the main aim of the research described in this thesis was to study the performance of RA mixtures with biobinders at binder and mixture scale in order to gain further understanding of their suitability to be used in actual pavements. For this purpose, biobinders manufactured from pine resin, linseed oil and by-products of the paper industry have been investigated as binders for the total replacement of the virgin bitumen needed in high RA content asphalt mixtures.

The research initially focused on the design of the blend of RA binder and biobinders through the study of their conventional and rheological properties which were subsequently used as an input in the design of the asphalt mixtures. Once the design parameters were fixed, the blends of RA binder and biobinders were characterised in terms of their rheological, ageing and adhesion properties, and their performance tested in terms of study rutting, fatigue and thermal cracking resistance. Then, 50% RA mixtures and 70% RA mixtures were characterised for the same properties and the relationships between binder blends and asphalt mixtures were studied.

The results showed that the biobinders studied are viscoelastic materials able to efficiently restore some of the properties of the RA binder in an equivalent or better way than conventional bitumens, increasing its viscous component and decreasing its stiffness. The mechanical performance of biobinders and bio-asphalt mixtures regarding rutting, fatigue, thermal cracking and moisture damage was found to be comparable to conventional mixtures. Good relationships were found between the binder blends and asphalt mixtures performance under the assumption of full blending, even though the exact degree of blending remained unknown. In this regard, the blend design performed as the first step was found to satisfactorily work as the input for the design of high RA content asphalt mixtures. Biobinders and bio-asphalt mixtures showed the same ageing tendency as conventional materials although ageing occurred at a faster rate, which can be considered the main drawback of their performance.

In the light of the results obtained in this thesis for the materials studied, high RA content asphalt mixtures with biobinders can be considered promising materials to be used in

pavement engineering. Full-scale experiments could be the final step for their development.

Acknowledgments

The first two persons that I would like to thank are my supervisors: Prof Gordon D. Airey and Dr Davide Lo Presti. Without their guidance and persistent help this thesis would not have been possible. Thank you for giving me the opportunity of being part of NTEC and SUP&R ITN. The research presented in this thesis was carried out as part of the Marie Curie Initial Training Network (ITN) action, FP7-PEOPLE-2013-ITN. This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement number 607524.

During the development of this thesis I have had the chance to collaborate with fantastic professionals. Thanks to all professors, colleagues and technicians at NTEC for making these years easier. I also have to thank the Ifsttar team (Nantes, France), where I spent three great months that helped me develop this thesis, in particular thanks to Dr Emmanuel Chailleux for his assistance and dedication. Thanks to Eiffage for all the technical support provided and to Dr Simon Pouget for having being involved in the project. Thank you to all LabIC.ugr group (University of Granada), where I started the adventure of pavement engineering research, and in particular to Prof Mayca Rubio, Dr Fernando Moreno and Dr Miguel del Sol. Thanks to all supervisors and colleagues in SUP&R ITN, you made this experience unforgettable.

But these years I have not only met good professionals but good friends. Thanks to all of you in Nottingham who have listened to so many stories so many times about this thesis.

Thanks Helena, Giacomo, Laura, Domenico, Andrea, Sara, Gaspare, Mo, Gustavo, Diana, Breixo, María and Antonio.

And not everything has been new. Thanks to all my friends from Granada. Thanks Ampi, Ana, Che, Fani, Glo, Maca, María, Marta, Nacho, Ro and Silvia for being an essential and indispensable part of my life. You know you charge my battery.

Thank you Alessio, for being always there ready to listen and to say the perfect words. Thank you for your energy and smile. Thank you for being you.

Last but most important, thanks to my family. Thanks to those who are not here in presence, but taught me so many things. Thanks to Luismi and Fátima for your listening and understanding in every single moment. Thank you Juan for the joy. Thank you mum and dad, for giving me your passion about academia and research since ever. Thank you for your unbeatable guidance and unconditional support. This is thanks to you.

Ana
Nottingham, August 2017

Declaration

I declare that the contents and the work described in this thesis were performed at the University of Nottingham, Faculty of Engineering from June 2014 to August 2017. I hereby certify that this thesis is my own and has not been submitted in whole or in part to any other university or any other educational association for a higher degree.

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We declare that the contents and the work described in this thesis were performed at the University of Nottingham, Faculty of Engineering from June 2014 to August 2017 and under our supervision.

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CHAPTER 1. INTRODUCTION

1. INTRODUCTION

1.1. Background of the thesis

Most pavements around the world are built with asphalt mixtures. The function of these materials, depending on where they are located in the pavement structure, is to provide the structural strength of the road as well as a smooth, safe and impermeable surface in order to ensure road users' safety. In this regard, asphalt mixtures have to be able to resist climate changes and heavy traffic loads without suffering excessive damage.

Asphalt mixtures are mainly composed of two materials: aggregates and binder. Aggregates are mineral particles which provide the mixture with resistance to compression due to friction between them, while binders are viscoelastic materials that provide tensile resistance and cohesion. In order to guarantee the right performance of the mixture, aggregates and binder have to work together. In this sense, binders play an essential role in asphalt mixture behaviour.

Commonly, bitumens and modified bitumens have been used as binders in asphalt mixtures. However, current concern about environmental issues and scarcity of these raw materials has motivated the search for different recycled and renewable resources to be used in pavement engineering. In this respect, the relatively new concept of biobinders is gaining force in this field. Biobinders are asphalt binder alternatives made from non-petroleum-based renewable resources, which should not rival any food material, and have environmental and economic benefits (Peralta et al., 2012a). For example, researchers have produced biobinders from algae, soy fatty acids or swine manure. According to

literature, biobinders can be utilized in three different ways to decrease the demand for fossil fuel based bituminous binders: (1) as a bitumen modifier (<10% bitumen replacement), (2) as a bitumen extender (25% to 75% bitumen replacement), and (3) as a direct alternative binder (100% replacement) (Airey et al., 2008; Raouf, 2010). To date, biobinders have shown great potential not only to reduce bitumen demand, but also exhibit good performance in terms of resisting the main distresses affecting mixtures: rutting, fatigue cracking, thermal cracking, ageing and moisture damage.

A recently developed approach for the use of biobinders is to combine them with Reclaimed Asphalt (RA). In this sense, it is possible to take advantage of the bitumen already present in recycled pavements while reducing the consumption of virgin materials. Moreover, biobinders have already shown the potential to be able to restore part of the initial properties of RA binders (Hill et al. 2013), which have been exposed to climate changes and traffic loads during the service life of the pavement and therefore may exhibit some performance issues.

The combination of RA with biobinders in new asphalt mixtures is therefore an innovative technique which should be further studied in order to understand whether they are suitable materials to be used in asphalt pavements. Furthermore, if high-RA contents are to be used in order to maximise its advantages, the presence of the aged binder cannot be ignored and a careful binder design previous to the asphalt mixture design should be undertaken. Within this framework, the performance of two biobinders in high-RA content mixtures is studied in this thesis.

“Design and characterisation of Reclaimed Asphalt mixtures with biobinders” is part of the European project SUP&R ITN (Sustainable Pavements and Railways Initial Training Network) within the Marie Curie Initial Training Network (ITN) action, FP7-PEOPLE-2013-ITN. This project has received funding from the European Union’s Seventh Framework Programme for research, technological development and demonstration under grant agreement number 607524.

1.2. Outline of the thesis and declaration

The present thesis covers the design and characterisation of RA mixtures with biobinders. Therefore, the first part is dedicated to the study and design of RA and biobinders’ blends and asphalt mixtures. Next, blends and asphalt mixtures are characterised in terms of their most important engineering properties.

To this end, the thesis is divided into eight chapters. In Chapter 1 the objectives, materials studied and methodology followed during the development of the thesis are explained. Chapter 2 reviews the existing literature about the different topics addressed: binders, asphalt mixtures, mechanical and rheological performance of those materials, RA and biobinders. Chapters 3 to 7 show the results and discussion obtained during the development of the thesis. Firstly, Chapter 3 shows the characterisation of the binders. Chapter 4 deals with the design performed for the blends and asphalt mixtures with RA and biobinders. In Chapter 5, the rejuvenating effect of biobinders over RA binder is analysed. Chapter 6 details the characterisation carried out in terms of linear-viscoelastic properties, rutting, fatigue, thermal cracking, moisture damage and ageing of biobinders

and RA binder blends and asphalt mixtures, including the study of their relationship. Chapter 7 studies the influence of RA content in the mechanical performance of the asphalt mixtures. Finally, Chapter 8 draws the conclusions of the work carried out and recommendations for further research.

Author's declaration: Some chapters of this thesis have been partly based on the following scientific publications:

1. A. Jiménez del Barco Carrión, D. Lo Presti & G.D. Airey (2015): Binder design of high RAP content hot and warm asphalt mixture wearing courses, Road Materials and Pavement Design, DOI: 10.1080/14680629.2015.1029707
2. D. Lo Presti, A. Jiménez del Barco Carrión, G.D. Airey & E. Hajj (2016): Towards 100% recycling of reclaimed asphalt in road surface courses: binder design methodology and case studies, Journal of Cleaner Production, 131:43-51 DOI: http://dx.doi.org/10.1016/j.jclepro.2016.05.093
3. A. Jiménez del Barco Carrión, D. Lo Presti, S. Pouget, G.D. Airey & E. Chailleux (2017): Linear viscoelastic properties of high reclaimed asphalt content mixes with biobinders, Road Materials and Pavement Design, DOI: 10.1080/14680629.2017.1304253
4. A. Jiménez del Barco-Carrión, M. Pérez-Martínez, A. Themeli, D. Lo Presti, P. Marsac, S. Pouget, F. Hammoum, E. Chailleux & G.D. Airey (2017): Evaluation of bio-materials' rejuvenating effect on binders for high-reclaimed asphalt content mixtures, Materiales de Construccion, 67 [327], e130, DOI: http://dx.doi.org/10.3989/mc.2017.04516

1.3. Objectives

Within the context described in Section 1.1, the main aim of this thesis is to provide further insight into the use of biobinders in Reclaimed Asphalt (RA) mixtures to promote the utilisation of these materials towards a post-petroleum society. For this purpose, the overall aim of the thesis is:

- ✓ To study the performance of biobinders and RA at binder and asphalt mixture level for pavement engineering purposes.

In this regard, the specific objectives of the thesis are:

- → To characterise the conventional and rheological properties of biobinders
- → To develop a biobinders and RA binders' blend design to be used in asphalt mixture design
- → To evaluate the rejuvenating effect of biobinders on RA binders through rheological assessment
- → To study and relate the linear visco-elastic properties of biobinders and RA blends and asphalt mixtures through mechanical models
- → To characterise the mechanical and linear-viscoelastic performance of RA blends and mixtures with biobinders in terms of the main distresses affecting asphalt pavements: rutting, fatigue, thermal cracking, moisture damage and ageing
- → To study the suitability of using high RA contents in these types of asphalt mixtures

Moreover, it has to be highlighted that the biobinders studied in this thesis would totally replace the virgin bitumen used in RA mixtures. This means that the asphalt mixtures

would be manufactured with biobinders, RA materials and virgin aggregates, avoiding the use of any virgin conventional bitumen.

1.4. Materials

In this section, the materials used during the development of the thesis are described including the conventional binders and biobinders, the source of RA selected and the virgin aggregates.

1.4.1. Conventional binders

Two different conventional binders were studied and used for different purposes. Firstly, a 50/70 penetration grade bitumen (50/70) was selected as a reference for the study in terms of the blend of biobinders and the RA binder. This type of binder is commonly used in Europe in base and binder layers in asphalt pavements.

Secondly, the control binder to be compared with biobinders was selected as a high-performance binder in order to compare the bio-materials with a high-quality binder. Therefore, this material was chosen to be a cross-linked SBS polymer modified binder (PMB) which is used in practice in France to recycle asphalt pavements, especially on large motorway projects.

The conventional properties of these two binders are shown in Table 1.

Table 1. Conventional properties of binders

Binder	Penetration at 25°C (x 0.1 mm)	Softening point (°C)	Fraass breaking point (°C)	Rotational viscosity at 135°C (mPa.s)
50/70	68	47.6	-7	275
PMB	85	67.0	-16	1151

1.4.2. Biobinders

1.4.2.1. BioBinder (BB)

The first biobinder is a 100% renewable binder composed of pine resin and linseed oil, named BB. The resin is made from stabilized and deodorized ester-pentaerythritol rosin. The rosin is a solid residue obtained from turpentine oleoresin which is a natural secretion harvested from coniferous trees, especially pines. The resin has a light colour and is particularly recommended for hot melt adhesives.

Figure 1 shows an example of the extraction process and the final resin.

Linseed oil is a yellow oil extracted from cultivated flax seeds (rapidly growing plant with blue flowers, cultivated for its fibres and oilseeds). The flax oil extraction is carried out by pressing the mature and dried flax seed after they are crushed. Linseed oil has several industrial and artistic applications. It is usually used with drying agents, which play a catalytic role in accelerating its drying or curing. Figure 2 shows the blue lin flowers, grains and the final oil.



Figure 1. Pine forest, rosin extraction and final resin

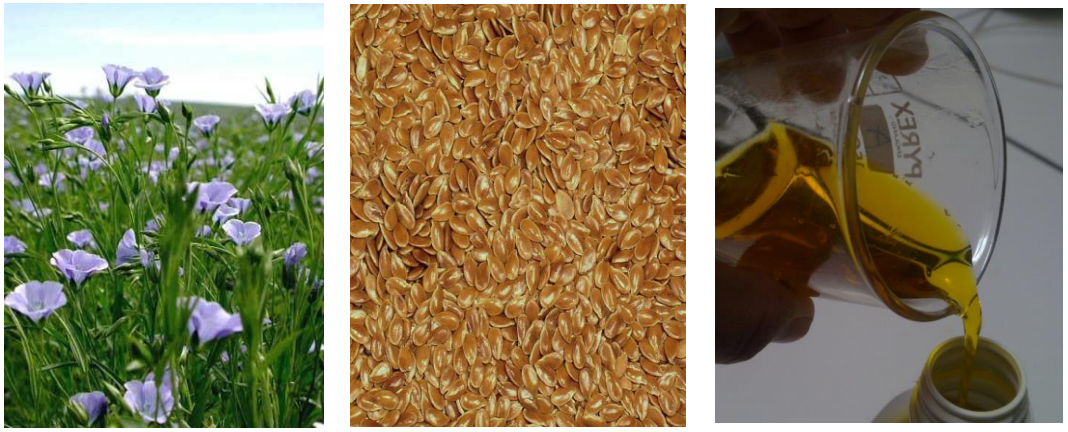


Figure 2. Lin field, grains and linseed oil

For the manufacture of the BioBinder BB, resin and oil are heated together at a 30^0C higher temperature than the ring and ball softening point of the resin. Resin softening point was determined to be 96.5^0C; therefore, the heating temperature selected was 126.5^0C. During the heating time, materials are blended through manual stirring for approximately 15 minutes to ensure complete homogenization. Figure 3 illustrates this process.

During the development of the thesis, this biobinder was used as an example of renewable material for the total replacement of virgin bituminous binders in RA mixtures. However, this material is expensive and its use in the field would not be currently viable. In this regard, the purpose of using this material is that the pine resin and linseed oil can be combined in different proportions to achieve specific desirable properties to be combined with RA and be used as a model biobinder.

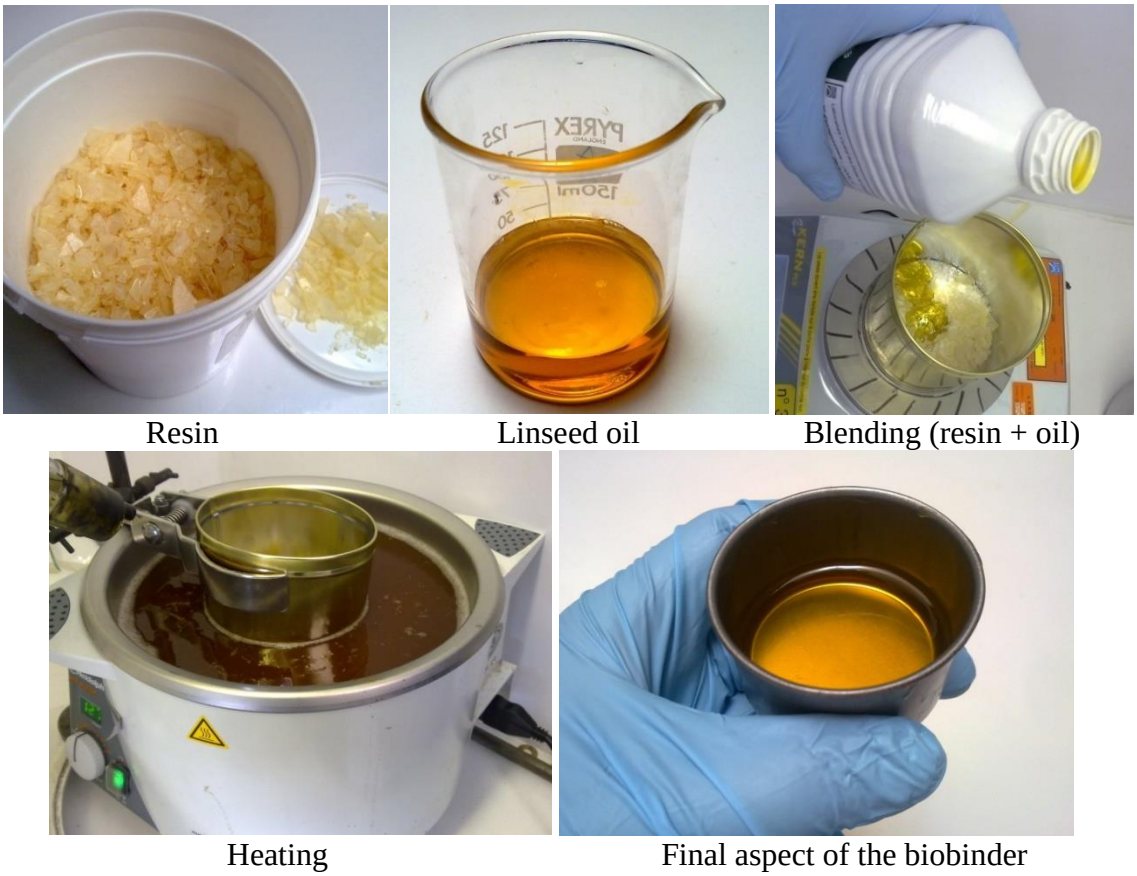


Figure 3. BioBinder (BB) manufacturing process

1.4.2.2. Biophalt® (BP)

Biophalt® is a patented material produced by EIFFAGE company and manufactured from the waste of paper industries containing rosin (pine resin) and SBS polymers (8% content) (Antonie Jean & Marcilloux 2008). The manufacturing process is similar to that of polymer modified bitumens (PMBs) so it can be produced and used in conventional asphalt plants. Biophalt® has a light colour which allows its pigmentation with different products. In the same way as BB, this binder would totally replace the virgin bituminous binder used in RA mixtures.

1.4.3. Reclaimed Asphalt (RA)

RA was received from a stockpile in France called “La Touraine”. Two fractions were used during the development of the thesis: 0/8 and 8/12.

The RA binder was recovered from each fraction following the standard procedure EN 12697-4: 2005 Fractionating Column by Distillation. The solvent used for this process was Dichloromethane (DCM). The characteristics of each RA fraction and binders are shown in Table 2. The RA fraction gradations are shown in Figure 4.

1.4.4. Virgin aggregates

Diorite-crushed virgin aggregates were selected from “La Noubleau” quarry in France in two fractions: 10/14 and 0/2. Limestone was used as mineral filler.

Table 2. Characteristics of RA fractions

Property	0/8	8/12
D (mm)	6.3	14
Binder content (%)	5.38	2.78
Penetration of extracted binder at 25^{0}C (dmm)	7	10
Softening point of extracted binder (^{0}C)	78.6	76.2
Max Bulk density (kg/m^3)	2513	2662

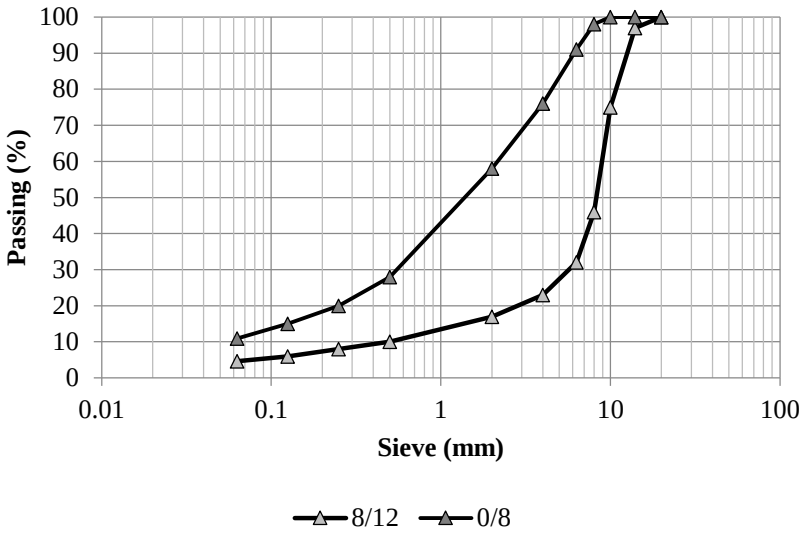


Figure 4. RA fractions gradation

1.4.5. Asphalt mixture type

The asphalt mixture type was chosen to be a High-Modulus mixture with optimum aggregate packing. This asphalt mixture type was developed by Olard & Pouget (2013) with the purpose of obtaining high modulus asphalt mixtures with high resistance to fatigue. The gradation of this type of asphalt mixture is developed using the French Gyratory Compactor with three fractions of aggregates (coarse, intermediate and fine) and Reclaimed Asphalt. The interaction between the fractions is analysed and the optimum content of each one is chosen based on wall and loosening effects of particles interaction (Furnas 1928). This particular process is beyond the scope of this thesis and is described in detail in Olard & Pouget (2013). The void content is 3-4%. This type of asphalt mixture was selected for this thesis in order to provide the asphalt mixture with RA and biobinders with a strong mineral skeleton which would positively contribute to achieve a suitable mechanical performance.

1.5. Methodology

The methodology of this thesis is divided into different steps/tasks related together as shown in Figure 5. As it can be seen in Figure 5, there are two different levels of materials' evaluation: binders/blends and asphalt mixtures. These two levels are connected through the development of the blend design of binders and asphalt mixture design. In this regard, the first step of the methodology is the characterisation of the binders. Next, this characterisation is used to perform the blend design of the RA binder and biobinders. The results of the blend design are used as inputs for the asphalt mixture design. Finally, blends of binders and asphalt mixtures are manufactured according to the asphalt mixture design, tested and related. The four steps are explained in detail in the following sections.

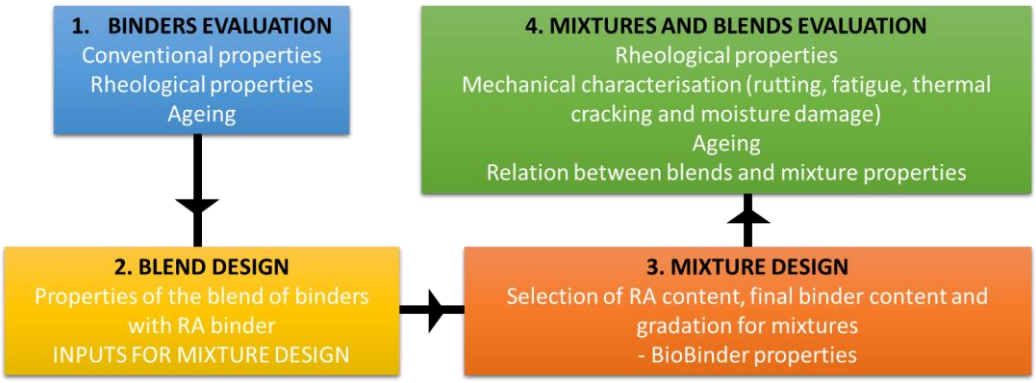


Figure 5. Summarised methodology

1.5.1. Binders evaluation

The first step of the methodology was focused on the characterisation of the binders. For this purpose, the conventional binders, biobinders and the recycled binder extracted from RA were conventionally and rheologically characterised in their neat and aged (RTFOT and PAV) state. To this end, the tests in Table 3 were performed. In this way, the conventional properties of the binders are obtained in their neat state as common

characterisation in Europe and rheology is characterised after short and long term ageing (RTFOT and PAV respectively). This allowed studying of how the binders' properties would evolve during their use in pavement engineering and obtaining their high, intermediate and low critical temperatures which will be related to the performance of the binders in the road as following:

- High critical temperature (T_c(High)). This temperature is related to the rutting resistance of the binder defining the maximum temperature at which it should not exhibit rutting issues. Therefore, the higher T_c(High) the higher resistance to plastic deformations.
- Intermediate critical temperature T_c(Int). This temperature is related to the fatigue resistance of the binder defining the minimum temperature at which it should not exhibit fatigue issues. Therefore, the lower T_c(Int) the higher resistance to fatigue.
- Low critical temperature T_c(Low). This temperature is related to the thermal cracking resistance of the binder defining the minimum temperature at which it should not exhibit thermal cracking issues. Therefore, the lower T_c(Low) the higher resistance to thermal cracking.

Each temperature is calculated using a specific parameter from the results of Dynamic Shear Rheometer and Bending Beam Rheometer tests and threshold defined in Superpave (Anderson et al. 1994) and described in Section 2.3.5.1 of the literature review.

Table 3. Testing matrix for binders

Test/Ageing level	Neat	RTFOT	RTFOT+PAV
Determination of the needle penetration at 25^{0}C (EN 1426 2015)	X		
Determination of softening point with the Ring & Ball method (EN 1427 2015)	X		
Determination of the rotational viscosity (EN 13302 2010)	X		
Determination of Fraass breaking point (EN 12593 2015)	X		
Determination of the shear complex modulus and phase angle in a Dynamic Shear Rheometer (DSR)	X	X	X
Determination of the stiffness and m-value in a Bending Beam Rheometer at different temperatures depending on the blend			X

1.5.2. Binders' blend design

This task deals with the study of the blend design of binders for asphalt mixtures with high RA content. Blend design can be defined as the theoretical evaluation of different properties of the blend of binders by means of blending laws. In this thesis, the blend design is undertaken to evaluate the conventional and performance-related properties of the blend of biobinders and the RA binder in different scenarios to finally obtain some inputs for the asphalt mixture design.

Most countries have developed their own blending laws for the use of RA binder and fresh binders in RA mixtures. For example, European countries use conventional properties to design blends (EN 13108-1 2016), while USA use performance-related properties (NCHRP 2001) and viscosity is used in Australia (Austroads 2013). These

blending models/laws were put together in Jiménez del Barco Carrión et al. (2015) and are as follows:

$$\log pen_{mix} = x \cdot \log pen_1 + (1 - x) \cdot \log pen_2 \quad (1)$$

where
pen_1 = penetration of the binder recovered from the RA (dmm)
pen_2 = penetration of the added fresh binder (dmm)
pen_{mix} = calculated penetration value of the binder in the mixture containing RA (dmm)
x = amount of RA binder in decimals

$$T_{R\&B\ mix} = x \cdot T_{R\&B\ 1} + (1 - x) \cdot T_{R\&B\ 2} \quad (2)$$

where
$T_{R\&B\ 1}$= softening point of the binder recovered from the RA (ºC)
$T_{R\&B\ 2}$= softening point of the added fresh binder (ºC)
$T_{R\&B\ mix}$= softening point of the binder in the mixture containing RA (ºC)
x = amount of RA binder in decimals

$$log\mu_{mix} = x \cdot \log \mu_1 + (1 - x) \cdot \log \mu_2 \quad (3)$$

where
μ_1 = rotational viscosity at 135ºC of the binder recovered from the RA (mPa.s)
μ_2 = rotational viscosity at 135ºC of the added fresh binder (mPa.s)
μ_{mix} = calculated rotational viscosity at 135ºC of the binder in the mixture containing RA (mPa.s)
x = amount of RA binder in decimals

$$T_{Fraass,mix} = x \cdot T_{Fraass,1} + (1 - x) \cdot T_{Fraass,2} \quad (4)$$

where
$T_{Fraass,1}$= Fraass breaking point of the binder recovered from the RA (ºC)
$T_{Fraass,2}$= Fraass breaking point of the added fresh binder (ºC)
$T_{Fraass,mix}$= Fraass breaking point of the binder in the mixture containing RA (ºC)
x = amount of RA binder in decimals

$$T_{critical,mix} = x \cdot T_{critical,1} + (1 - x) \cdot T_{critical,2} \quad (5)$$

where

$T_{critical,1}$= high, intermediate or low critical temperature of the binder recovered from the RA (°C)
$T_{critical,2}$= high, intermediate or low critical temperature of the added fresh binder (°C)
$T_{critical,mix}$= high, intermediate or low critical temperature of the binder in the mixture containing RA (°C)
x = amount of RA binder in decimals

The linear and logarithmic blending laws presented in Equations (1) to (5) according to EN 13108-1 (2016) and NCHRP (2001) for conventional materials were used in the binder blend design to obtain inputs for the asphalt mixture design and then validated to corroborate that their use was adequate in this thesis for biobinders.

Considering Equations (1) to (5), the properties of the RA binder and the fresh binder were needed to perform the blend design and were obtained from the binders' evaluation (first step of the thesis methodology). Then, Equations (1) to (5) were in preliminary assessment of the properties that the blend would have in the RA mixture under different conditions of RA content, final binder content and Degree Of Blending (DOB). DOB is the amount of RA binder that would be active in the asphalt mixture and blending with the fresh binder added. This concept is further explain in Section 2.5. In these equations, "x" is the amount of fresh binder that will be replaced by RA binder. This amount is called "Replaced Virgin Binder" (RVB) and it is not the same as the amount of RA in mass which is to be added in the mixture. Instead, the RVB depends on:

1. Binder content in the RA, which can be determined in the laboratory.
2. Total percentage of RA to add in the mixture, which is selected by the mix designer.
3. Final binder content of the mixture, which is selected by the mix designer.

4. DOB, which is the percentage of RA binder that will actually blend with the fresh binder and may not be 100%.

In this sense, the RVB (%) is obtained following Equation (6) (Lo Presti et al. 2016):

$$RVB\ (\%) = 100 \cdot \frac{RA\ content\ in\ the\ mixture \cdot DOB \cdot RA\ binder\ content}{binder\ content\ in\ the\ mixture} \quad (6)$$

where, RA content in the mixture is the total RA percentage to add in the asphalt mixture by mass, DOB is the assumed degree of blending between RA and virgin binders, RA binder content is the binder content in the RA and binder content in the mixture is the designed final binder content in the mixture, with all the parameters being expressed in decimals.

The inclusion of the DOB in the calculation of RVB is an approach recently developed by Jiménez del Barco Carrión et al. (2015) and Lo Presti et al. (2016) which takes into account what would happen if full blending (100% DOB) does not occur between the fresh binder and the RA binder in the asphalt mixture. The different variables in Equation (6) were selected so different RVBs were obtained and introduced in Equations (1) to (5).

Thereby, having the properties of the fresh binder and RA binder and the RVB(%), the blend design could be carried out. As a result of this procedure, blending charts and laws are obtained as a function of the RVB(%) for the properties studied. Figure 6 shows an example of a blending chart and law. Having this, it is possible to assess the properties that the binder would have in the new asphalt mixture under different conditions such as RA content and final binder content and therefore, make decisions for the asphalt mixture

design on this basis (i.e. select these parameters). Finally, the blend design was validated by testing the actual blends in the laboratory.

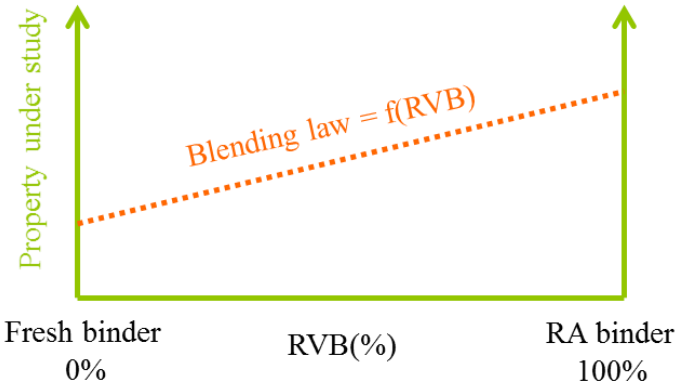


Figure 6. Example of blending chart and law

1.5.3. Asphalt mixture design

Following the asphalt mixture type described in Section 1.4.5., the asphalt mixture design step consisted of firstly: selection of the RA percentage and total binder content to have in the asphalt mixtures to meet the properties of the target binder (50/70 penetration grade). Secondly, the definition of the gradation. RA percentage and total binder content were chosen based on the results of the blend design. The gradation was fixed following the procedure in Olard & Pouget (2013), in EIFFAGE. The asphalt mixture design was then fixed for the three binders (two biobinders and reference) in order to highlight the influence of the binder in the asphalt mixture performance through keeping the other variables constant.

It has to be noticed that the properties of BB are adaptable by changing the proportions of resin and oil in the binder. Therefore, in order to keep the asphalt mixture design fixed to allow better comparison for asphalt mixtures and blends performance, RA content and

binder content were selected based on BP properties, and then BB resin/oil proportions were adjusted to meet the same target binder when blended with the RA.

Moreover, in order to maximise the use of RA and to study its influence, a second RA percentage (higher than the first one) was selected from the blend design to produce the same type of asphalt mixtures. For this, the binder content and the gradation had to be the same as that of the first RA percentage, in order to highlight the influence of RA as content. This methodology would thereby produce six different asphalt mixtures as summarised in Table 4.

Table 4. Mixtures matrix

Mix	Binder	RA (%)	Binder content (%)
X% RA PMB	PMB	X	a
X% RA BB	BB	X	a
X% RA BP	BP	X	a
Y% RA PMB	PMB	Y	a
Y% RA BB	BB	Y	a
Y% RA BP	BP	Y	a

1.5.4. Asphalt mixtures and blends evaluation

1.5.4.1. Manufacturing

Binders' blends and asphalt mixtures of RA with biobinders and the reference PMB were manufactured in the laboratory according to the asphalt mixture design fixed in the previous step. Blends were manufactured for the first RA percentage using the full blending assumption.

For the production of the blends of RA and bio or reference binder, the RA binder was heated to 160°C (due to its hardness) and the other binders were heated to 140°C. Once

the proportions of each material were weighed and put together in a tin, they were introduced into an oven at 150°C for half an hour. After that, all blends were stirred in a temperature-controlled environment using heating plates at 200 rpm for 15 minutes.

The asphalt mixtures were manufactured at NTEC and Ifsttar (Nantes, France) following the same conditions for heating temperatures and mixing times (Table 5). However, two different methods were used for compaction. At NTEC, asphalt mixtures were compacted using the gyratory and roller compactor (depending on the specimen geometry needed for the testing) to achieve the target density. At Ifsttar, the asphalt mixtures were compacted with a pneumatic compactor to produce slabs following a specific sequence of wheel passes and efforts required for high-modulus asphalt mixtures (see Figure 7).

Table 5. Temperatures, times and sequence for mixtures manufacture

Material	Heating Temperature (ºC)	Time in the oven (h)	Mixing sequence
RA	130	4	1. Introduce RA in the mixer and mix for 15 seconds 2. Add virgin aggregates and mix for 15 seconds 3. Add binder and mix for 60 seconds TOTAL TIME: 90s
Fresh binder	150	3	
Virgin aggregates	165	8	



a) All components in the mixer | b) Mix after manufacture | c) Mix before compaction | d) Compaction | e) Mix after compation

Figure 7. Asphalt mixtures manufacturing and compaction in Ifsttar

1.5.4.2. Testing

Blends

The blends of RA binder and bio or reference binders were tested for three main purposes:

1. To obtain their conventional properties and critical temperatures to validate the blend design
2. To understand their rheology and ageing
3. To obtain their performance-related properties

For this, the blends were manufactured and subjected to two levels of ageing: short-term (RTFOT) and long-term (RTFOT+PAV). In this regard, blends were tested at different levels of ageing depending on the property studied as shown in Table 6.

Regarding Table 6, the determination of the shear complex modulus and phase angle was performed at the three ageing levels in order to understand how the rheology of the materials changes with ageing. MSCR test results are related to the rutting resistance of the binder, therefore, these tests should be performed after short-term ageing (i.e. when

the asphalt mixtures have been manufactured). On the other hand, time sweep and BBR results are related to the fatigue and thermal cracking resistance of binders respectively. Therefore, these tests are carried out on long-term aged samples (i.e. simulating the ageing during some years of service life of the pavement). Finally, BBS tests were undertaken on neat samples to understand cohesion and adhesion properties of the binders and how these are affected by moisture damage.

Table 6. Testing matrix for blends

Test/Ageing level	Neat	RTFOT	RTFOT+PAV
Determination of the shear complex modulus and phase angle in a DSR	X	X	X
Multiple Stress Creep Recovery test (MSCR) at 40^0C and 60^0C		X	
Time sweep at 20°C and 10 Hz			X
Determination of the stiffness and m-value in a Bending Beam Rheometer at different temperatures depending on the blend			X
Binder Bond Strength (BBS) in dry and wet condition	X		

Mixtures

The asphalt mixtures were tested for two main purposes:

1) To understand their rheology
2) To obtain their mechanical properties and ageing performance

Therefore, the six asphalt mixtures were subjected to the following testing:

→ Determination of the complex modulus and phase angle in two-point bending mode from -10 to 40°C and from 1 to 40 Hz (EN 12697-26 2012 - Annex A).

→ Indirect Tensile Stiffness Modulus (ITSM) at 20°C (EN 12697-26 2012 - Annex C).

→ Indirect Tensile Strength (ITS) at 25°C (EN 12697-23 2003)

→ Water Sensitivity (EN 12697-12 2008).

→ Repeated Loading Axial Tests (RLAT) at 40°C for rutting resistance (BS DD 226 1996).

→ Indirect Tensile Fatigue Test (ITFT) at 20°C for fatigue resistance (BS DD ABF 2003)

In addition, the asphalt mixtures with the first RA percentage were tested using the Thermal Stress Restrained Specimen Test (TSRST) and were subjected to an ageing process to complete their characterisation.

CHAPTER 2. LITERATURE REVIEW

2. LITERATURE REVIEW

2.1. Introduction

Roads are the main means of transport all over the world. The main types of road pavement are rigid (concrete) and flexible pavements. Flexible pavements are made of asphalt mixtures and they represent around the 90% of pavements. Asphalt pavements provide numerous advantages in terms of sustainability, comfort and safety (AsphaltAdvantages 2017).

In terms of sustainability, the Asphalt Pavement Alliance (APA) states that "asphalt is the pavement of choice for sustainability". Asphalt pavements are 100% recyclable and able to reuse waste materials and industrial byproducts saving landfill space. In addition, their production emits less greenhouse gases than concrete pavements (APA 2017).

Asphalt pavements provide the road with a smoother and less noisy surface than other paving technologies. Flexible pavements are continuous materials which do not need joints like concrete pavements avoiding disturbances to users while driving. In addition, in terms of safety, asphalt pavements are the best option for hostile weather conditions. Their smooth surface, in addition to the comfort, provide the user with an easier and more relaxed drive for safety (APA 2017).

These advantages are only some of many which make asphalt pavements the first choice for roads. Asphalt pavements are made of asphalt mixtures which are compound materials made of aggregates and binder. Aggregates are mineral particles which provide the asphalt mixture with resistance to compression due to friction between them. Binders are

usually thermoplastic and viscoelastic materials that keep the aggregates bounded and provide tensile resistance and cohesion to the asphalt mixture (Thom 2008; Moreno-Navarro 2013).

The main binder used in asphalt mixtures is bitumen. The World Road Association defines bitumen as "a very viscous or nearly solid, virtually involatile, adhesive and waterproofing organic material derived from crude petroleum or present in natural asphalt, which is completely or nearly completely soluble in toluene" (PIARC 2017). The two main sources of natural bitumen are rock asphalt, defined as "mineral matter impregnated with bitumen by a natural process", and lake asphalt, defined as "a highly viscous natural asphalt found in well-defined surface deposits" (PIARC 2017). However, currently natural bitumen is barely used in pavement engineering and most bitumen comes from crude oil refining. In 2015, approximately 300Mt of bitumen were used in Europe for the production of asphalt mixtures (EAPA 2015). Nevertheless, crude oil is a finite resource whose production is predicted to decrease in the future. In fact, this has already produced changes in some refineries strategies which are installing cokers towards the production of lighter products and consequently the bitumen supply could decrease (Lavoie 2011). In view of this, two main actions are being undertaken in pavement engineering:

- The use of recycled asphalt pavements to take advantage of the bitumen already present in it (over the last decades)
- The use of alternative binders from renewable resources to replace bitumen as binder in new asphalt mixtures (more recently developed)

In this thesis, both recycling and alternative binders (biobinders) are studied. Therefore, this literature review covers the main features of asphalt mixtures and binders and then move to current tendencies on the use of recycled materials and biobinders.

2.2.Asphalt mixtures for pavements

Road pavements are structures composed of different horizontal layers which have been compacted and are made of different materials (Figure 8). These layers are supported by the subgrade and should be able to resist traffic loads and climate changes during several years without suffering any damage that could affect users comfort and safety or the pavement integrity.

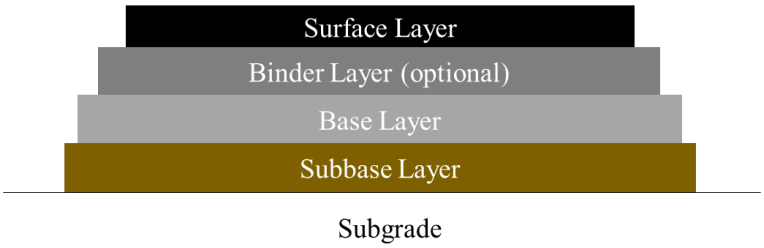


Figure 8. Road pavement section

Most pavements over the world are flexible pavements made of asphalt mixtures and unbound materials. Four main layers can be differentiated in flexible pavements (Kraemer 2009):

- Surface layer: usually thin layer (4-6cm) made of asphalt mixture which should mainly provide skid resistance and drainage and permeability to the pavement section.

- Binder and base layers: they are located under the surface layer and their function is mainly to provide resistance to the pavement supporting most of the vertical stresses from repetitive traffic loads. The division into binder and base layer is optional depending on the traffic the pavement is meant to support.
- Subbase layer: it is situated under the base layer and above the subgrade. Its function is to provide the base layer with a uniform support and constitute a suitable platform during the construction and compaction. This layer is made of unbound materials.

Asphalt mixtures are comprised of four components: aggregates, binder, filler and air voids. Aggregates are mineral particles which provide the asphalt mixture with resistance to compression due to friction between them. Binders are usually viscoelastic materials that keep the aggregates bound together with the filler providing tensile resistance and cohesion to the asphalt mixture. Filler are the finest granular particles (<0.063mm). The fourth component of asphalt mixtures is air, which fills the voids that remain between the aggregate skeleton and are not filled with the binder (Thom 2008; Moreno-Navarro 2013).

Different countries use different parameters and procedures for the design of asphalt mixtures. However, in general, the three main features affecting the design and performance of an asphalt mixture are:

- Aggregates properties and gradation
- Binder properties and content
- Air voids content

Varying these features, different asphalt mixture types can be distinguished. This distinction also depends on countries. For instance, in France, asphalt mixtures are divided into BB (“Bétons Bitumineux”), for mixtures with binder content between 5% and 7% usually for surface layers, GB (“Graves Bitumes"), for mixtures with binder content between 3% and 4% usually for base and binder layers, and EME (“Enrobés à Module Élevé”), for high modulus mixtures (Delorme et al. 2007). On the other hand, in the United Kingdom there exist 8 types of mixtures: asphalt concrete, asphalt concrete for very thin layers, soft asphalt, hot rolled asphalt, stone mastic asphalt, mastic asphalt, porous asphalt and mixtures containing reclaimed asphalt. These mixtures are different in aggregate gradation curve, binder content and functionality (EN 13108 - Part 1 to 8).

2.2.1. Loads affecting asphalt pavements

The main distresses affecting asphalt mixtures are conditioned by the loads they are exposed to during their service life due to traffic and climate conditions. Regarding traffic, vehicles passing induce the bending of layers in the pavement creating horizontal tensile stresses and strain in the bottom of each bound layer and vertical compressive stresses and strain in the bulk section (Figure 9). Due to the properties of asphalt mixtures and binders, this repetitive loading can produce fatigue cracking at the bottom of the bound layer and rutting (permanent deformation) of the vertical section. The stiffness of the material of each layer is needed in order to calculate the stress and strain they are suffering under the loading (Mangiafico 2014).

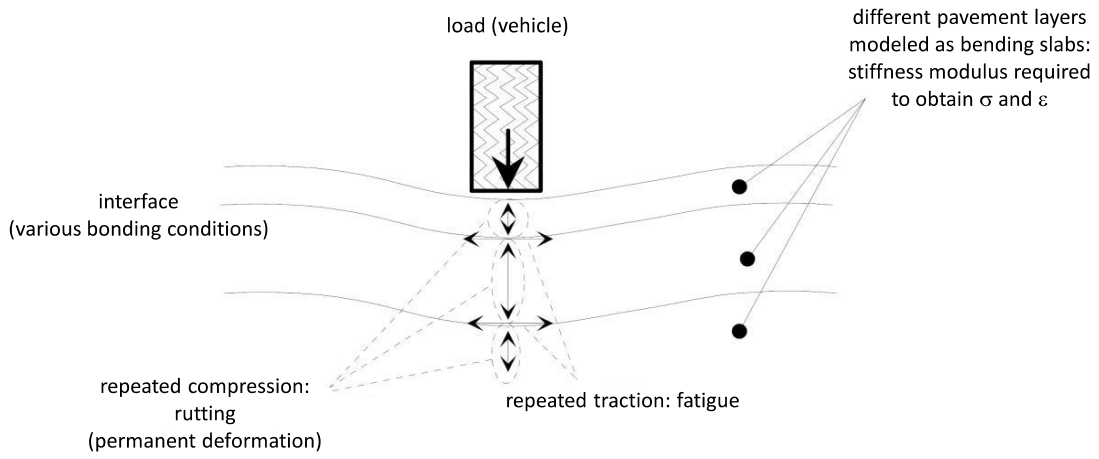


Figure 9. Traffic load and pavement response (Mangiafico 2014)

In terms of climatic conditions, depending on the area they are placed in, pavements can be exposed to extreme temperatures, temperature changes, rain and freeze-thaw cycles. The behaviour of asphalt mixtures and binders is temperature dependant. Asphalt mixtures and binders are stiffer and more elastic at low temperatures, while they become softer and more viscous at higher temperatures. Consequently, temperature will always influence the performance of the pavement and the likely appearance of different distresses. In addition, asphalt mixtures exhibit thermal expansion and contraction when they are subjected to temperature changes, particularly at low temperatures. In pavements, because of the layered structure, the thermal contraction is restrained by the friction with the layers in contact and stress is build up in the mixture. This phenomenon is called thermal cracking. Moreover, repeated thermal expansion and contraction can generate repeated strains resulting in thermal fatigue. Finally, rain has two effects. On one hand, the presence of water due to the lack of drainage can induce moisture damage in the asphalt mixtures causing the loss of adhesion between aggregates and binder or loss of

cohesion in the mixtures. On the other hand, if water is present, temperature changes can lead to freeze-thaw cycles which can deteriorate the materials (Mangiafico 2014).

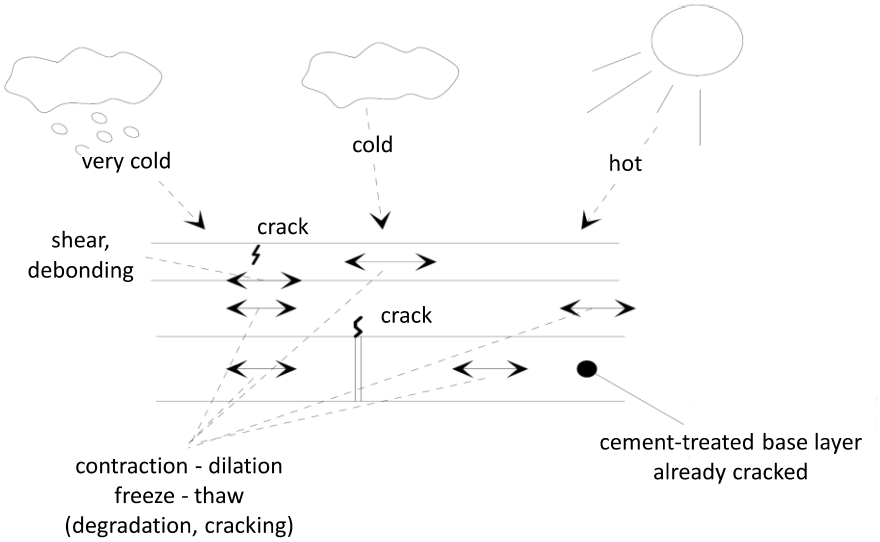


Figure 10. Climate condition loads and pavement response (Mangiafico 2014)

Finally, the exposure to climate conditions of asphalt mixtures also ages the binder present on them as explained in Section 2.3.3. This ageing influences the performance of the pavement and may lead to its premature failure.

Thereby, in summary, the main distresses affecting asphalt mixtures are fatigue, rutting, thermal cracking, moisture damage and ageing.

2.3.Binders for asphalt mixtures

2.3.1. Bituminous binders

The most common binder used for asphalt mixtures is bitumen. In 1990, BS 3690: Part 3 defined this material as follows:

"A viscous liquid, or a solid, consisting essentially of hydrocarbons and their derivatives, which is soluble in carbon disulphide and is substantially non-volatile and softens gradually when heated. It is black or brown in colour and possesses waterproofing and adhesive properties. It is obtained by refinery processes from petroleum, and is also found as a natural deposit or as a component of naturally occurring asphalt, in which it is associated with mineral matter".

In this definition, the main features of bitumen behaviour are established: chemical composition ("hydrocarbons and derivatives"), viscoelasticity and temperature dependency ("viscous liquid or solid").

Bitumen is mainly a hydrocarbon material composed by hydrogen (82-88%) and carbon (8-11%), but also contains other components in lower concentrations such as sulphur (0-6%), oxygen (0-1.5%) and nitrogen (0-1%) (Whiteoak & Read 2003).

Although the elemental composition of bitumen is important, it does not provide enough information about its molecular structure in order to further understand the way it may affect the physical and engineering properties and its chemical reactivity (Whiteoak & Read 2003).

Bitumen is a viscoelastic material which exhibits elastic properties at intermediate/low temperatures (<40°C) typical of heavy molecules (high molecular weight) and viscous properties at higher temperatures. However, if the molecular weight of the particles is determined, relatively low values are obtained. It is therefore generally assumed that smaller molecules create strong associations and perform as high molecular weight

compounds. The main molecules present in bitumen are aromatic, naphthenics and aliphatics. In addition, some researchers hypothesized that the similar behaviour to high molecular weight compounds is due to polar and π-π bonds, which are weaker than covalent bonds, making bitumen therefore sensitive to temperature and shear forces (Petersen et al. 1994; Airey 1997).

The exact chemical structure of a bitumen is highly dependent on its source of origin and manufacturing process. It is usually determined by fractional composition techniques which divide bitumen's molecules into groups based on their size, polarity and solubility. The most common technique is known as SARA analysis, whose name comes from the different fractions it provides: Saturates, Aromatics, Resins and Asphaltenes (Figure 11). SARA analysis separates the asphaltenes from the other fractions by n-heptane precipitation, and saturates, aromatics and resins are obtained by silica gel or alumina chromatography. Saturates, aromatics and resins are known as a group as maltenes. The main features of each group are as follows (Whiteoak & Read 2003):

- Asphaltenes: insoluble in n-heptane black or brown amorphous solids. They have high molecular weight ranging from 1000g/mol to 100000g/mol with a particle size of 5nm to 30nm. They generally constitute 5% to 25% of the bitumen mass. Asphaltene content play an important role in bitumen properties since higher asphaltene content produces a harder bitumen (lower penetration). Conventional bitumen increases its asphaltene content with ageing, increasing its molecular weight (Lesueur 2009).

- Resins: soluble in n-heptane dark brown solid or semi-solid particles. They are very adhesive and dispersing or peptisers agents for asphaltenes. Their molecular weight ranges from 500g/mol to 50000g/mol with a particle size of 1nm to 5nm. They are generally 13% to 25% of the bitumen mass.
- Aromatics: lowest molecular weight naphtenic aromatic compounds in bitumen ranging from 300g/mol to 2000g/mol. They represent the major proportion of the dispersion medium for the asphaltenes. They are generally 40% to 65% of the bitumen mass.
- Saturates: straight and branched-chain aliphatic compounds with alkyl-naphthenes and some alkyl-aromatics. They are white with similar molecular weight to aromatics. They are generally 5% to 20% of bitumen mass.

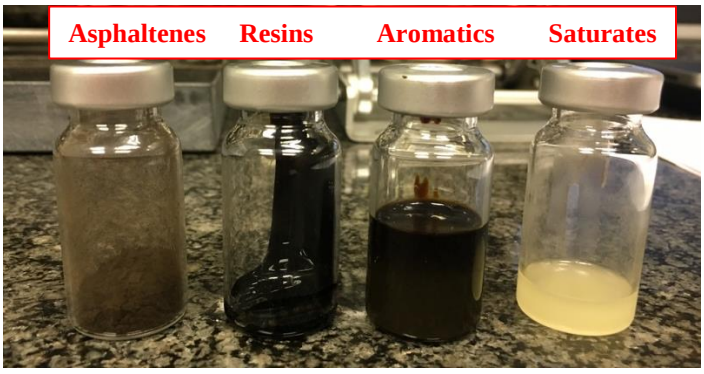


Figure 11. Bitumen SARA fractions

Bitumen is responsible for the visco-elastic character of asphalt mixtures (Olard & Di Benedetto 2003; Di Benedetto et al. 2004), and therefore its linear-viscoelastic (LVE) properties are critical for the LVE properties of the whole. Consequently, bitumen has a strong influence on the mechanical properties of asphalt mixtures (Moreno-Navarro et al. 2015). The relationship between the properties of binders and asphalt mixtures is one of

the main topics of research in pavement engineering. The reason for this is that testing binders is less time and material consuming than testing asphalt mixtures. Therefore, predicting the performance of asphalt mixtures from binder testing or at least using the binder results as criteria for selecting binders for asphalt mixtures represents a great advantage in terms of time and material savings.

In this regard, in general, hard binders can resist deformation and therefore help for rutting resistance but may be more sensitive to fatigue due to their high stiffness. On the other hand, soft binders are flexible to cope with fatigue distresses but prone to exhibit early rutting problems. Binders' elastic component helps rutting and fatigue resistance in asphalt mixtures, while the viscous response is related to the resistance to thermal cracking because of the relaxation properties (Gogula et al. 2003; Moreno-Navarro et al. 2015; Hafeez et al. 2012). Moisture damage is mainly affected by binders/aggregate adhesion properties, which depends on their affinity (Bahia et al. 2012; Moraes et al. 2011; Zhang et al. 2015).

Binder content is also an essential parameter in asphalt mixtures design. There are different methods to determine the optimum binder content of asphalt mixtures relying on volumetric properties, such as Marshall, or performance-related properties, such as the French methodology. In Marshall methodology, the optimum binder content is found as a compromise between air voids and Marshall stability. Voids versus binder content curves find a minimum value while the stability finds a maximum. It is recommended to select the binder content within the decreasing part of the voids curve and close to the maximum stability.

Regarding mechanical and viscoelastic properties, the most common observation is that higher bitumen contents lead to improved fatigue resistance. Regarding complex modulus, only the asymptotic values at very high temperature and very low frequency (static modulus) and very low temperature and very high frequency (glassy modulus) of asphalt mixtures do not seem to be strongly influenced by bitumen content, since they depend mainly on the granular matrix (Mangiafico 2014). Rutting resistance can be adversely affected if binder content is too high and prevents the existence of air voids (Lira et al. 2013).

2.3.2. Bituminous binders' modification

In order to improve some of the properties that conventional bitumens confer to asphalt mixtures, bitumen modification has been undertaken for decades. Desirable characteristics of modified binders include greater elastic recovery, a higher softening point, greater viscosity, greater cohesive strength and greater ductility (Yildirim 2007).

Nowadays, the most common bitumen modification is the addition of polymers. The use of these materials in asphalt mixtures was patented in 1843 and over the last decades it has become a very common practice all over the world due to the improvements they confer to bitumen for pavement engineering. Polymers modify bitumen properties and rheology so that pavements with polymer modification exhibit greater resistance to rutting and thermal cracking, and decreased fatigue damage, stripping, plastic deformations and temperature susceptibility (Yildirim 2007; Kök & Çolak 2011).

Polymers are added to neat bitumen as small particles and blended in different manners. The degree of modification that polymers provide to bitumen always depends on the

nature of the base bitumen, nature of polymer, compatibility of both materials and concentration of modifier. Some of the most used polymers are styrene-butadiene-rubber (SBR), styrene-butadiene-styrene (SBS), crumb rubber, polyethylene, ethylene-vinyl-acetate (EVA) and ethylene-glycidyl-acrylate (EGA).

Styrene-butadiene-styrene (SBS) is currently the most common modifier of bitumen and consist of a block copolymer that increases the elasticity of bitumen (Airey 2003; Yildirim 2007). SBS polymers produce a highly elastic network in the binder which increases viscosity, complex modulus and elastic response, especially at high temperatures (Airey 2003a). In this sense, SBS modification improves rutting, thermal and cracking resistance of asphalt mixtures (Kalantar et al. 2012; Singh et al. 2013; Alataş & Yilmaz 2013).

The rheological study of binders becomes more complicated when they are modified. The presence of modifiers in chains of small particles in binders can make them highly stress dependent at high temperature (Wasage et al. 2011) and, depending on the concentration of modifier, they could become thermo-rheologically complex (Yusoff et al. 2011). Black diagrams are useful tools to identify bitumen modification by means of rheology. Figure 12 shows typical Black curves for SBS-modified bitumens versus non-modified bitumen.

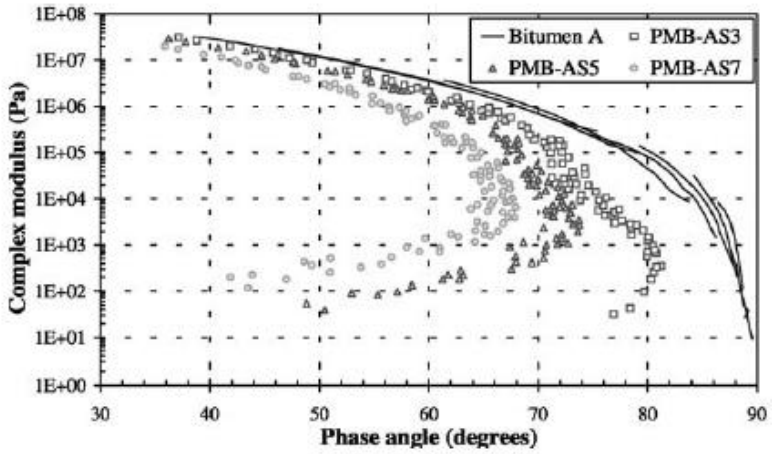


Figure 12. Black Diagram of conventional and SBS-modified bitumens (Airey, 2003)

2.3.3. Bituminous binders' ageing

Bitumen ageing is one of the major factors producing pavement deterioration and shortening service life of roads. This phenomenon affects binder behaviour having great consequences on main pavement distresses such as fatigue and rutting (Lu & Isacsson 2002; Ali et al. 2013).

Bitumen ageing takes place during the manufacture, laying and service life of the asphalt pavement due to its exposure to climate conditions. In this sense, when bitumen is laid in form of an asphalt mixture in the road, it has been already aged and its properties will have changed in comparison to the original ones.

The main mechanisms related to ageing are oxidation, evaporation, exudation and physical hardening (Karlsson & Isacsson 2006). Among those, oxidation is considered the main cause of bitumen ageing. Generally, conventional bitumens become stiffer and more elastic after ageing. These effects are due to the chemical composition and structure of bitumens. During ageing, asphaltene content increases, producing changes in bitumen

properties and rheology and obtaining a harder binder (Lesueur 2009). Figure 13 shows an example of these changes in bitumen rheology after ageing. As it can be observed, complex modulus increases and phases angle decreases when the sample is aged. However, the influence of ageing on physical and performance-related properties of binders depends on their nature and composition, and therefore, it has to be carefully studied (Lu & Isacsson 2000; Lu & Isacsson 2002).

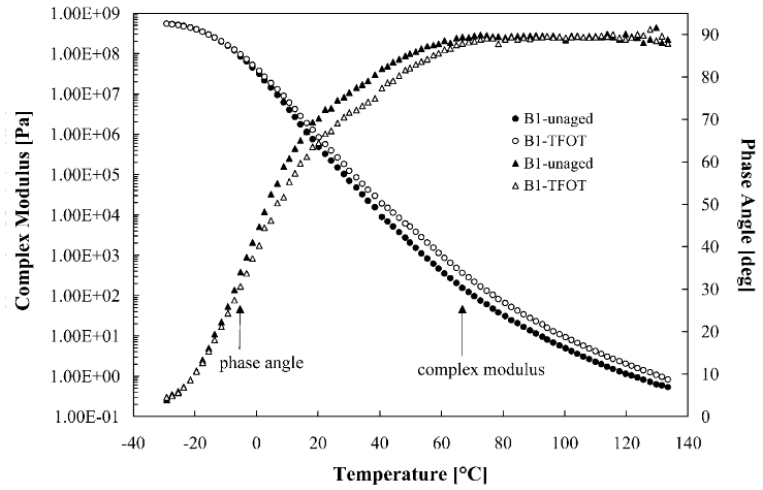


Figure 13. Effect of ageing on bitumen rheology (Lu & Isacsson 2000)

Rheological characterization of aged polymer modified bitumens (PMB) has been undertaken by different authors. Airey (2003), through the study of Black diagrams, master curves and isochronal plots, found that ageing had a different effect on PMBs than on conventional bitumen at high temperatures, since they became more viscous instead of more elastic. This fact was attributed to polymer deterioration. Figure 14 shows how changes due to ageing may be visible in Black Diagrams. In accordance to this, Ruan et al. (2003) concluded that ageing dramatically decreases the benefit of polymers to ductility in comparison with conventional bitumens due to the stiffening of the base

bitumen and deterioration of polymers. In the same way, Wu et al. (2009) reported that aged PMB behaviour tended to be closer to aged conventional bitumen behaviour due to the damage in the polymer network.

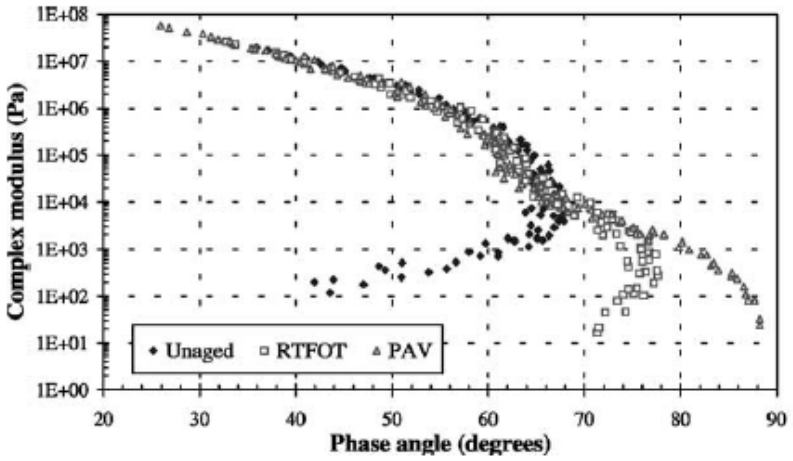


Figure 14. Black diagram of unaged, RTFOT and PAV aged SBS-modified bitumen (Airey, 2003)

In order to study bitumen ageing, two types of ageing can be distinguished: short-term ageing, which simulate changes in the bitumen after the manufacture of the asphalt mixture, and long-term ageing, which simulates ageing after several years of service life of the road. The procedures to characterise the ageing of bitumen are explained in Section 2.4.6 of this literature review.

2.3.4. Conventional properties

For the purpose of characterising bitumen behaviour from an engineering point of view, diverse properties are measured at different temperature ranges and loading times. Conventional properties are referred to bitumen physical features. The most common ones are described below.

Fraass breaking point

It is used at the brittleness range of temperature and is defined as the temperature (^{0}C) at which a film of binder breaks under a specific load. The test carried out to measure this low temperature fracture is known as the Fraass breaking point (EN 12593 2015).

Penetration

Penetration is a measure of bitumen stiffness. The test carried out to obtain this value consists of the vertical application of a standard load with a needle over a tin of bitumen at a specific loading time and temperature. The result of the test is the length (decimillimetres, dmm or 0.1mm) of the needle which has been introduced into the bitumen. In this sense, it is assumed that the higher the penetration the stiffer the bitumen. As a standard, penetration is measured at temperatures in which the binder is semi-solid, usually 25^{0}C (EN 1426 2015), but it can be obtained at different temperatures.

Softening point

Softening point (SP) can be defined as the temperature (^{0}C) at which binders change their consistency and begin to be more fluid-like. It is usually obtained using the Ring & Ball method (EN 1427 2015). In this test, bitumen is poured and trimmed in a ring and conditioned at 5^{0}C. Next, the ring is located in a frame inside a glass beaker with water or glycerine (depending on the expected softening point: water for SP<80^{0}C and glycerine for SP>80^{0}C) with a ball placed in the centre of the ring touching the binder. Temperature is increased under control at a certain rate. The temperature at which the ball drops and touches a sensor is considered as the softening point of the material.

2.3.5. Binder Specifications

In Europe, binder specifications are based on the different properties explained in the previous section. Bitumens are usually denominated by their penetration value (i.e. pen 50/70, pen 100/160, etc.) expressed in decimillimeters which is known as penetration grading (EN 12591 2009).

However, those binder specifications have some limitations in order to classify binders for its use in asphalt mixtures. Therefore, in the Superior Performing Asphalt Pavement research (Superpave), undertook by the Strategic Highway Research Program (SHRP) in the United States of America (USA), great efforts were carried out in order to develop a new binder specification (including modified binders) which took into account performance-related bitumen properties. This means that this specification classifies binders regarding their field performance for some of the main distresses in pavement such as rutting, fatigue and thermal cracking. Binders are denominated by the initials PG (Performance Grade) followed by two temperatures, one positive and one negative, which define the range of temperature for which the binder should adequately perform (i.e. a binder PG64-12 would satisfactorily behave between 64ºC and -12ºC). These temperatures are obtained based on the binder critical temperatures.

2.3.5.1. Critical temperatures

Superpave (Anderson et al. 1994) defines three critical temperatures for binders: high, intermediate and low. Each critical temperature is related to the binder performance in field as following:

- High critical temperature (T_c(High)). This temperature is related to the rutting resistance of the binder defining the maximum temperature at which it should not exhibit rutting issues. Therefore, the higher T_c(High) the higher resistance to plastic deformations.
- Intermediate critical temperature T_c(Int). This temperature is related to the fatigue resistance of the binder defining the minimum temperature at which it should not exhibit fatigue issues. Therefore, the lower T_c(Int) the higher resistance to fatigue.
- Low critical temperature T_c(Low). This temperature is related to the thermal cracking resistance of the binder defining the minimum temperature at which it should not exhibit thermal cracking issues. Therefore, the lower T_c(Low) the higher resistance to thermal cracking.

In order to obtain these temperatures, Superpave requires to test neat and aged samples in a Dynamic Shear Rheometer and in a Bending Beam Rheometer (see Section 2.4.1.2 and 2.4.4) to obtain the complex modulus (G*), phase angle (δ), stiffness (S) and m-value. Next, the following threshold for aged and unaged binders are used:

High critical temperature:	$\|G^*\|/\sin\delta$ (neat) = 1 kPa
	$\|G^*\|/\sin\delta$ (RTFOT-aged)) = 2.2 kPa
Intermediate critical temperature:	$\|G^*\|\cos\delta$ (PAV-aged) = 5000 kPa
Low critical temperature:	S (PAV-aged) = 200 MPa
	m (PAV-aged) = 0.300

For the high and low critical temperatures, the most conservative one out of the two criteria are selected. The critical temperatures define the continuous PG. However,

binders are usually denominated the standardised PG, which is calculated according to Figure 15.

PERFORMANCE GRADE	PG 46-			PG 52-							PG 58-					PG 64-					
	34	40	46	10	16	22	28	34	40	46	16	22	28	34	40	10	16	22	28	34	40
Average 7-day Maximum Pavement Design Temperature, °C[a]	<46			<52							<58					<64					
Minimum Pavement Design Temperature, °C[a]	>-34	>-40	>-46	>-10	>-16	>-22	>-28	>-34	>-40	>-46	>-16	>-22	>-28	>-34	>-40	>-10	>-16	>-22	>-28	>-34	>-40
ORIGINAL BINDER																					
Flash Point Temp, T48: Minimum °C	230																				
Viscosity, ASTM D4402:[b] Maximum, 3 Pa•s, Test Temp, °C	135																				
Dynamic Shear, TP5:[c] G*/sinδ, Minimum, 1.00 kPa Test Temp @ 10 rad/s, °C	46			52							58					64					
ROLLING THIN FILM OVEN (T240) OR THIN FILM OVEN RESIDUE (T179)																					
Mass Loss, Maximum, percent	1.00																				
Dynamic Shear, TP5: G*/sinδ, Minimum, 2.20 kPa Test Temp @ 10 rad/s, °C	46			52							58					64					
PRESSURE AGING VESSEL RESIDUE (PP1)																					
PAV Aging Temperature, °C[d]	90			90							100					100					
Dynamic Shear, TP5: G*sinδ, Maximum, 5000 kPa Test Temp @ 10 rad/s, °C	10	7	4	25	22	19	16	13	10	7	25	22	19	16	13	31	28	25	22	19	16
Physical Hardening[e]	Report																				
Creep Stiffness, TP1:[f] S, Maximum, 300 MPa, *m* - value, Minimum, 0.300 Test Temp @ 60s, °C	-24	-30	-36	0	-6	-12	-18	-24	-30	-36	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30
Direct Tension, TP3:[f] Failure Strain, Minimum, 1.0% Test Temp @ 1.0 mm/min, °C	-24	-30	-36	0	-6	-12	-18	-24	-30	-36	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30

Figure 15. Superpave specification for binders (ASTM D6373-13 2013)

2.4. Characterisation of asphalt mixtures and binders for engineering purposes

The behaviour of asphalt mixtures under the main distresses affecting them are determined by their linear and non-linear viscoelastic properties. Therefore, a full characterisation of asphalt mixtures and binders from the pavement engineering point of view should consider all these properties and distresses. For the purpose of characterising asphalt mixtures and binders, laboratory tests are designed to simulate the traffic loading and climate conditions in the pavement to assess its response under traffic and climatic

conditions. The following sections describe these properties and how they can be characterised.

2.4.1. Linear viscoelastic properties

Asphalt mixtures and bituminous binders are viscoelastic materials. Viscoelastic materials are characterised by having a time-dependent response to loads showing partially elastic and viscous behaviours. The viscoelastic response of a material can be exemplified by performing a test in which a stress is applied at time t_0, hold constant for a period and totally removed at time t_1. In terms of strain response, a viscoelastic material will first suffer an immediate elastic deformation at t_0 followed by creep until t_1. At time t_1 the elastic strain will be instantaneously recovered, some of the creep deformation will be recovered with time but some permanent deformation will remain (Figure 16) (Abbas 2004). Viscoelasticity is linear if the response of the material to a superposition of loads is equal to the superposition of the individual responses to the individual loads. This is known as the Boltzmann superposition principle (Boltzmann 1874) and the main consequence is that strain and stress are proportional (Salencon 2016). There are several important features to describe the LVE materials response to loads: creep, relaxation, complex modulus and phase angle.

Creep strain is defined as the gradual increase in strain of a material with time under a constant stress or load while stress relaxation is defined as the gradual decrease in stress with time under a constant deformation or strain.

Due to the further use of complex modulus and phase angle concepts in this thesis, these parameters are further explained in the next subsection.

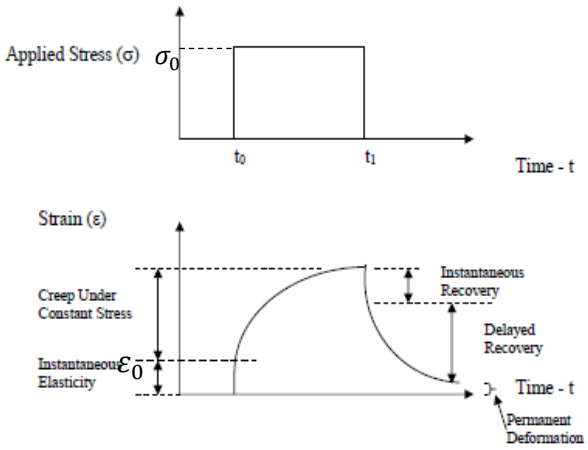


Figure 16. Viscoelastic response (modified from Abbas (2004))

2.4.1.1. Complex Modulus and Phase Angle

The LVE properties of asphalt mixtures and binders can be analysed using dynamic tests. Dynamic tests apply a sinusoidal stress or strain at a specific frequency ω (rad/s) within the LVE region of the material. The case of the applied stress will be further used (being analogous for the applied strain). The sinusoidal stress is represented using the following complex notation:

$$\sigma^* = \sigma_0 e^{i\omega t} \quad (7)$$

$$\omega = 2\pi f \quad (8)$$

$$i = \sqrt{-1} \quad (9)$$

where σ^* is the dynamic stress, σ_0 is the peak stress, ω is the angular frequency in rad/s and f is the frequency in Hz.

Equation (7) can be also written as:

$$\sigma^* = \sigma_0 \sin(\omega t) \quad (10)$$

The strain response of the material to this loading for LVE is a sinusoidal strain out of phase with the stress by an amount δ (phase angle) following the equivalent Equations (11) and (12):

$$\varepsilon^* = \varepsilon_0 e^{i(\omega t - \delta)} \tag{11}$$

$$\varepsilon^* = \varepsilon_0 \sin(\omega t - \delta) \tag{12}$$

where ε^* is the dynamic stress, ε_0 is the peak strain and δ is the phase angle in degrees. The phase angle represents the gap between the applied stress and the strain response. If a material is purely elastic, this gap does not exist and the phase angle is 0º, while if the material is purely viscous the phase angle is 90º. Thereby, for viscoelastic materials like bituminous binders and asphalt mixtures, the phase angle will be within this range, being a valuable measure of the elasticity and viscosity of the material.

The ratio between the applied stress and the resulting strain is called complex modulus:

$$E^*(\omega) = \frac{\sigma^*}{\varepsilon^*} = \frac{\sigma_0}{\varepsilon_0} e^{i\delta} \tag{13}$$

where $E^*(\omega)$ is the complex modulus in Pa whose norm is the ratio of the peak stress and strain:

$$|E^*(\omega)| = \frac{\sigma_0}{\varepsilon_0} \tag{14}$$

The complex modulus is also known as stiffness. Equation (13) can be written as:

$$E^*(\omega) = \frac{\sigma_0}{\varepsilon_0} cos\delta + i\frac{\sigma_0}{\varepsilon_0} sin\delta = E'(\omega) + iE''(\omega) \tag{15}$$

where E' is called storage modulus in Pa (also known as E_1) and E'' is the loss modulus in Pa (also known as E_2). Thereby, the norm of the complex modulus can also be written as:

$$|E^*(\omega)| = \sqrt{(E')^2 + (E'')^2} \tag{16}$$

Having that:

$$E' = E^* cos\delta \tag{17}$$

$$E'' = E^* sin\delta \tag{18}$$

The storage modulus represents the energy elastically stored and released in each dynamic cycle. Therefore, it can be also called as elastic modulus or elastic component of the complex modulus. On the other hand, the loss modulus represents the average dissipated energy rate in every dynamic cycle. Therefore, it is also known as viscous modulus or viscous component of the complex modulus (Airey 1997).

If the loading mode is shear stress or strain, the complex modulus is denominated shear complex modulus G^* and follows an analogous expression to Equation (19) (Pink et al. 1980):

$$G^*(\omega) = \frac{\tau_0}{\gamma_0} cos\delta + i\frac{\tau_0}{\gamma_0} sin\delta = G'(\omega) + iG''(\omega) \tag{19}$$

where $G^*(\omega)$ is the shear complex modulus in Pa, τ_0 is the peak shear stress, γ_0 is the peak shear strain, $G'(\omega)$ is the shear storage modulus and $G''(\omega)$ is the shear loss modulus.

If the material under study is isotropic, E* and G* are related as following:

$$G^* = \frac{E^*}{2(1+\nu^*)} \quad (20)$$

where ν^* is the Poisson ratio.

2.4.1.2. Dynamic Shear Rheometer

Most of the binders' testing in this thesis, including the testing to obtain the LVE properties, has been performed using a Dynamic Shear Rheometer (DSR) (Figure 17). Therefore this section is dedicated to explain its functionality.

DSR is a shear strain/stress controlled device which allows studying bitumen rheology at a wide range of loads, frequencies and temperatures. For this purpose, a rounded sample of bitumen is sandwiched between two plates allocated inside a temperature control system. The lower plate is fixed while the upper plate is allowed to move at different frequencies in order to apply a shear stress/strain to the sample. Figure 18 shows the functioning principle of DSR. The equipment is able to control torque (T) and displacement (θ), so stress and strain are calculated according to Equations (21) and (22). From this data, the shear complex modulus and phase angle of the same are obtained for the temperatures and frequencies tested.



Figure 17. Dynamic Shear Rheometer

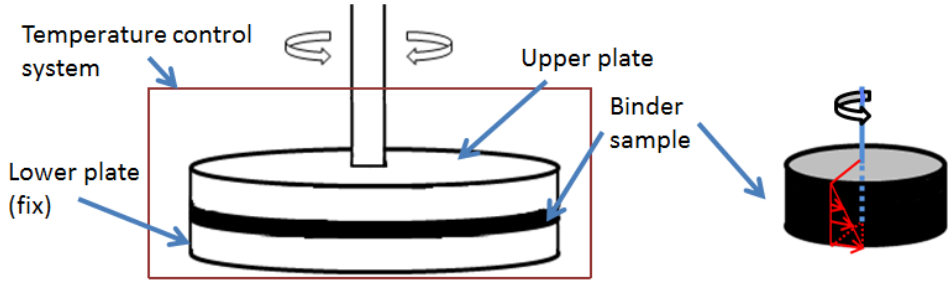


Figure 18. DSR functioning principle

$$\tau_r = \frac{2T}{\pi r^3} \quad (21)$$

$$\gamma_r = \frac{r\theta}{h} \quad (22)$$

Where τ_r is the stress in a r distance from the centre of the sample, γ_r is the strain in a r distance of the centre of the sample, T is the torque (N·m), θ is the displacement (rad), r is the radius (m) and h is the height of the sample (m), known as gap.

Due to torque limitations of DSR, for bitumen testing it is usually necessary to use different plate sizes for different temperature ranges, in order to allow the equipment to apply the desired strain or stress. Two main sizes are commonly used: ø 25 mm (at high temperatures) and ø 8 mm (at low temperatures). The 25 mm – geometry is usually used with 1 mm gap, while the 8 mm is usually used with 2 mm gap (Figure 19).

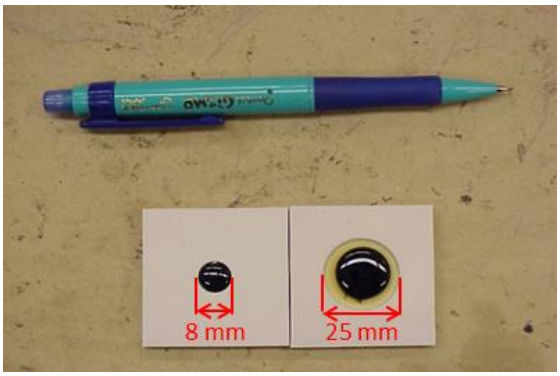


Figure 19. Different DSR geometries

2.4.1.3. Two-point bending

The LVE properties of asphalt mixtures can be obtained by means of two-point bending tests (Di Benedetto et al. 2001). In this test, a trapezoidal asphalt mixture specimen is subjected to a dynamic sinusoidal two point bending load. Figure 20 shows the test device for testing four specimens at the same time.



Figure 20. Two-point bending device

Two-point bending tests allow studying the LVE properties of asphalt mixtures at a wide range of temperatures and frequencies. The trapezoidal shaped cantilever beam specimen is fixed at its base with the top of the beam being cyclically loaded. The functioning principle of this test is shown in Figure 21. The bending stress varies continually along the length of the beam with the maximum bending stress located towards the centre of the beam, its position being dependent upon the chosen geometry (Rowe 1996). The complex modulus of the asphalt mixture is determined using two factors (EN 12697-26 2012):

- A shape factor γ that depends on the dimensions of the specimen as shown in Equation (23), where γ is the shape factor and the rest are the specimen dimensions as shown in Figure 21.

$$\gamma = \frac{12L^3}{b(h_1 - h_2)^3}\left[\left(2 - \frac{h_2}{2h_1}\right)\frac{h_2}{h_1} - \frac{3}{2} - ln\frac{h_2}{h_1}\right] \quad (23)$$

- A mass factor μ that takes into account (if necessary) the effects of inertia related to the mass of the movable parts (attachment helmets, specimen-loading frame coupling, etc.). For classical tests (less than 30Hz) this factor is negligible. Equation (24) shows the mass factor.

$$\mu = 0.135M + m \quad (24)$$

where μ is the mass factor, M is the mass of the specimen and m is the mass of the movable parts.

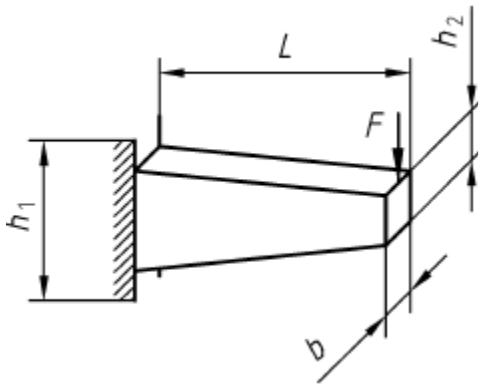


Figure 21. Two-point bending principle

The real and imaginary parts of the complex modulus (storage and loss modulus) are then given by Equations (25) and (26):

$$E' = \gamma\left(\frac{F}{D}cos\varphi + \mu\omega^2\right) \quad (25)$$

$$E'' = \gamma\left(\frac{F}{D}sin\varphi\right) \quad (26)$$

where E' and E'' are the storage and loss modulus respectively in MPa, γ is the shape factor, F is the amplitude of the load in N, D is the amplitude of the displacement in mm, φ is the phase angle, μ is the mass factor and ω is the frequency in Hz.

2.4.1.4. LVE properties' testing and representation

Using the DSR and two-point bending device for binders and asphalt mixtures respectively, different tests can be carried out to determine their LVE properties and their representation.

- Strain sweep

A strain sweep test consists of the application of a range of strains to the sample at a fixed frequency. These tests are usually undertaken to obtain the LVE strain limit of asphalt mixtures and binders. For binders, this limit is assumed to be the strain for which the complex modulus drops 5% from its initial value at a specific temperature (Anderson et al. 1994). Figure 22 displays an example of a strain sweep test.

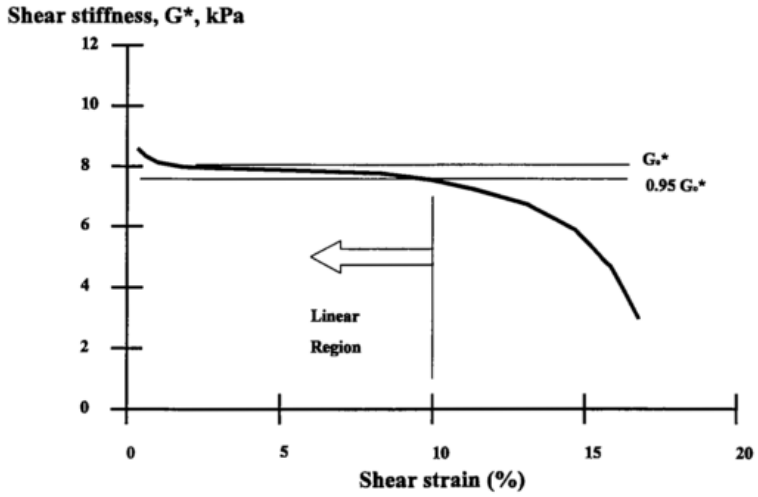


Figure 22. LVE strain limit for a bitumen (Airey 1997)

- Frequency sweep

In a frequency sweep test, the dynamic loading equipment applies a range of frequencies to the sample at a fixed strain/stress. In order to obtain representative results, the strain/stress applied has to be within the limit of the LVE. Therefore, frequency sweeps are usually undertaken after strain sweeps. Figure 23 shows an example of frequency sweep results at different temperatures (0 to 80ºC) for a binder tested in a DSR.

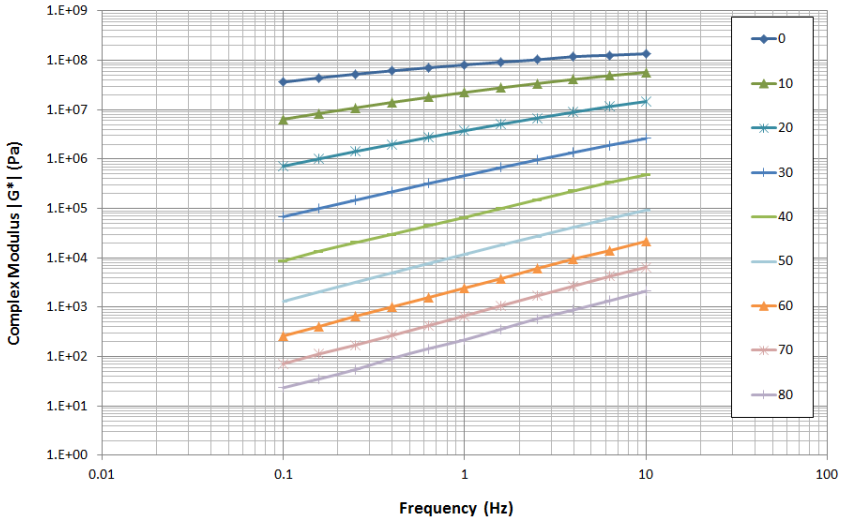


Figure 23. Example of frequency sweep results (Isotherms)

- Temperature sweeps

Temperature sweeps are used to study the temperature susceptibility of asphalt mixtures and binders. In this test, frequency and strain are fixed, and temperature changes in the desired range. Usually, this test is combined with frequency sweep (see Figure 22) so that a more complete characterisation of the material is obtained.

- LVE properties representation

There exist different types of representation to characterise and identify the LVE properties of materials. The most common plots are (Airey 1997):

- Black diagrams. These curves represent complex modulus versus phase angle in the so-called Black space. Usually, complex modulus is plotted in log-scale. These diagrams are useful to identify material behaviour at high temperature/low frequency (Mangiafico 2014). In addition, these diagrams can be used to assess whether a material is thermorheologically simple. Thermorheological simplicity

implies that the curves at different temperatures of a material plotted in the Black space have to smoothly overlap. Figure 24 displays an example of these plots for the shear complex modulus and phase angle of a thermorheologically simple bitumen.

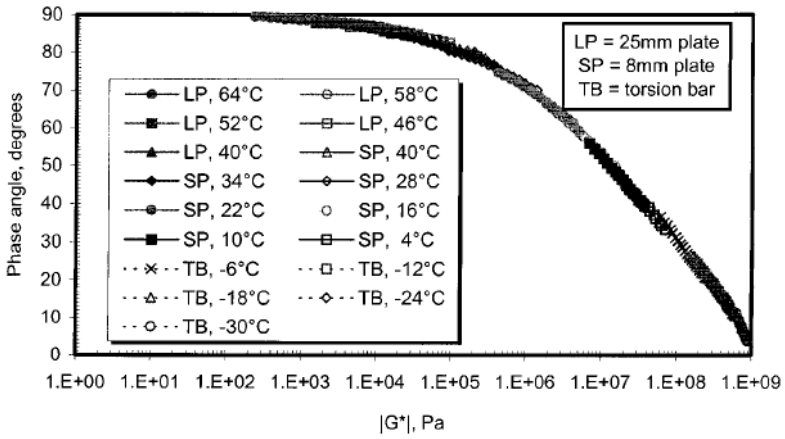


Figure 24. Black Diagram of a binder in the Black Space (Marasteanu & Anderson 2001)

- Isochrones are curves which display any material property versus temperature at a fixed frequency. These curves can be used to assess temperature dependency at different frequencies.
- Isothermss are curves which display any material property versus frequency at a fixed temperature. These curves can be used to assess frequency dependency at different temperatures.
- Cole-Cole diagram shows elastic modulus versus viscous modulus. In this way, the viscoelastic balance of the material is represented without including other variables. These plots are useful to highlight the behaviour of binders and mixtures at low temperature/high frequency (Mangiafico 2014).

In addition to these, master curves are used to study and compare the rheology of asphalt mixtures and binders. In order to build them, Time-Temperature Superposition Principle needs to be applied.

2.4.1.5. Time-Temperature Superposition Principle

One of the main techniques for the analysis of LVE data is the construction of master curves. Different authors have found that there exists a relationship between temperature and frequency which allows measurements done at different temperatures to fit a single curve at a wide range of reduced frequencies by the use of shift factors. This relationship is reflected in the fact that some materials show unique curves in the Black space and Cole-Cole diagram regardless of the test temperature and frequency (see Figure 24). Materials showing this behaviour are called thermorheologically simple (Airey 1997).

Complex modulus curves of different materials crowd together at high frequencies tending to a unique horizontal asymptote, called glassy modulus G_g. On the other hand, at low frequencies the complex modulus of different materials does not converge to a viscous asymptote because viscosity strongly depends on temperature. Because of this, it is possible to separate the effect of frequency (loading time) and temperature in the LVE behaviour of materials (Airey 1997). This is the Time-Temperature Superposition Principle (TTSP) which can be expressed as:

$$E^*(\omega, T) = E^*(\omega f(T)) = E^*(g(\omega)T) \quad (27)$$

Equation (27) means that there is an equivalency of complex modulus values measured at different frequencies and temperatures such as:

$$E^*(\omega_1, T_1) = E^*(\omega_2, T_2) \quad (28)$$

having:

$$\omega_1 f(T_1) = \omega_2 f(T_2) \quad (29)$$

$$g(\omega_1) T_1 = g(\omega_2) T_2 \quad (30)$$

Thereby, the TTSP allows the representation of a continuous curve of the binder behaviour over a wide range of frequencies at a reference temperature (T_{ref}) using shift factors (a(T)). This curve is called a master curve. The extended frequency scale in a master curve is called the reduced frequency defined as:

$$\log f_r = \log f + \log a(T) \quad (31)$$

where f_r is the reduced frequency in Hz, f is the frequency in Hz and $a(T)$ is the shift factor at temperature T. Therefore, the TTSP can be expressed as:

$$E^*(\omega, T) = E^*\left(\omega a(T), T_{ref}\right) \quad (32)$$

For the construction of the master curve, frequency sweeps have to be carried out at different temperatures. Next, a reference temperature is selected and the rest of isotherms are shifted over the frequency axis a distance log a(T) (Figure 25).

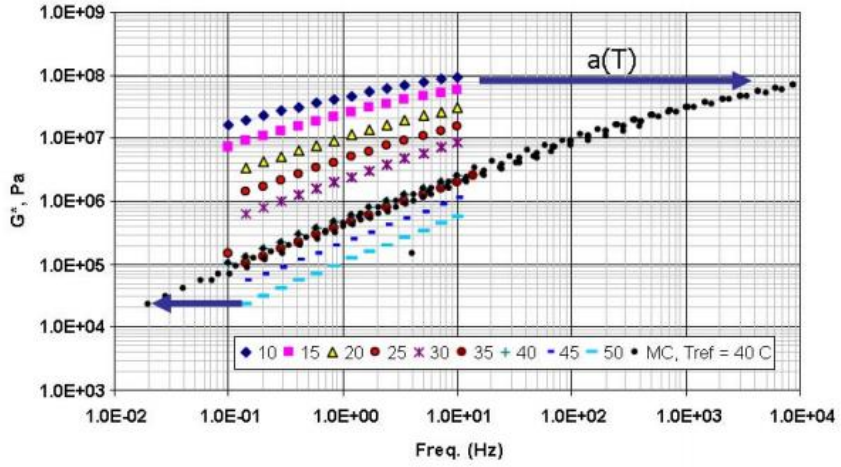


Figure 25. Master curve construction for the norm of the shear complex modulus of binders (Time Temperature Superposition Principle) (Rowe & Sharrock 2011)

Shift factors (a(T)) are functions of temperature and can be either manually obtained or following different equations. Among others, Arrhenius (Equation (33)) (Arrhenius 1889) and William-Landel-Ferry (WLF) (Equation (34)) (Williams, Landel, & Ferry 1955) equations are used to obtain shift factors. Recently, some authors have developed mathematical-based approaches for the optimisation of shift factors (Chailleux et al. 2006).

$$\log a_T = C\left(\frac{1}{T} - \frac{1}{T_R}\right) = \frac{0.4347\ E_a}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right) \quad (33)$$

$$\log a_T = \frac{-C_1(T - T_R)}{C_2 + (T - T_R)} \quad (34)$$

Where a_T is the shift factor at T temperature, T_R is the reference temperature, R is Boltzmann constant, E_a is the activation energy of the binder and C, C_1 and C_2 are constants. From Equations (33) and (34) it can be observed that shift factors have a logarithmic relation with temperature (Figure 26).

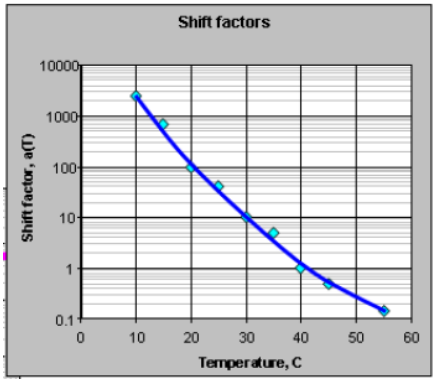


Figure 26. Shift factors versus temperature (Rowe & Sharrock 2011)

Master curves can be built for every viscoelastic property of asphalt binders and mixtures and represent a powerful tool for the comparison of the LVE properties of different materials.

Some materials such as polymer modified binders exhibit a more complicated rheology (Section 2.3.2) not showing thermorheological simplicity (i.e. their Black curve is not unique). This would prevent the use of the TTSP and consequently the construction of master curves. However, researchers (Olard & Di Benedetto 2003; Di Benedetto et al. 2004) have found that is possible to apply a Partial Time-Temperature Superposition Principle (PTTSP) and obtain shift factors to shift isothermal curves to a single master curve.

2.4.1.6. Linear viscoelastic models

Due to the different behaviour of asphalt mixtures and binders at different temperatures and loading times (frequencies), the characterisation of their LVE properties requires the time consuming process of obtaining master curves with the corresponding testing. In order to provide these master curves over a full range of frequencies and temperatures,

LVE models are able to simulate master curves using a limited amount of rheological data (Airey 1997).

There exist many different models for the simulation of master curves which can be divided into: nonlinear multivariable models, empirical algebraic equations and mechanical element models (Yusoff et al. 2011). Hereafter, some of the most used empirical algebraic equations and mechanical element models are described (for further use during the analysis of results of the present thesis).

Empirical Algebraic Equations

- Christensen and Anderson (CA) model

CA model was developed during the SHRP A-002A study through the analysis of the LVE properties of bitumens in order to develop an equation able to describe them. They stated that the glassy modulus G_g, the steady state viscosity η_{ss}, the cross over frequency ω_0, and the rheological index R (or R-value) were required to fully characterise the LVE properties of binders. The cross over frequency is the frequency in a master curve at which the phase angle is 45º (i.e. at which the storage and the loss modulus are equal). The R-value is the log distance between the glassy modulus and the modulus at the cross over frequency. These parameters are represented in Figure 27.

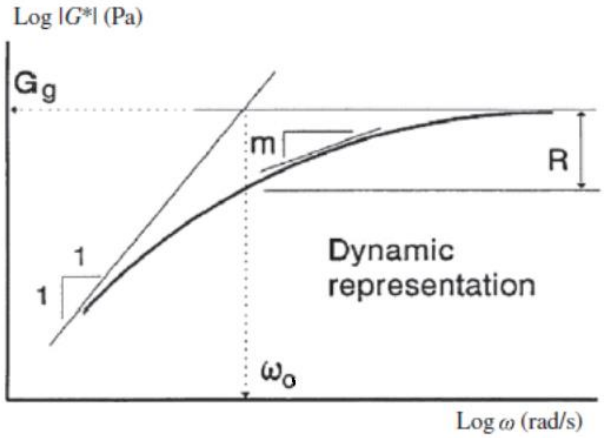


Figure 27. Dynamic representation of CA model parameters (adapted from (Yusoff et al. 2011))

This model is defined by a series of equations for the main LVE parameters of binders:

$$|G^*| = G_g \left[1 + \left(\frac{\omega_0}{\omega}\right)^{\frac{\log 2}{R}}\right]^{-\frac{R}{\log 2}} \tag{35}$$

$$\delta = \frac{90}{\left[1 + \left(\frac{\omega}{\omega_0}\right)^{\frac{\log 2}{R}}\right]} \tag{36}$$

$$R = \frac{(\log 2) \times \log\left(\frac{|G^*|}{G_g}\right)}{\log\left(1 - \frac{\delta}{90}\right)} \tag{37}$$

This model is relatively simple and more accurate than others, such as Jongepier and Kuilman, Dobson or Dickinson and Witt. However, it has some limitations due to the only used of parameters related to the shape of the relaxation spectrum and it presents some difficulties to simulate LVE properties of modified binders (Yusoff et al. 2011).

With the purpose of simplifying the visual analysis of rheological data and comparison, Rowe et al. (2009) used the parameters defined in this model to characterise the ageing and rejuvenation of binders. The ageing (and consequently the rejuvenation) of binders change the shape of their master curves. This fact implies that the rheological parameters controlling the shape of the master curve also change and could reflect the effect of ageing and rejuvenation. In fact, Rowe et al. (2009) observed that generally after ageing, cross over frequencies decrease and R-value increases for conventional (non-modified binders). In view of this, they proposed to plot R-value versus cross over frequencies to visually evaluate the influence of ageing and rejuvenation in the LVE properties of binders. Figure 28 shows an example of this plot. This approach is used to simplify and help to quickly assess the effect of ageing and different additives such as rejuvenators in the rheology of binders (Rowe et al. 2015; Rahbar-Rastegar et al. 2017).

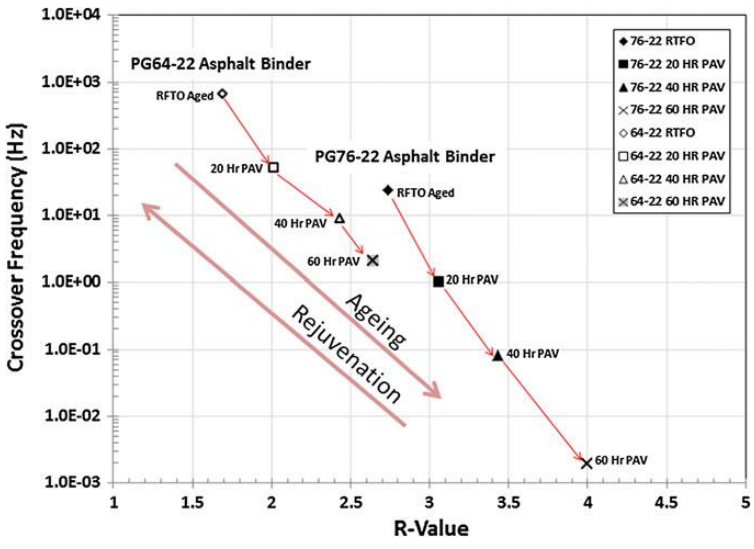


Figure 28. Example of R-value versus crossover frequency for ageing and rejuvenation evaluation (Rowe et al. 2015)

- Sigmoidal model

The Mechanistic-Empirical Pavement Design Guide (ME PDG), developed in the National Cooperative Highway Research Program (NCHRP) Project A-37A, suggested a new dynamic modulus function called the Sigmoidal Model (Medani et al. 2004; Bonaquist & Christensen 2005).This model is described as following:

$$\log|G^*| = v + \frac{\alpha}{1 + e^{\beta+\gamma(\log\omega)}} \quad (38)$$

Where $\log\omega$ is the log reduced frequency, v is the lower asymptote, α is the difference between the upper and lower asymptote, β and γ are the shape parameters of the master curve between the asymptotes and define the inflection point. The representation of these parameters is shown in Figure 29.

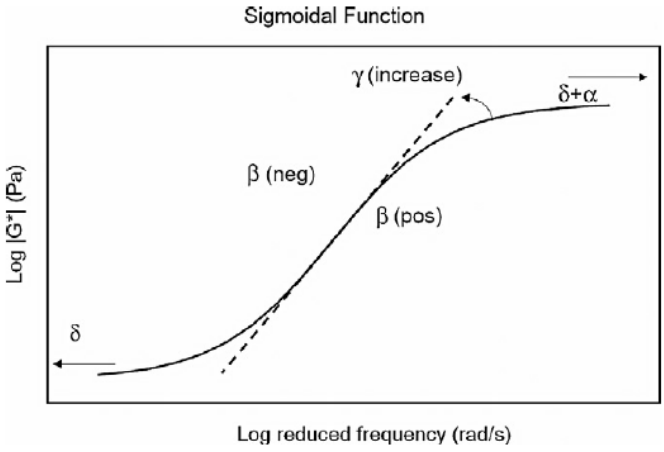


Figure 29. Sigmoidal Model parameters (Garcia & Thompson 2007)

With the same purpose as Rowe et al. (2009) for the evaluation of binders ageing, Mensching et al. (2017) recently used the parameters of the sigmoidal model to study the ageing of asphalt mixtures. In this regard, the master curve of asphalt mixtures becomes

flatter after ageing which means that γ increases. On the other hand, the inflection point moves to lower frequencies and is controlled by the β parameter. Figure 30 shows a representation of these changes. Therefore, the crossover frequency parameter (– β/ γ) versus relaxation spectra width parameter (γ) plot for mixtures can be similar to crossover frequency versus R-value plot for binders for the visual assessment of ageing (Rowe et al. 2015).

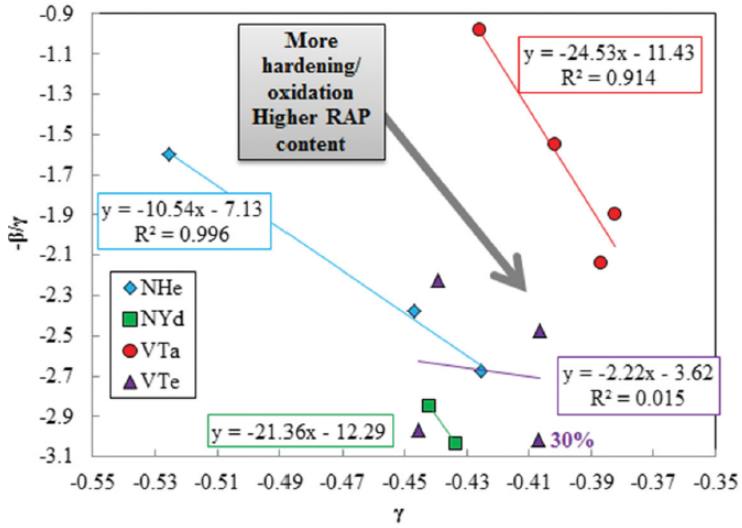


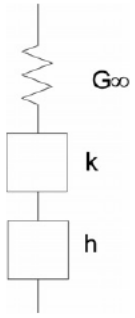
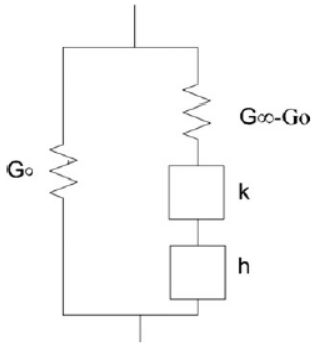
Figure 30. Influence of β and γ parameters in the shape of mixtures master curves (Mensching et al. 2017)

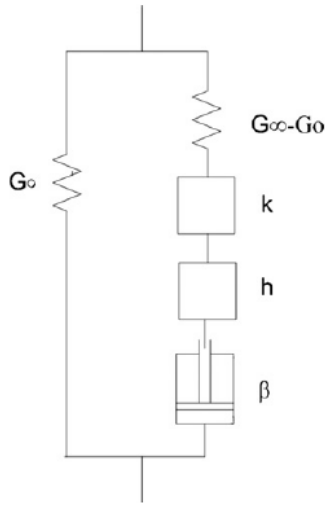
Mechanical element models

Mechanical element models use different arrays of springs, dashpots and parabolic elements to describe the LVE properties of asphalt mixtures and binders. Springs are ideal elastic elements which obey the linear force-extension relation (Hooke's Model) while dashpots are ideal viscous element which spreads at a proportional rate to the applied stress (Newton's Model). Parabolic elements are analogical models with a parabolic creep function (Di Benedetto et al. 2004). The most common models used for the simulation of

the LVE behaviour of asphalt mixtures and binders are summarised in Table 7 which shows the equations for obtaining the complex modulus of the materials according to Huet, Huet-Sayegh and 2S2P1D models. The complete mathematical development of these models can be found in Huet (1963), Sayegh (1965) and Olard & Di Benedetto (2003) respectively. In Table 7, in the different equations, G^* is the complex modulus, G_∞ is the limit of the complex modulus, τ is the characteristic time (which varies only with temperature), h and k are the dimensionless constant for the parabolic elements such as 0<h<k<1, o is a dimensionless constant, G_0 is the elastic modulus and β is the dashpot dimensionless constant.

Table 7. Mechanical element models for the LVE behaviour of asphalt mixtures and binders

Name	Graphical representation	Complex modulus equation
Huet Model (Huet 1963)		$G^* = \frac{G_\infty}{1 + o(i\omega\tau)^{-k} + (i\omega\tau)^{-h}}$ (39)
Huet-Sayegh Model (Sayegh 1965)		$G^* = G_0 \frac{G_\infty - G_0}{1 + o(i\omega\tau)^{-k} + (i\omega\tau)^{-h}}$ (40)

2S2P1D Model (Olard & Di Benedetto 2003)		$G^* = G_0 \frac{G_\infty - G_0}{1 + o(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\tau\beta)^{-1}}$ (41)

Regarding the suitability of the models to simulate the LVE behaviour of asphalt mixtures and binders, Huet was found to be precise in simulating the response of the materials to monotonic loading in terms of Cole-Cole diagrams. However, it lacks viscous elements to include the permanent deformation of bituminous materials. This is also the case of the Huet-Sayegh model, which includes a second spring in parallel with a small rigidity in comparison to G_∞ (Yusoff et al. 2011). In fact, Olard & Di Benedetto (2003) found that G_0 has a very close value to zero for bitumens such as it can be neglected. They also found that Huet-Sayegh model could not fit the data at very low frequencies, where the behaviour should be like a dashpot and not like a parabolic element. For this reason, they introduced the dashpot in the 2S2P1D model.

2S2P1D model has been used by many researchers to obtain the LVE properties of asphalt mixtures and binders. Di Benedetto et al. (2004) found that the parameters of the model should be the same for the mixture and the binder used in its production, except G_0 which is zero for binders but not for mixtures and G_∞. This fact confirms that the LVE properties

of asphalt mixtures are provided by the binder. However, when it comes to RA mixtures, this relationship is not direct. Researchers (Mangiafico 2014; Mangiafico et al. 2013) have studied the relationship between the LVE properties of asphalt mixtures containing RA and the corresponding blends of RA binder and fresh binder under the hypothesis of full blending. They found that the relationship stated by Di Benedetto et al. (2004) was not applicable in these cases, attributing it to the possible not full blending occurring between the RA binder and the fresh binder.

The three models presented have some limitations to be applied to modified binders. However, Olard & Di Benedetto (2003) introduced the use of PTTSP to construct the master curves of modified binders and allowed their modelling.

Recently, Themeli et al. (2015) developed a methodology to relate the rheological properties of binders with their molecular weight distribution by means of mechanical element models. This methodology is based on the fact that bitumen is a continuum of molecular weight species. Each molecule has its own relaxation frequency below which the molecule relaxes and does not contribute to the complex modulus of the material anymore. Consequently, a direct analogy can be made between the rheological response of the bitumen and its molecular weight distribution. As the oscillation frequency decreases in a dynamic test, heavier molecules relax and the modulus decreases. At the same time, the response to the external forces becomes slower and the phase angle increases. In addition, phase angle has been found to be very sensitive to the molecular weight of bitumens. Therefore, this methodology, called δ-method, relies on the hypothesis that the cumulative molecular weight distribution curve and the phase angle

master curve are proportional. The use of mechanical element models is justified by the fact that continuous phase angle curve is needed to derive the cumulative molecular weight distribution curve of the bitumen. The full development of the method and validation by means of gel permeation chromatography can found in Themeli et al. (2015).

2.4.2. Rutting

Rutting (Figure 31) in asphalt mixtures appears due to plastic deformations taking place in the material because of the repetitive loading of traffic. Therefore, its evaluation has to be performed under dynamic cyclic loading.



Figure 31. Example of rutting in an asphalt pavement

Rutting tests are usually conducted at medium-high temperature (30-60ºC) at which ruts are prone to appear because of the softer and more viscous behaviour of asphalt mixtures and binders. There are many different rutting tests to assess the rutting resistance of asphalt mixtures and binders.

In terms of binders, the Multiple Stress Creep Recovery Test (MSCRT) (AASHTO TP 70-13 2009) and rheological parameters such as $|G^*|/\sin\delta$ are widely used. $|G^*|/\sin\delta$ is the Superpave rutting parameter usually obtained at 1.59Hz which also defines the high critical temperature for binders with thresholds of 1kPa for unaged binders and 2.2kPa for RTFOT aged binders (Anderson et al. 1994). Although this parameter has been used for decades to study the rutting potential of binders, researchers have found that there exist a poor correlation between it and the rutting performance of asphalt mixtures (Dongre & D'Angelo 2003), specially for modified binders.

In this regard, new tests have been developed to better relate the rutting behaviour of binders and asphalt mixtures. Multiple Stress Creep Recovery Test (MSCRT) was developed in the early 2000s for this purpose. This test assesses binder ability to recover deformation, and consequently, their potential resistance to rutting in the asphalt mixture.

MSCRT is carried out using a DSR with the parallel-plate geometry of 25mm diameter. The original test consists on the application of ten creep-recovery cycles to a sample at two specific stress levels: 0.1kPa and 3.2kPa. The use of those two stress levels is meant to characterise the rutting performance within and outside the LVE region response of binders. Each cycle lasts 10 seconds, during which the stress is applied for 1 second (creep) and then the sample is allowed to recover during 9 seconds (recovery). Figure 32 shows the evolution of the strain during 10 cycles in MSCRT.

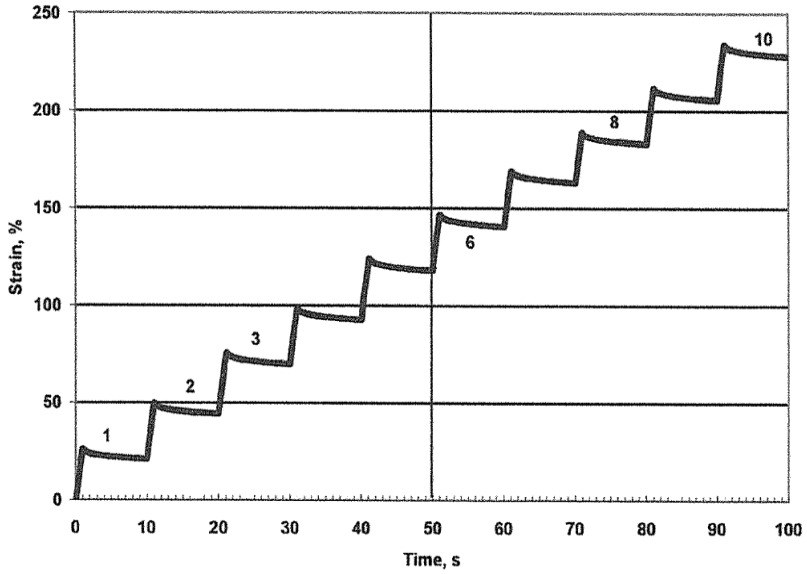


Figure 32. Evolution of strain during 10 cycles in MSCR (AASHTO TP 70-13 2009)

As results, two parameters at each stress level are obtained: average percentage of strain recovery R (%) and average Non-Recoverable Creep Compliance J_{nr} (1/Pa). The percentage of recovered strain at each stress level is obtained as:

$$R(\%) = \frac{\sum_{n=1}^{10} R_n(\%)}{n} = \frac{\sum_{n=1}^{10} \frac{\gamma_{n,1} - \gamma_{n,10}}{\gamma_{n,1}} \cdot 100}{n} \quad (42)$$

where $R(\%)$ is the average percentage of recovered strain at the stress level, $R_n(\%)$ is the percentage of recovered strain at cycle n, $\gamma_{n,1}$ is the strain after 1 second (creep) at cycle n, and $\gamma_{n,10}$ is the strain after 10 seconds (recovery) at cycle n.

Non-Recoverable Creep Compliance J_{nr} is a measure of the potential of the binder to suffer permanent deformations. J_{nr} is obtained as:

$$J_{nr} = \frac{\sum_{n=1}^{10} J_{nr,n}}{n} = \frac{\sum_{n=1}^{10} \frac{\gamma_{n,10}}{\tau}}{n} \quad (43)$$

where J_{nr} is the average non-recoverable compliance at the stress level, $J_{nr,n}$ is the non-recoverable compliance at cycle n, and $\gamma_{n,10}$ is the strain after 10 seconds (recovery) at cycle n, which represents the non-recovered strain, and τ is the stress level.

In addition to the recovery capacity and non-recoverable compliance, the stress susceptibility of binders can be assessed using this test. For this purpose, a stress susceptibility parameter ($J_{nr,diff}$) was defined according to Equation (44).

$$J_{nr,diff} = \frac{J_{nr,3.2kPa} - J_{nr,0.1kPa}}{J_{nr,0.1kPa}} \times 100 \leq 75\% \quad (44)$$

Golalipour (2011) suggested increasing the number of cycles to 30, in order to permit the sample to stabilize, finding better results. In addition, other researchers (Wasage et al. 2011) have applied different stress levels than the original ones in order to obtain more information about the binder.

This test have been found to provide good correlations with rutting resistance of asphalt mixtures (Zoorob et al. 2012), as well as the ability to identify modified binders (Bukowski et al. 2011). In this sense, MSCRT test can also be used to evaluate whether the dosage of modifier in a binder is correct or not using the plot in Figure 33 where high polymer content PMBs will tend to lie in the passing % recovery section of the plot.

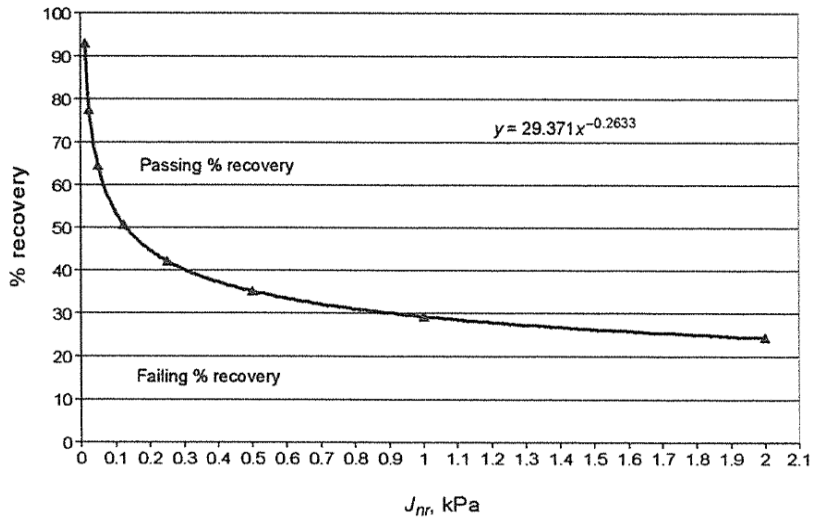


Figure 33. Non-recoverable compliance versus percentage of recovery (AASHTO TP 70-13 2009)

In order to study the rutting performance of asphalt mixtures, the most common tests used in Europe are the Repeated Loading Axial Test (RLAT), Wheel Tracking Tests (WTT) and Hamburg Wheel Tracking Test (HWTT).

In RLAT, a cylindrical specimen is subjected to an unconfined repeated axial stress. In WTT and HWTT, a slab of asphalt mixture is exposed to the repetitive loading of a wheel. For the purpose of this thesis, RLAT was selected to evaluate the rutting of asphalt mixtures because of its loading mode. The asphalt mixtures in this thesis are meant to be placed as binder or base layers in the pavement, therefore, they would not be exposed to wheel loading in field. Instead, they would be subjected to compression cycles as RLAT simulated.

RLAT was developed in the mid 1990s (Gibb 1996) using the Nottingham Asphalt Tester (NAT). The test was developed to overcome limitations found in WTT such as the large dimensions of the specimens needed and the price of the specific equipment. During the

development, RLAT was found to be easy to perform and able to discriminate between the performances of asphalt mixtures with respect to their resistance to rutting producing representative results especially for comparison purposes. Gibb (1996) suggested to obtain two parameters as result of the test: mean and minimum strain rates. Figure 34 shows typical results from RLAT.

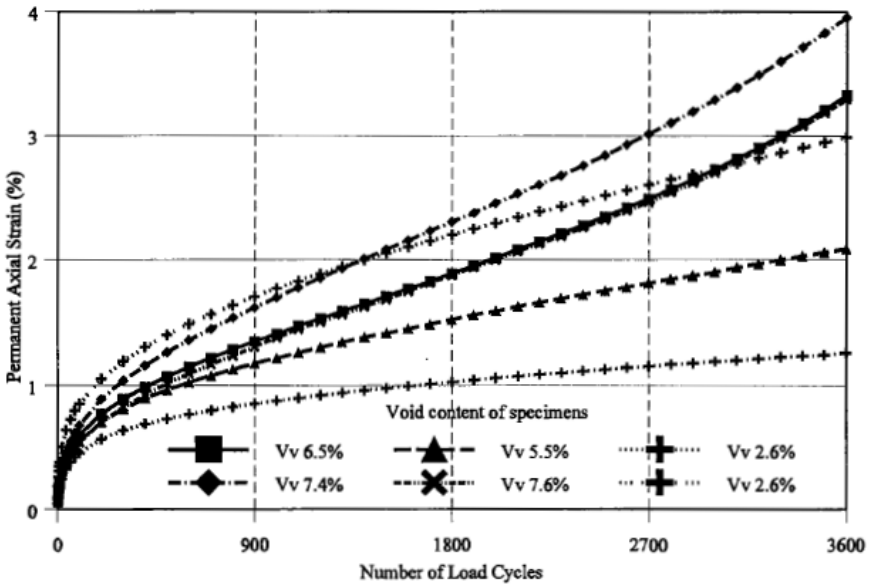


Figure 34. Example od RLAT results: Permanent Axial Strain vs. Number of Load Cycle

Following the initial research, the standard BS DD 226 (1996) was created establishing the tests conditions. Thereby, RLAT applies an unconfined axial stress of 100kPa ± 2kPa to cylindrical specimens in cycles of "1s stress application – 1s rest" for a total of 3600 cycles. During the tests, the axial deformation of the specimen is measured by means of two vertical LVDTs and recorded as shown in Figure 35. In the standard, the main parameter obtained after RLAT is the permanent axial strain that the specimen had suffered at the end obtained as shown in Equation (45).

$$\varepsilon_{d(n,T)} = \frac{\Delta h}{h_0} \quad (45)$$

where $\varepsilon_{d(n,T)}$is the axial strain caused to the specimen after n applications of load at temperature T, h_0 is the original distance between the specimen loading surfaces (in mm) and Δh is the axial deformation (change in the distance between the specimen loading surfaces) (in mm).

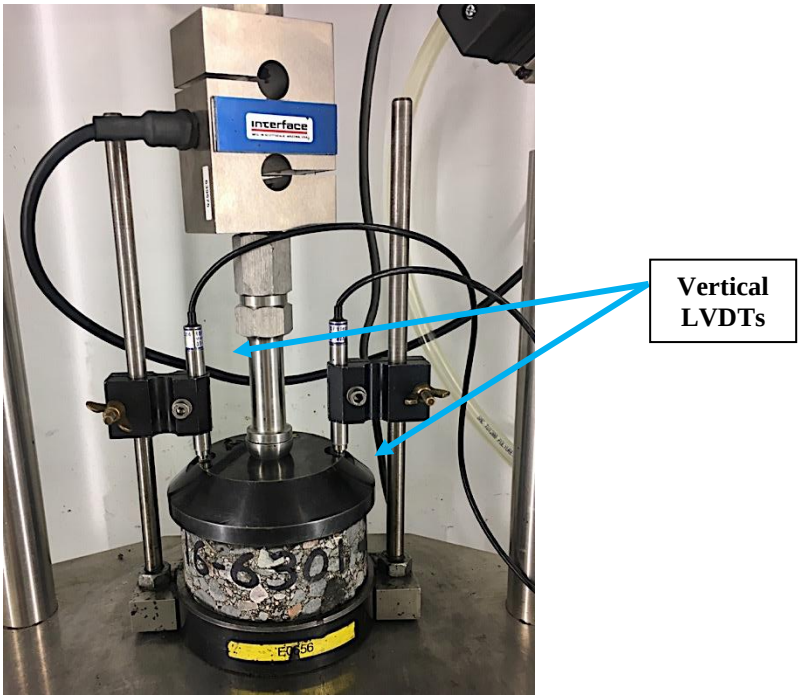


Figure 35. RLAT set up

2.4.3. Fatigue

"Fatigue in bituminous pavements is the phenomenon of cracking (Figure 36). It consist of two main phases, crack initiation and crack propagation, and is caused by tensile strains generated in the pavement by not only traffic loading but also temperature variations and construction practices" - Read (1996).



Figure 36. Example of fatigue cracking on an asphalt pavement

Fatigue tests are usually carried out at intermediate temperatures (10-30ºC) at which fatigue cracking takes place. There exist different fatigue tests under different loading modes. The main distinction is made between stress-controlled and strain-controlled tests. Stress-controlled tests apply a constant cyclic stress and measure the increasing strain, while strain-controlled tests apply a constant cyclic strain and record decreasing the stress. In stress-controlled mode, once the crack appear its propagation is fast due to the stress concentration in the tip. In strain-controlled mode the progression of the crack is slower (Mangiafico 2014).

For the study of the fatigue of binders, $|G^*|\sin\delta$ is the Superpave fatigue parameter which provides the potential of the material to fail because of fatigue. In the same way as for rutting, this parameter has been widely used for decades, however, currently, other specific tests have been developed to better correlate the fatigue of binders with the fatigue of asphalt mixtures.

According to several studies (Shen et al. 2006; Bonnetti et al. 2002), the characterisation of the fatigue resistance can be carried out by performing Time Sweep Tests using the

DSR in the classical configuration of parallel plates of 8 mm diameter and 2 mm gap. These tests apply a repetitive shear loading to the binder in stress or strain-controlled mode at a constant frequency. In this way, the properties of the binder evolve during the tests generally showing a decrease in the complex shear modulus and an increase in phase angle, which may then be followed by a decrease. These changes in complex modulus and phase angle are understood as fatigue damage (Wang et al. 2016). Figure 36 shows an example of these results during a Time Sweep test.

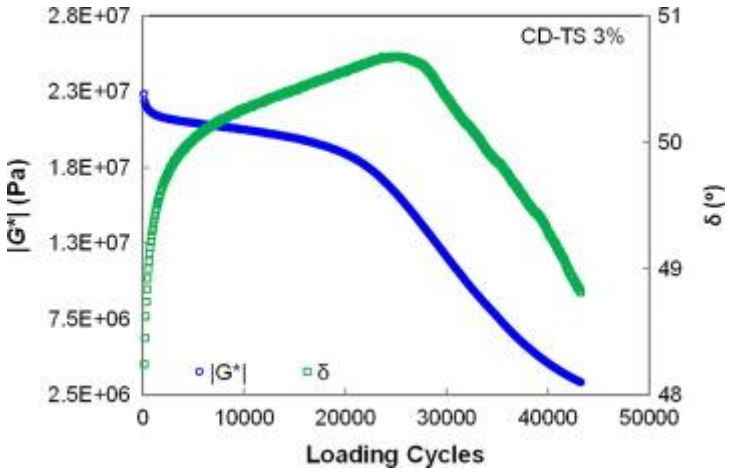


Figure 37. Example of Time Sweep results (Wang et al. 2016)

The classical criterion to determine the fatigue failure of binders is to consider the failure cycle at the 50% drop of the initial complex modulus and is usually termed as N_{f50} (Wang et al. 2016). However, more recent approaches have focused on the use of the dissipated energy concept to define the fatigue failure of binders (Bonnetti et al. 2002; Shen et al. 2006). Dissipated energy is defined as the area within a hysteresis loop, and for LVE materials can be obtained as shown in Equation (46).

$$W_i = \pi \sigma_i \varepsilon_i \sin(\delta_i) \quad (46)$$

where $W_i$is the dissipated energy at cycle i, σ_i is the stress at cycle i, ε_i is the strain at cycle i and δ_i is the phase angle at cycle i. Researchers found that the evolution of the dissipated energy of a binder during a fatigue test can be used to define its fatigue life. This evolution is characterised by the Dissipated Energy Ratio (DER) shown in Equation (47).

$$DER = \frac{\sum_{i=1}^{n} W_i}{W_n} \quad (47)$$

where $W_i$is the dissipated energy at cycle i and $W_n$is the dissipated energy at cycle n. As explained in Bonnetti et al. (2002), DER evolves in different way in strain and stress controlled tests and different criteria can be defined according to the deviation of DER from the non-damage line for the selection of the failure cycle. The most common one is to consider the failure when the DER is deviated 20% from the non-damage line, known as N_{p20} (Martono 2008, Bahia and Delgadillo, 2005; Bonetti et al., 2002). This parameter was introduced during the NCHRP 9-10 project (NCHRP 459, 2001) and it is independent of the loading mode. In addition, it results in a more conservative fatigue response respect to the approach based on Nf50 or based on Np value, which represents the number of cycles to crack propagation and can be estimated as the number of cycles resulting in maximum DER value (Riccardi et al. 2017). Figure 38 illustrates this parameter in stress-controlled mode tests.

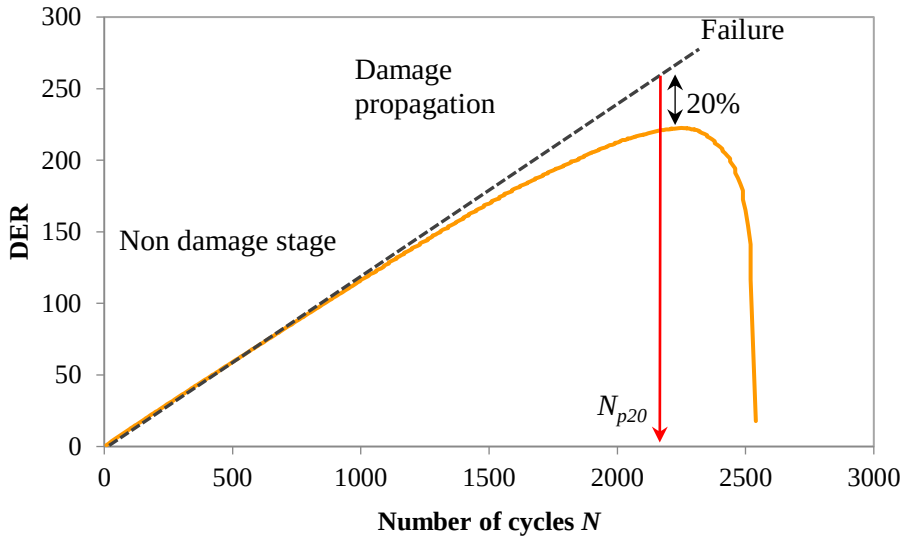


Figure 38. Dissipated Energy Ratio (DER) versus the number of cycle (Riccardi et al. 2017)

More recently, other tests have been developed for the study of the fatigue performance of binder such as Linear Amplitude Sweep (LAS) test. This test is also carried out in the DSR and is a combination of a frequency sweep and a strain sweep up to 30% strain (Johnson 2011). LAS is considered an accelerated test due to the high percentage of strain reached which leads to a short duration of the test (approximately 5 minutes). However, some limitations have to be considered when testing stiff materials such as RA. If the material is too stiff, the sample would have a brittle fracture instead of experimenting fatigue.

Finally, fatigue test results are usually expressed in terms of fatigue laws of the materials, which plot the failure criteria selected versus the number of cycles as shown in Figure 39 as an example for N_{p20}. Fatigue laws are obtained as shown in Equations (48) and (49) for N_{f50} and N_{p20} respectively.

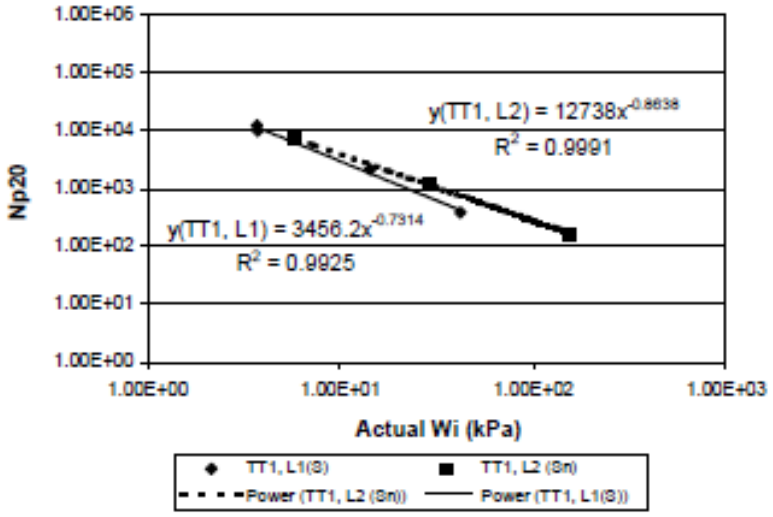


Figure 39. Fatigue law example for N_{p20} failure criteria (Bonnetti et al. 2002)

$$N_{f50} = a(\gamma_i)^b \tag{48}$$

$$N_{p20} = a(W_i)^b \tag{49}$$

where N_{f50} is the cycle at which the shear complex modulus of the binder has dropped 50% of its initial value, γ_i is the initial shear strain, N_{p20} is the cycle at which the DER deviates 20% of the non-damage line, W_i is the initial dissipated energy and a and b are fitted coefficients in each equation.

In addition to the tests described, Rowe (2011) recently defined a fatigue cracking parameter which combines the complex modulus and phase angle of binders at 15ºC and 0.005rad/s as shown in Equation (50). This parameter, known as the Glover-Rowe (G-R) parameter, defines a cracking limit and warning in the Black Space for the evaluation of the cracking potential of binders. The G-R parameter gives a boundary value of 0.18 MPa, which is considered as cracking warning, while a value of 0.45 MPa or more is suggested as cracking limit. These values at this temperature-frequency combination were

developed for a PG 58-28 climate region; current work is ongoing to determine how these should be adjusted to other climactic conditions. Figure 40 shows an example of the representation in the Black Space of the G-R parameter and the cracking warning allowing the fatigue cracking potential of binders to be eoaluated (Mensching et al. 2016). In addition, this parameter has been used to identify the ageing of binders as their G-R parameter moves towards the cracking warning and limit.

$$\frac{G^*(\cos\delta)^2}{\sin\delta} \tag{50}$$

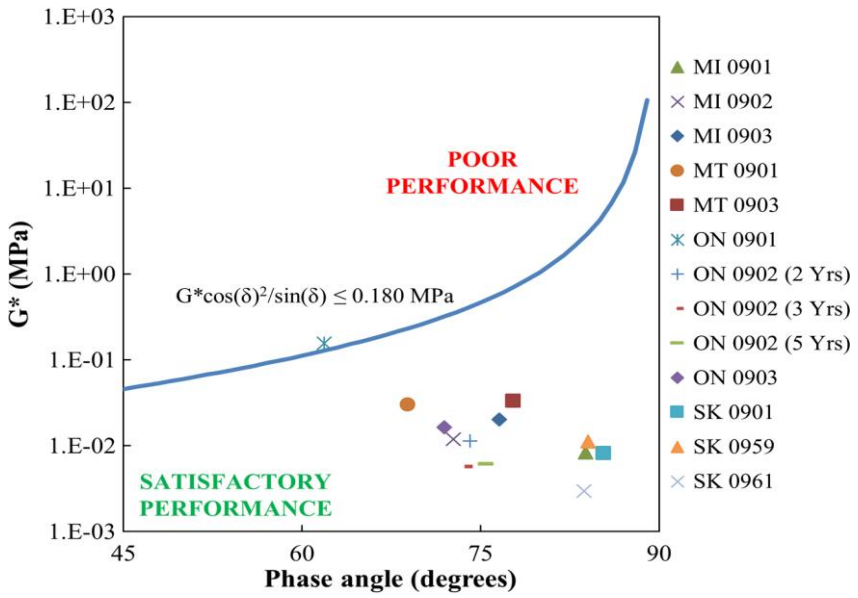


Figure 40. Example of G-R parameter (Mensching et al. 2016)

Regarding the fatigue study of asphalt mixtures, among the most common tests, Indirect Tensile Fatigue Test (ITFT), two-point bending test, three-point bending and four-point bending tests are performed in Europe (EN 12697-24 2012). ITFT is performed on cylindrical specimens subjected to a repeated load with a constant indirect tensile load. Two-point bending tests can be carried out with either prismatic or trapezoidal specimens

which are tested in fatigue mode with controlled displacement. Three-point bending tests use prismatic specimens subjected to controlled displacement loads. Four-point bending tests are carried out on prismatic specimens under four-point periodic bending with free rotation and translation at all load and reaction points.

ITFT is the most commonly used fatigue test in the UK and is performed according to BS DD ABF (2003). The test is widely used because of several reasons:

- The test is simple
- The equipment used (NAT) is applicable for other tests
- The test can be performed on field cores allowing the correlation between lab specimens and cores to be done
- The repeatability for cycles to failure is high (better than tests on either trapezoidal or beam flexure)
- It discriminates between asphalt mixtures containing different binders based upon stiffness and cycles to failure

According to BS DD ABF (2003), ITFT is performed at 20°C ± 0.5°C and different stress levels (depending on the asphalt mixture) at a frequency of 40 ± 1 load repetitions per minute. The vertical deformation of the specimen is measured by embedded LVDTs and recorded (Figure 41). The test is set to stop when the deformation is larger than 10mm.

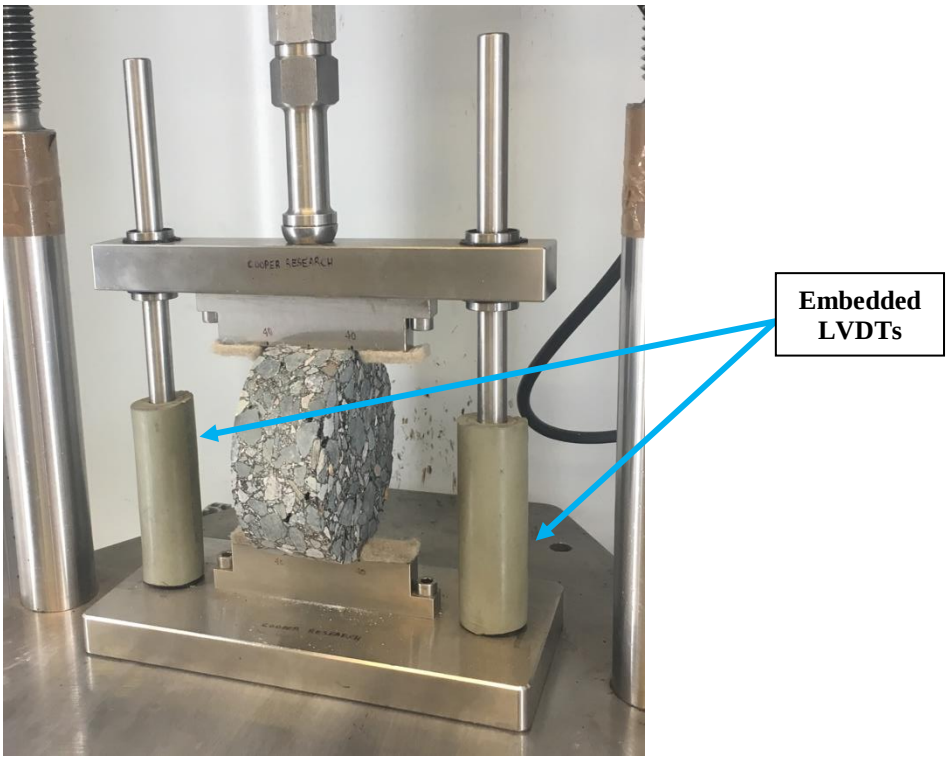


Figure 41. ITFT set up

The main outcome of ITFT is the fatigue law of the asphalt mixtures for comparison. In the same way than for binders, fatigue laws represent the failure criteria versus the failure cycle. In ITFT, the failure cycle is termed N_f and is the cycle at which the vertical deformation of the specimen is 9mm. Figures Figure 42 and Figure 43 show the typical result of an ITFT and fatigue law respectively. The fatigue law is as shown in Equation (51).

$$N_f = a(\varepsilon_i)^b \tag{51}$$

$$\varepsilon_i = \frac{\sigma}{S}(1 + 3\nu) \tag{52}$$

where N_f is the failure cycle, ε_i is the initial strain in the centre of the specimen determined as shown in Equation (52) and a and b are fitted parameters. In Equation (52), σ is the stress applied during the test, S is the stiffness of the specimen and ν is the Poisson ratio.

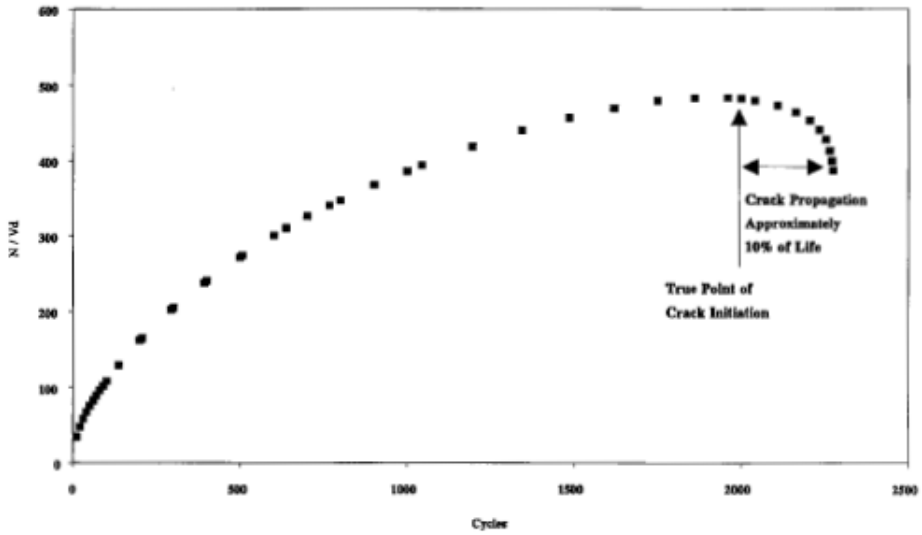


Figure 42. Typical result of an ITFT (Read 1996) at a specific stress level

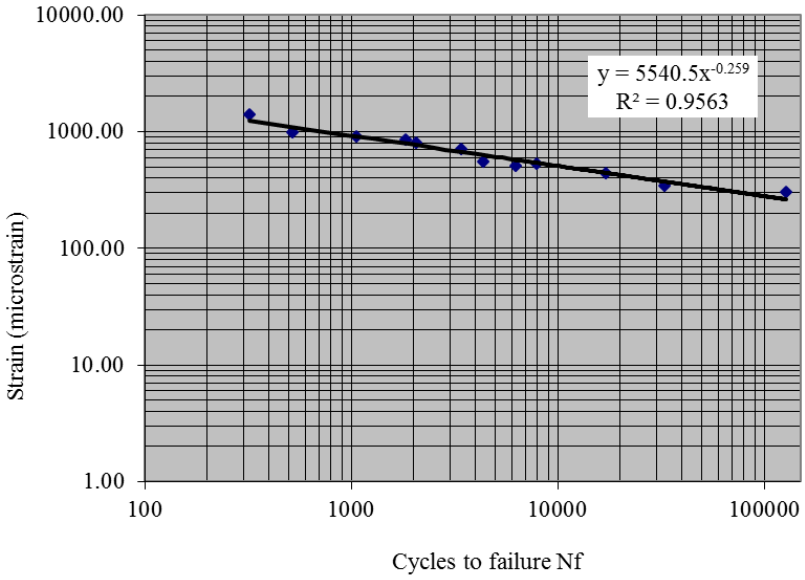


Figure 43. Example fatigue law of an asphalt mixture after ITFT

2.4.4. Thermal cracking

Thermal cracking phenomenon (Figure 44) in asphalt mixtures is related to the relaxation capability of binders. This phenomenon is usually studied at low temperatures (<0ºC) to subject the materials to extreme conditions to test their relaxation capability.



Figure 44. Example of thermal cracking

In order to characterise binders at low temperature, the Bending Beam Rheometer is widely used over the world. In this device, a beam of bitumen is subjected to a bending load at different times (from 8 to 240 seconds) (EN 14771 2012). The outputs of the test are the flexural creep stiffness (S, in MPa) and m-value of the binder. The measured flexural stiffness is obtained using Equation (53) for the different loading times. Then, its logarithmic value is fitted to a second-degree polynomial function to the logarithmic of the loading times as shown in Equation (54). The calculated flexural stiffness is obtained from the fitted Equation (54) according to EN 14771 (2012).

$$S_m(t) = \frac{PL^3}{4bh^3\delta(t)} \quad (53)$$

$$logS_c(t) = A + B \cdot log(t) + C \cdot [log(t)]^2 \quad (54)$$

where $S_m(t)$ is the measured flexural stiffness at time t in MPa, $S_c(t)$ is the calculated flexural stiffness at time t in MPa P is the measured test load in N, L is the distance between supports in mm, b is the width of the test specimen in mm, h is the thickness of the tests specimen in mm, $\delta(t)$ is the deflection of the test specimen at a time t in mm and A, B and C are regression coefficients.

The m-value is the absolute slope of the curve of the logarithm of the stiffness versus the logarithm of time as shown in Equation (65).

$$m(t) = \left|\frac{dlog[S(t)]}{dlog(t)}\right| \quad (55)$$

As reference values, S and m-value are taken at a loading time of 60 seconds. For the characterisation of the performance of binders at low temperature, BBR test are usually carried out at least at two temperatures. If this is the case, the Superpave critical temperatures for S and m-value can be obtained as explained in Section 2.3.5.1. Recently, researchers have presented a new parameter that uses those two critical temperatures as a measure of the cracking potential of the binders following Equation (56) (Anderson et al. 2011).

$$\Delta T_{cr} = T_{cr}(Stiffness) - T_{cr}(m - value) \quad (56)$$

According to Equation (56), if ΔT_{cr} > 0, the low critical temperature of the binder is controlled by the stiffness, while if ΔT_{cr} < 0, the low critical temperature is controlled by

the m-value. Researchers have found that ΔT_{cr} and G-R parameter are interrelated and therefore, the cracking warning and limit of the G-R parameter (see Section 2.4.3) could be extrapolated to obtain the same type of limits to use ΔT_{cr} as an indicator of potential cracking. Anderson et al. (2011) proposed 2.5ºC as warning and 5.0ºC as limit value for ΔT_{cr}. However, Rowe (2011) discussed these values noting that instead they should be 2.4ºC and 5.7 ºC, as shown in Figure 45.

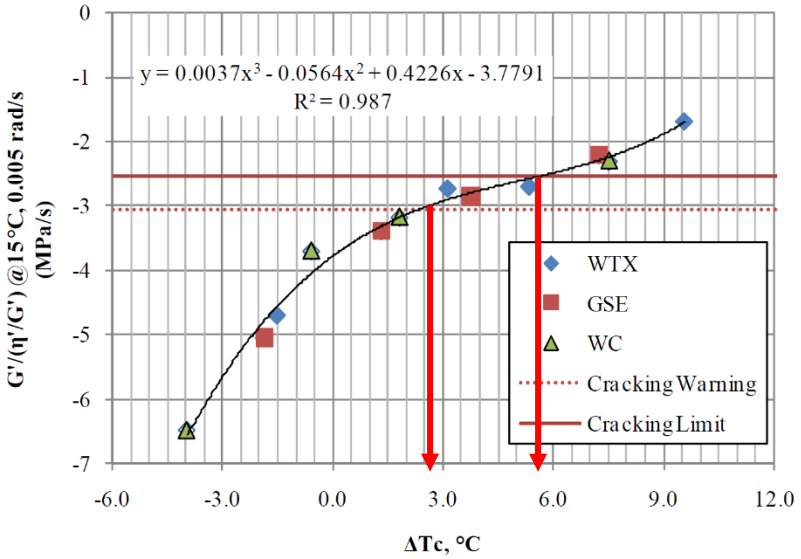


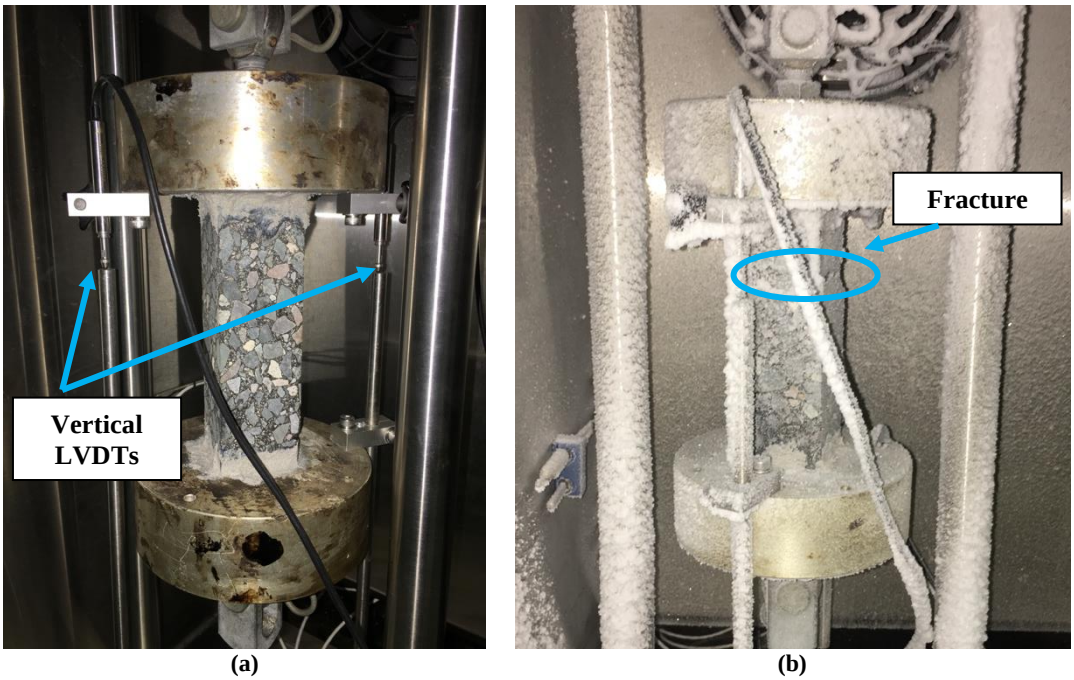
Figure 45. G-R parameter versus ΔT_{cr} (Rowe 2011)

In addition, authors have shown that ΔT_{cr} can be related with the ageing of binders, and therefore with rejuvenation. In this regard, as an asphalt binder ages, ΔT_{cr}value becomes more negative, indicating a loss of its relaxation properties (Hanz & Services 2015; Anderson 2016).

Regarding the thermal cracking properties of asphalt mixtures, they can be characterised by means of Thermal Stress Retained Specimen Test (TSRST) (EN 12697-46 2012). This test reproduces the conditions in the pavement structure for binder and base layers

constraining the movement of a specimen subjected to a decrease of temperature. Thereby, in the same way as in the road, a cryogenic stress is built up in the specimen until it fractures.

TSRST uses prismatic specimens with section 50x50mm and 160mm length and applies a temperature decrease at a constant rate of 10K/h starting at 20ºC. Two vertical LVDTs control the position of the specimen (Figure 46). The main results of the test are the evolution of the cryogenic stress with the decrease in temperature, the failure stress and the failure temperature. The cryogenic stress is the tension stress induced in the specimen by the prohibited thermal shrinkage. The failure stress and failure temperature are the stress and temperature at the moment of fracture.



(a) (b)

Figure 46. TSRST device: (a) specimen before testing; (b) specimen after testing at -30ºC

2.4.5. Moisture damage

Moisture damage is one of the main causes of failure in asphalt mixtures (Figure 47). If

a pavement is not able to properly drain, the presence of water can induce a loss of the adhesive bonding between aggregates and binder and/or a loss of cohesive strength of the asphalt binder.



Figure 47. Moisture induced damage induced in asphalt mixtures (Hamzah et al. 2015)

In this regard, the binder bond strength properties of binders with aggregates can be studied by means of Bitumen Bond Strength (BBS) tests, evaluated with the upgraded PATTI device (Pneumatic Adhesive Testing Instrument).

In these tests, a certain amount of binder is poured on an aggregate surface and the PATTI equipment is used to evaluate the fracture strength of the geometry either in terms of the cohesive bond strength of the binder or the adhesive bond strength of the binder–aggregate interface. This equipment was developed by the National Institute of Standards and Technology (NIST) with the equipment used for the PATTI test shown in Figure 48a). A camera is used to take graphical evidence of the aggregate substrate after testing to record the type of failure. Figure 48b) shows a cross-sectional schematic of the setup of the PATTI with the piston attached to a pull-stub which in turn is attached by means of the binder coating to the aggregate substrate (Santagata et al. 2009).

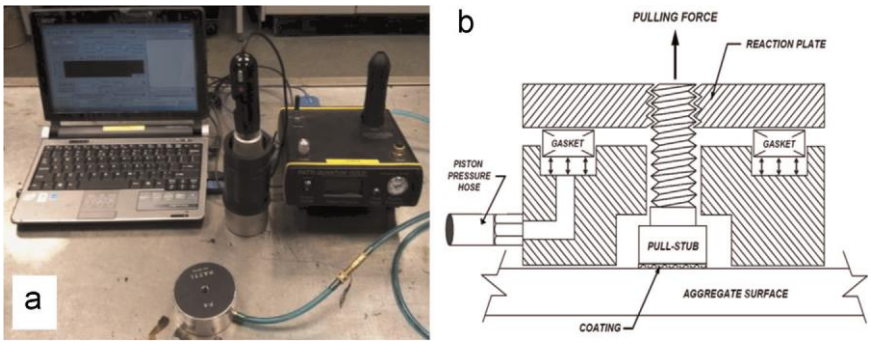


Figure 48. PATTI test: (a) set-up; (b) cross-section of piston attached to pull stub (Santagata et al. 2009)

During testing, air pressure generated by the PATTI is transmitted to the piston which is placed over the pull stub and screwed onto the reaction plate. The air pressure induces an air-tight seal formed between the piston gasket and the aggregate surface. A constant rate of pulling pressure, which is set in the pressure control panel, is applied to the sample. The test generates data in the form of tensile pressure versus testing time which is recorded by the data acquisition system. The maximum tensile pressure to separate the binder from the substrate is captured by the software. This pressure is converted to its pull-off tensile strength, as expressed using Equation (57).

$$POTS = \frac{(AP \cdot A_g) - C}{A_{ps}} \tag{57}$$

where, POTS is the pull-off tensile strength (kPa), AP is air pressure (kPa), A_g is the contact area of gasket with relation plate (mm^2), C is the piston constant and A_{ps} is the area of pull-stub (mm^2).

The POTS and the type of failure are the main results obtained from the PATTI tests. The type of failure is visually identified as shown in Figure 49:

a) Cohesive: the inner cohesion of the binder fails

b) Adhesive: the aggregate-binder surface adhesion fails

c) Cohesive/adhesive: a mix of the two previous types of failure



Figure 49. BBS test type of failure (Canestrari et al. 2010)

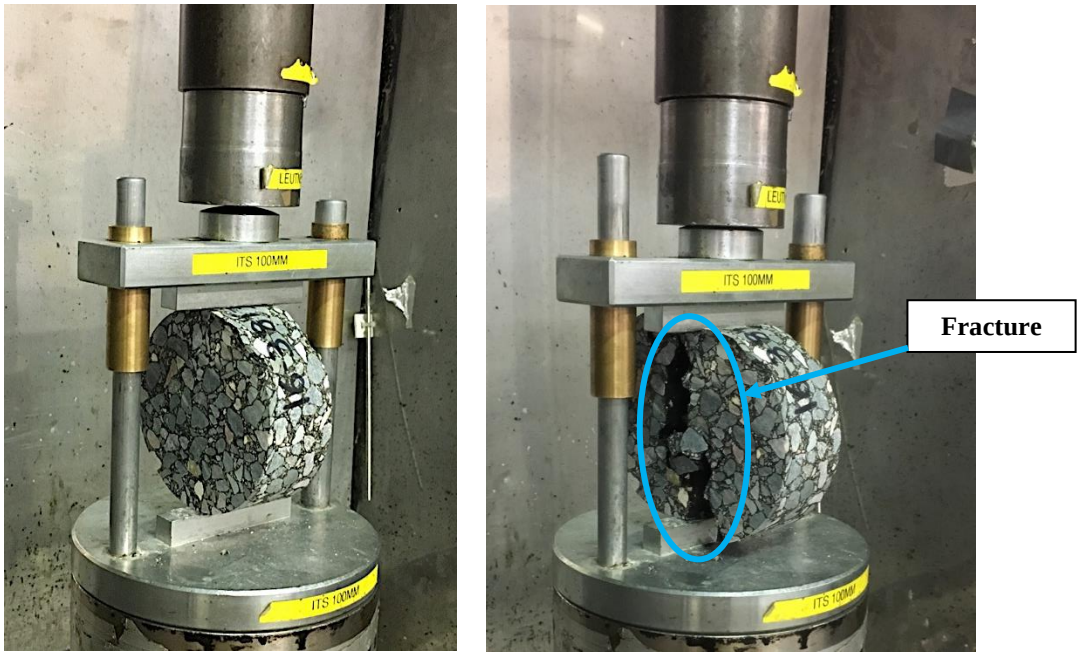
PATTI or BBS tests have been used by different researchers to study the moisture damage of binders (Canestrari et al. 2010; Moraes et al. 2011). For this purpose, the tests are performed before and after water conditioning of the specimen. In this way, the change in the POTS and the type of failure because of the water conditioning can be evaluated as a sign of moisture damage.

The moisture damage of asphalt mixtures is commonly studied in Europe according to EN 12697-12 (2008) – Method A for the determination of water sensitivity. In this test, two sets of three cylindrical specimens are subjected to dry and wet conditioning respectively and tested to obtain their Indirect Tensile Strength (ITS) at 25°C according to EN 12697-23 (2003). During this test, the specimen is located in a loading frame and a diametrical load is continuously applied at a constant speed of deformation of (50 ± 2)

mm/min (Figure 50). The load applied is recorded and the loading continues until the specimen breaks. Next, the ITS of the specimen is calculated as shown in Equation (58).

$$ITS = \frac{2P}{\pi DH} \tag{58}$$

where, P is the peak load during the test (kN), D is the diameter of the specimen in mm and H in the height of the specimen in mm.



(a) **(b)**

Figure 50. ITS test set up: (a) specimen before testing; (b) broken specimen after testing

Therefore, two values of ITS are obtained: dry (ITSd) and wet (ITSw), and compared to determine the Indirect Tensile Strength Retained (ITSR) in percentage after moisture damage as shown in Equation (59).

$$ITSR(\%) = \frac{ITS_w}{ITS_d} \cdot 100 \tag{59}$$

2.4.6. Ageing

As explained in Section 2.3.3, bitumen and consequently the whole asphalt mixture age during its manufacturing and service life in the road changing their initial properties (i.e. conventional bitumen become stiffer and increases its elastic component while decreasing its relaxation properties). Ageing is one of the major distresses in pavements which may cause its failure. Therefore, from an engineering point of view, it is essential to characterise the ageing performance of binders and asphalt mixtures prior to their use. For this purpose, different laboratory methods are used to simulate the ageing that these materials suffer.

In order to study binder ageing, two types of methods can be distinguished: short-term ageing, which simulate changes in the binder after the manufacture of the asphalt mixture, and long-term ageing, which simulates ageing after several years of service life of the pavement. Among the tests that simulate short-term ageing, the most frequently used are the Thin Film Oven Test (TFOT) and Rotating Thin Film Oven Test (RTFOT). Regarding long-term ageing, Pressure Ageing Vessel (PAV) test and Rotating Cylinder Ageing Test (RCAT) have shown the best results in terms of simulating the process that takes place in the field (Airey 2003a). The most widely used methods are RTFOT and PAV.

TFOT consists on the exposition of a 3.2 mm film of binder to heat (163^0C) during 5 hour (EN 12607-2 2014). RTOFT introduced clear improvements over the TFOT regarding ageing simulation due to the changes of test conditions (Whiteoak & Read 1973; Hveem et al. 1963). During RTFOT, a film of binder is subjected to rotation and heating inside an oven at a constant temperature (usually 163^0C) and a specific supply of air during a

certain period of time (EN 12607-1 2014), better reproducing the conditions in an asphalt plant.

PAV method is used to simulate long-term ageing of binders during their service life. In this method, a static film of binder is heated to a specified temperature (usually between 80 and 115 ^{0}C) under a specified air pressure (usually 2.1 MPa) for a given period of time (EN 14769 2012). In order to fully characterise binders, their properties must be analysed in the neat (virgin) state and after RTFOT and RTFOT+PAV.

Regarding ageing of asphalt mixtures, although many studies exist undertaking this topic, currently there is no standard methodology to simulate it. According to Partl et al. (2013), the main features to consider when ageing asphalt mixtures are:

- To age compacted or loose material
- Ageing cycles (temperature and time)
- UV effect
- Air pulses or oxygen pulses

The ageing of compacted specimens is used to determine the end-characteristics of the asphalt mixture in the road, while the ageing of loose material is used to re-use the aged asphalt mixture as artificial RA and simulate ageing during the production stage. In terms of ageing cycles, temperatures lower than 100ºC are recommended and the duration should be determined according to the targeted ageing degree. The UV effect is still uncertain and the inclusion of air or oxygen pulses may accelerate the ageing.

Thus, for the purpose of determining the end-characteristics of the asphalt mixture in the road, compacted asphalt mixture specimens should be studied. Then, temperature, time and the introduction of air or oxygen pulses must be decided.

2.5.Reclaimed Asphalt (RA)

After a certain time of service life, depending on pavement conditions, road wearing courses need to be maintained and sometimes totally changed due to the appearance of damage (such as ruts, potholes, cracks, etc.). In the latter case, asphalt mixture layers are removed from the road through milling. The by-product obtained after milling is known as Reclaimed Asphalt (RA). Thereby, RA is the primary recycled product of the aged asphalt mixture pavements (West 2010) (Figure 51).



Figure 51. Samples of fractioned RAP (West 2010)

This section of the literature review is divided into three subsection to address the different aspects of RA practices that are relevant for this thesis.

2.5.1. RA performance

RA has been re-used in pavement engineering for decades. This technique is considered a valuable approach due to environmental and economic reasons. On one hand, the use of RA decreases the amount of new material needed for the construction or maintenance of roads. This fact represents a great advantage due to the current scarcity of natural resources in terms of aggregates and bitumens. In addition, it helps to reduce disposal problems reducing landfill space. In the same way, the use of RA decreases costs due to the savings in virgin materials (Al-Qadi et al. 2007; Zaumanis et al. 2014a).

However, despite all these benefits, the use of RA has been limited due to the uncertainties found in its behaviour (Zaumanis et al. 2014). Asphalt mixtures containing RA can show very different performance due to the properties of the aged binder in the RA and RA content in the asphalt mixture, among other factors. Generally, an increase of RA content implies an increase in uncertainties about the asphalt mixture behaviour (Li et al. 2004). In order to reduce those worries, RA performance has been widely studied regarding the main distresses affecting pavements.

Asphalt mixtures containing RA are stiffer and have higher complex modulus than those which only have virgin material (Li et al. 2004). This fact is due to the hardening process that the binder in the RA has suffered during its service life. In this sense, because of the increased stiffness of the binder, RA mixtures usually exhibit better (or at least equivalent) resistance to rutting than conventional mixtures (Hajj et al. 2009).

Fatigue cracking behaviour of asphalt mixtures with RA is still uncertain. There exist research in which asphalt mixtures containing RA have shown less fatigue resistance than

conventional mixtures due to the stiff and brittle binder of the RA (Shah et al. 2007). However, Shu et al. (2008) conducted a study with mixtures containing 10, 20 and 30% of RA and considering different fatigue failure criteria. They concluded that depending on the criterion used, the addition of RA seemed to either increase or decrease fatigue life of pavements. In addition, Hajj et al. (2009) reported that the inclusion of RA could result in a worse or better fatigue resistance depending on the RA source and content. On the other hand, and contrary to general thinking, some authors have found that RA could improve fatigue life of mixtures (Huang et al. 2004; McDaniel et al. 2012; Tabaković et al. 2010). Nevertheless, these results could not be totally reliable due to the diffusion phenomenon that appears when rejuvenating agents are used (Zaumanis et al. 2014a).

Concerning low temperature performance, mixtures containing RA are more susceptible to thermal cracking due to the presence of the aged binder (Mensching et al. 2014). However, some studies have shown that up to 25% of RA could be added in mixes without adversely affecting low temperature behaviour (McDaniel et al. 2012). The use of additives to improve low temperature performance of mixtures with high RA content is one of the current major issues in this field.

Regarding moisture damage, given that RA aggregates are already covered with the binder, water sensitivity is expected to decrease in mixes with high percentages of RA (Mogawer et al. 2012; Karlsson & Isacsson 2006; Tran et al. 2012).

Another current concern about the use of RA is its interaction with the virgin material, especially the interaction between the RA binder and the virgin binder. This interaction is known as Degree Of Blending (DOB). There exist different approaches about this

phenomenon. Black rock approach supports that there is no blending between the RA and the virgin binder. This fact implies that the virgin binder covers the RA and does not blend with it. On the opposite side, the full blending approach considers that all the RA binder is detached from the aggregates and blends with the virgin one. In between these extremes, the partial blending approach suggests that some RA binder remains in the aggregates and some blends with the virgin one. Understanding the DOB between old and virgin binders is crucial in order to properly design RA mixes with a good long-term performance (Bowers et al. 2014; Shirodkar et al. 2011).

In this respect, some researches have shown that for high RA contents (≈40%) almost full blending occurs (Soleymani et al. 2000; McDaniel et al. 2012; Shirodkar et al. 2011; Kriz et al. 2014; Zhao et al. 2016). However, other authors (Al-Qadi et al. 2009; Bowers, Huang, et al. 2014; Bowers et al. 2014a; Liphardt et al. 2015) determined that layers were formed between RA and virgin binders, being stiffer in the inner part, so partial blending took place. The fresh binder used, mixing temperature, time and additives also affect the DOB. It has been shown that blending increases using soft binders (high penetration), increasing mixing temperature and time as well as in the presence of warm mix additives (Bowers et al. 2014a; Navaro et al. 2012).

2.5.2. RA and virgin binders blend design

Given that RA comes from the recovery of pavements that have been in service, considerations about its properties have to be taken into account. Therefore, in order to be re-used, RA is usually required to meet some specifications depending on the country in which it will be used. In order to meet these specifications and when the desired

percentage of RA in the mix is high, blending models for the RA binder and the virgin binder have to be used to design the final content of RA or to design a final binder with certain desired properties. Mollenhauer (2010) provides an excellent summary of the different approaches used for the blend design of RA binders from all over the world. This section provides a summary of the three most commonly used methodologies found.

2.5.2.1. EU methodology

European blending models are based on the penetration and softening point properties of the RA recovered binder and the virgin binder. European Standard BS EN 13108-8 (2005) for reclaimed asphalt sets out that the binder class of the virgin binder may be used unaltered if the mix design includes less than 10% RA for surfacing layers and less than 20% RA for base layers and binder courses. If higher proportions of RA are used, the penetration and softening point values of the binder blend are to be determined using Equations (60) and (61) respectively:

$$a \log pen_1 + b \log pen_2 = (a + b) \log pen_{mix} \quad (60)$$

where

pen_1 = penetration of the binder recovered from the RA

pen_2 = penetration of the added virgin binder

pen_{mix} = calculated penetration value of the binder in the mixture containing RA

a, b = ratios by mass of the binder from the RA and of the virgin binder respectively (a+b=1.0)

$$T_{R\&B\ mix} = a\ T_{R\&B\ 1} + b\ T_{R\&B\ 2} \quad (61)$$

where

$T_{R\&B\ 1}$= softening point of the binder recovered from the RA

$T_{R\&B\ 2}$= softening point of the added virgin binder

$T_{R\&B\ mix}$= softening point of the binder in the mixture containing RA

a, b = ratios by mass of the binder from the RA and of the virgin binder respectively (a+b=1.0)

2.5.2.2. USA methodology

NCHRP Report 452 (2001) specifies that for low RA contents (10 – 20%), it is not necessary to do tests because there is not enough of the old, hardened RA binder present in the mix to change the total binder properties. At higher RA contents, however, the RA binder will have a noticeable effect, and it must be accounted for by using a softer grade of binder. For intermediate ranges of RA, the virgin binder grade can simply be dropped one grade. However, for higher percentages of RA, RA binder has to be recovered and blend design has to be carried out. NCHRP (2001) Report 452 describes the procedure to obtain blending charts according to SUPERPAVE. This procedure is based on critical temperatures of materials and follows the prediction law (Equation (62)):

$$T_{blend} = T_{RA} * \%RA + T_{VB} * \%VB \quad (62)$$

where,

T_{blend} = critical temperature of the final blend of binders

T_{RA} = critical temperature of the RA binder

T_{VB} = critical temperature of the virgin binder used as rejuvenator

%RA = percentage of RA in the blend

%VB = percentage of virgin binder in the blend

Therefore, in order to construct blending charts, critical temperatures of the RA recovered binder have to be known. Thus, once the RA binder has been recovered, its properties have to be determined by undertaking DSR and BBR tests. Firstly, RA binder has to be tested on the DSR at high temperatures. Then, RA binder has to be aged through the RTFO test procedure and tested on the DSR at high and intermediate temperatures and on the BBR at low temperatures. With the results of these tests, critical temperatures can be determined as follows:

1. High critical temperature (T_c(High)). The slope of the stiffness-temperature curve of the unaged RAP binder is determined as ΔLog (G*/sinδ)/ΔT and Equation (63) is used:

$$T_C(High)_1 = \left(\frac{Log(1.00) - Log(G_1)}{a}\right) + T_1 \quad (63)$$

where,

G_1= the G*/sinδ value in kPa at a specific temperature T_1

a= the slope of the stiffness-temperature curve described above

The slope of the stiffness-temperature curve of the RTFOT RA binder is determined as ΔLog (G*/sinδ)/ΔT and Equation (64) is used:

$$\mathrm{T_C(High)_2} = \left(\frac{\mathrm{Log(2.2) - Log(G_1)}}{\mathrm{a}}\right) + \mathrm{T_1} \quad (64)$$

where,

G_1= the G*/sinδ value in kPa at a specific temperature T_1

a= the slope of the stiffness-temperature curve described above

$T_C(High)$is chosen between $T_C(High)_1$ and $T_C(High)_2$ as the most restrictive value (the lower one).

2. Intermediate critical temperature (Tc(Int)). The slope of the stiffness-temperature curve of the RTFOT RA binder is determined as ΔLog (G*sinδ)/ΔT and Equation (65) is used:

$$T_C(Int) = \left(\frac{Log(5000) - Log(G_1)}{a}\right) + T_1 \quad (65)$$

where,

G_1= the G*/sinδ value in kPa at a specific temperature T_1

a= the slope of the stiffness-temperature curve described above

3. Low critical temperature (Tc(Low)). The slope of the stiffness-temperature curve of the RTFOT RA binder is determined as ΔLog (S)/ΔT and Equation (66) is used:

$$T_C(Low)(S) = \left(\frac{Log(300) - Log(S_1)}{a}\right) + T_1 \quad (66)$$

where,

S_1= the S value in MPa at a specific temperature T_1

a= the slope of the stiffness-temperature curve described above

The slope of the m-temperature curve of the RTFOT RA binder is determined as Δ(m)/ΔT and Equation (67) is used:

$$T_C(\text{Low})(\text{m}) = \left(\frac{0.300 - m_1}{a}\right) + T_1 \quad (67)$$

where,

m_1= the m value at a specific temperature T_1

a= the slope of the stiffness-temperature curve described above

$T_C(Low)$is chosen between $T_C(Low)(S)$ and $T_C(Low)(m)$ as the most restrictive value (the higher one).

At this point, there are two methods to be followed depending on the available data for the mix design: RA percentage of the mix or properties of virgin binder. In the first case, when the RA content is known, an adequate virgin binder can be chosen in order to get a particular grade of the blend of the RA binder and the new one by using Equation (68):

$$T_{VB} = \frac{T_{Blend} - (\%RA \times T_{RA})}{(1 - \%RA)} \quad (68)$$

where,

T_{blend} = critical temperature of the final blend of binders

T_{RA} = critical temperature of the RA binder

T_{VB} = critical temperature of the virgin binder used as rejuvenator

%RA = percentage of RA expressed as a decimal

For the other case, when the virgin binder properties are known, the %RA can be determined as follows (Equation (69)) to obtain the desired grade of the blend:

$$\%RA = \frac{T_{blend} - T_{VB}}{T_{RA-T_{VB}}} \quad (69)$$

where each term represents the same as above.

2.5.2.3. Australian methodology

A recent report published by AUSTROADS (2013) describes a guideline for carrying out RA binder blend design. Once the RA binder has been recovered, they recommend determining the complex viscosity of the RA, the virgin binder and the rejuvenator (if it is the case) in the DSR at 60^{0}C and 1 rad/s according to AASHTO T315-12. Then, the viscosity of the blend can be predicted using the Chevron model with Equations (70) - (72):

$$VBI_i = \frac{log\vartheta_i}{3 + log\vartheta_i} \quad (70)$$

$$VBI_\beta = \sum_{i=1}^{n} x_i VBI_i \quad (71)$$

$$\mu = 10^{\left(\frac{3VBI_\beta}{1-VBI_\beta}\right)} \quad (72)$$

where,

ϑ_i = viscosity of ith component (cP)

VBI_i= viscosity blending index of ith component

VBI_β= viscosity blending index of ith component

x_i = volume fraction of ith component

μ = viscosity of the blend (cP)

In this model it is assumed for the material under study that the percentages by volume are equal to percentages by weight (neglecting differences in density). Therefore, the prediction law would follow the expression in Equation (73):

$$\mu^{1/3} = w_A \mu_A^{1/3} + w_B \mu_B^{1/3} \quad (73)$$

where,

μ = viscosity of the blend (cP)

μ_A = viscosity of component A (cP)

μ_B = viscosity of component B (cP)

w_A = weight fraction of component A (cP)

w_B = weight fraction of component B (cP)

2.5.3. RA with rejuvenating agents

Given the economic and environmental advantages of reusing RA, great efforts are currently being undertaken in order to promote its used and increase RA content in mixtures. For this purpose, when RA content is higher than a certain percentage (limitations depend on RA properties and local specifications) or when the RA contains particularly hard aged binder, it seems to be necessary to introduce another component in the asphalt mixture (in addition to the virgin binder) (Shen & Ohne 2002). This component will be responsible for restoring some of the properties that the reclaimed material had before its service life (Karlsson & Isacsson 2006; Romera et al. 2006; Tran et al. 2012; Zaumanis et al. 2013). Those materials are found in literature with different names such as rejuvenating, reclaiming, modifying, softening or recycling agents,

recycling modifiers, rejuvenators but also fluxing, extender or aromatic oils (Karlsson & Isacsson 2006).

Zaumanis et al. (2013) and Baghaee Moghaddam & Baaj (2016) highlighted the expected short and long term performance of rejuvenated binder as follows:

1. Short term. Rejuvenators should allow the production of high RA content mixtures by rapidly diffusing into the RA binder and mobilizing the aged asphalt in order to produce uniformly coated mixtures. Rejuvenators should soften the binder in order to produce a workable mixture that can be easily paved and compacted to the required density without the hazard of producing harmful emissions. Major part of diffusion process should be completed before the traffic is allowed, to avoid reduction of friction and increased susceptibility to rutting.

2. Long term. Rejuvenators should reconstitute chemical and physical properties of the aged binder and maintain stability for another service period. The binder rheology has to be altered to reduce fatigue and low temperature cracking potential without over softening the binder to cause rutting problems. Sufficient adhesion and cohesion have to be provided in the mix to prevent moisture damage and ravelling.

Rejuvenating agents are usually materials which have lower density than bitumen such as asphalt or petrol lubricants or soft bitumens (high penetration grade) (Shen & Ohne 2002). The three main current concerns about using rejuvenators in RA mixtures have been the determination of the amount of rejuvenating agent to add, the effect that it causes in the asphalt mixture performance and its diffusion process (Shen & Ohne 2002;

Karlsson & Isacsson 2006; Zaumanis, Rajib B Mallick, et al. 2013; Baghaee Moghaddam & Baaj 2016).

Carpenter & Wolosick (1980) hypothesized that the diffusion of rejuvenators into the old binder could be described in steps as follows. First, the rejuvenator created a very low-viscosity layer around the RA aggregate (coated with high viscosity binder). Then, the rejuvenator starts to penetrate into the aged binder softening the bitumen and reducing the rejuvenator layer on the surface. After a certain period of time, no raw rejuvenator remains and the diffusion of it continues. At the same time, the viscosity of the inner layer is lowered, and the viscosity of the outer layer is increased. At the end, equilibrium is achieved over the majority of the shell of binder. After a literature review on the topic, Karlsson & Isacsson (2006) concluded that this phenomenon does not restrain the creation of homogeneous recycled binder films, even though it can be time consuming (especially in cold recycling).

Regarding the rejuvenator content needed in the mixture, the traditional way to determine it has been by means of penetration and viscosity specifications, ensuring that the final binder (blend of RA binder, virgin binder and rejuvenator) had the same grade as the required target binder. However, some researchers have focused on obtaining the rejuvenator content using other methods. Shen & Ohne (2002) carried out a study to determinate the rejuvenator content basing on performance-related properties of binders using the three temperatures defined in the SHRP specification. They found linear correlations between critical temperatures and an oily rejuvenator dosage concluding that linear blending charts for SHRP properties could be used to obtain the rejuvenator

content. Furthermore, on one hand, the addition of the rejuvenator decreased the high critical temperature of the binder, meaning that the maximum rejuvenator content has to be controlled by this parameter. On the other hand, binder behaviour at intermediate and low temperatures improved with increasing rejuvenator content. The optimum rejuvenator dosage they found was later used to manufacture mixtures with RA content up to 48% (Shen et al. 2007). They concluded that rejuvenators improved mix performance in comparison to those mixtures that only contained soft virgin binder and that RA content could be increased by up to 10% by using rejuvenators.

Romera et al. (2006) undertook a study with three rejuvenating agents: aliphatic-aromatic commercial oil, aliphatic aromatic motor recycling oil and a 150/200 penetration grade bitumen. They chose the rejuvenator dosage by adjusting the final penetration grade of the blend to a target penetration. Through the use of rejuvenators, they managed to increase RA binder flexibility and therefore thermal cracking resistance. Furthermore, rutting resistance was not negatively affected and viscosity results showed that the manufacture temperature of a RA mix could be decreased with the addition of rejuvenating agents.

Tran et al. (2012) conducted an investigation with 50% RA mixtures and rejuvenating agents. Rejuvenator content was determined using the same approach as Shen & Ohne (2002) obtaining again good linear correlations between rejuvenator dosages and critical temperatures. They concluded that rejuvenating agents improved cracking resistance of mixture without adversely affecting rutting resistance and moisture damage.

Zaumanis et al. (2013) studied the performance of six rejuvenating agents including aromatic extract, waste engine oil, tall oil, organic oil, waste vegetable oil and waste vegetable grease. Rejuvenator dosage was chosen basing on previous work of the authors using penetration and binder film thickness as the design parameters (Zaumanis et al. 2013a). Their results showed that none of the rejuvenators used decreased the high critical temperature of the RA recovered binders arguing that if adequate dose of rejuvenator is used and good diffusion occurs in asphalt binder film, there is no danger of increased rutting susceptibility with the use of rejuvenators. In addition, all the recycling agents were able to improve low critical temperatures by around 10^0C and reduce binder viscosity allowing a decrease in the mixture manufacture temperature by 15-25^{0}C. Furthermore, all the rejuvenated binders met the SHRP fatigue resistance requirements.

Going further, Zaumanis at al. (2014b) manufactured 100% RA mixtures using the six rejuvenators and dosages explained above (Zaumanis et al., 2013). They found that all the rejuvenated RA mixtures exhibited good rutting resistance, improved thermal cracking resistance in comparison to non-rejuvenated RA mixtures and even equal or better performance than the virgin one. Mix workability was enhanced compared to RA although it remained worse than that of the virgin mixture. They concluded that the application of organic products as recycling agents require much lower dosage than petroleum ones and are able to obtain the same rejuvenating effect. In addition, based on the good results obtained, they proposed to use penetration to calculate the amount of rejuvenator needed, following Equations (74) and (75):

$$PEN = A \cdot e^{B \cdot Dose} \quad (74)$$

$$Dose = \frac{ln\frac{PEN}{A}}{B} \quad (75)$$

Where PEN is the penetration (dmm), Dose is the dose of rejuvenating agent (%), A is the penetration at 0% dose of rejuvenating agent and B is the constant calculated by least squares fit through data points.

Ongel & Hugener (2015) also studied the use of rejuvenators in 100% RA mixtures. They concluded that this practice is possible and that in fact, the ageing of RA binders with rejuvenators seems to be slower than that of virgin binders. Regarding the ageing of recycled materials with rejuvenators, Poulikakos et al. (2014) also showed the equivalent performance of an aged mixture with 40% RA to virgin ones.

Yang & Lee (2016) recently developed a methodology to determine the optimum amount of rejuvenator for RA mixtures whose RA binder is highly aged. For this purpose, they modified the Asphalt Institute methodology using viscosity as the design parameter for rejuvenator dosage. With the designed dosages, they obtained rejuvenated binders which showed improved rutting performance compared to virgin binders and that were able to bring the RA binder to the "safe" area according to the Glower-Rowe parameter in terms of fatigue cracking.

2.6.Biobinders

Peralta et al. (2012) defined biobinders as asphalt binder alternatives made from any non-petroleum-based renewable resources, which should not rival any food material, and have

environmental and economic benefits. The interest of using biobinders in pavement engineering has significantly grown over the last decades due to the increasing scarcity of raw materials and environmental concern about the use of non-recoverable natural resources from crude oil. Crude oil is a finite resource whose production is predicted to decrease in the future. In fact, this has already produced changes in some refineries strategies which are installing cokers towards the production of light products and the bitumen supply could decrease (Lavoie 2011). Thereby, environmental degradation, depleting petroleum reserves and price-spiking of bitumen encourage researchers to seek for alternative materials for asphalt mixtures (Aziz et al. 2015).

According to literature, biobinders can be utilized in three different ways to decrease the demand for fossil fuel based bituminous binders: (1) as a bitumen modifier (<10% bitumen replacement), (2) as a bitumen extender (25% to 75% bitumen replacement), and (3) as a direct alternative binder (100% replacement) (Airey, Mohammed, & Fichter, 2008; Peralta et al., 2012; Raouf, 2010). According to the review conducted by Mamat et al. (2015) on the use of biobinders for asphalt mixture, most of the current studies focus on the first use mentioned, adding <10% of biobinders in the mixture. These researchers established the need to go further in the use and study of biobinders in order to maximise their potential.

Biobinders could be produced from many different natural resources such as agricultural crops, municipal wastes, agricultural and forestry byproducts, sugar, molasses and rice, corn and potato starches, natural tree and gum resins, natural latex rubber and vegetable oils, lignin, cellulose, palm oil waste, coconut waste, etc. (Peralta et al. 2012). In this

sense, through the application of scientific research and development, a range of different vegetable oils have been investigated to determine their physical and chemical properties to study their applicability to be used as biobinders for roads (Airey et al., 2008; Airey & Mohammed, 2008; Tan & Man, 2002).

First of all, before considering the use of new materials as binders, Kluttz (2012) presented some considerations to take into account during a workshop entitled "Alternative Binders for Sustainable Asphalt Pavements", which took place in January 2012 in Washington D.C. Kluttz (2012) highlighted some of the issues around substituting other materials for some or all of the bitumen in conventional paving mixes. In this sense, he pointed out that the alternative materials should have predictable properties regarding ageing, rheology, adhesion to aggregates, coating behavior in a mix plant and flow characteristic during construction. Furthermore, Kluttz (2012) added other less obvious assumptions to take into account such as predictable leaching characteristics, water solubility, interaction with fuels or oils, environmental issues, odor and mixing with binders as in reclaimed asphalt mixtures. In addition, Raman et al. (2015) highlighted the need to study the relationship between the rheological properties and performance of biobinders and asphalt mixtures produced with them. Finally, Aziz et al. (2015) pointed out the importance of studying biobinders and bio-mixtures from the engineering point of view, analysing their mechanical performance in terms of rutting, fatigue, moisture damage, thermal cracking and ageing behaviour. These aspects could serve as a starting point for evaluating new binders for pavements.

2.6.1. 100% bitumen replacement studies

Studies present in this section include those whose aim is to completely substitute bitumen in asphalt mixtures.

In this sense, Airey & Mohammed (2008) carried out a first-step investigation on the potential of three types of acrylate-based polymer binders to replace bitumen and thereby reduce its demand. Binders consisted of polyethyl acrylate (PEA), polymethyl (PMA) acrylate and polybutyl acrylate (PBA). Chemical and rheological properties of the binders were analyzed. Results showed that PEA could simulate a 100/150 penetration grade bitumen, while PMA could be similar to a stiff 10/20 penetration grade bitumen. On the other hand, PBA was dismissed because of its high viscous nature and low dynamic moduli. Further studies with PEA and PMA (Airey et al., 2008) blended these materials with conventional bitumens in 1:1 or 3:1 ratios. Those blends were found to produce similar rheological properties to SBS polymer modified bitumens although not identical viscous behaviour.

Raouf (2010) developed his thesis on the use of non-petroleum binders derived from fast pyrolysis bio-oils in flexible pavements. In particular, he produced biobinders from oakwood, switchgrass and corn stover bio-oils. He found that biobinder performance-related properties may differ from those of conventional bitumen and their polymer modification changes those properties significantly. Moreover, biobinders could improve rutting resistance in comparison to bitumen but not low temperature behaviour.

In the case of the switchgrass bio-oil, Raouf & Williams (2010) showed that the relationship between viscosity and temperature and shear rate could be well described by

Arrhenius-type and Power law models, respectively, or by a log linear relationship. They concluded that the rheological properties of switchgrass bio-oils were similar and comparable to bitumen binders and represented a viable renewable alternative to petroleum derived asphalt binders.

Chailleux et al. (2012) proposed the use of residues of microalgae from which some proteins had been removed and studied the lipid fractions. They carried out a chemical and rheological analysis of samples with different algaenan (fatty acid polymer) percentages mixed with free fatty acid oil. The authors concluded that the design of microalgae-based road binders should be feasible. They found that these materials could show similar rheological properties to those of bitumen through the adjustment of the algaenans percentage in the oil.

Peralta et al. (2012a) aimed to develop a biobinder which could 100% replace bitumen in mixtures by using bio-oil and crumb rubber. This approach was developed in order to upgrade bio-oil behavior at low temperature to enhance its resistance to thermal cracking. Bio-oil was derived from the fast pyrolysis of red oak wood residues in the Iowa State University pyrolysis unit and two sources of crumb rubber from used tires from different suppliers were tested by adding them a 10% and 15%. They found that crumb rubber could be effectively blended with the bio-oil at 125^0C, which is a significantly lower temperature than those used for the blend with bitumens (usually around 180^0C). Regarding the performance, high and intermediate critical temperatures compared very well with those of a PG 64-16 bitumen. In addition, low critical temperatures of all

biobinders remained below -10^{0}C. Further work about ageing, mixtures and field performance still needs to be carried out.

Pouget & Loup (2013) studied the performance of two biobinders to totally replace bitumen in asphalt mixtures in terms of complex modulus, direct tensile strength and thermal cracking. In addition, they analysed the ageing and LVE properties of the mixtures. They found similar properties between the bio-mixtures and the reference one in terms of modulus, tensile strength and thermal cracking resistance. Regarding ageing, the bio-mixtures showed higher sensitivity than the conventional one being characterized by a significant stiffening and decrease in viscous response. They established that the ageing of bio-mixtures is a discriminatory issue and should be carefully studied.

2.6.2. Use of biobinders as bitumen extenders

This part reviews the current studies found which use biobinders as bitumen extenders in terms of 20% to 75% replacement.

Wen, Bhusal, & Wen (2012) carried out a laboratory evaluation of waste cooking oil-based biobinder. For their investigation, biobinder was mixed with PG 58-28 bitumen at 30% and 60% by weight of base binder, and at 10% and 30% with PG 76-16 and PG 82-16 bitumens. This distinction was made based on previous studies that suggested that biobinders could reduce thermal cracking resistance of bitumens. PG testing, critical strain energy density determination and MSCR tests were undertaken for the binders. All HMA mixtures were designed following the Superpave design method and manufactured by increasing conventional mixing temperature in 5^{0}C to obtain coating uniformity of the aggregates. In addition, mixtures were allowed to cure for 2h before compaction.

Dynamic modulus, flow number, indirect tensile and moisture damage tests were carried out for mixtures. After this testing, they found that for binders the addition of biobinders decreased rutting and fatigue resistance but increased thermal cracking resistance. Mixtures results were in accordance with those for binders, adding that the mixtures passed the AASHTO moisture damage requirements.

Mohammad et al. (2013) conducted a study on the use of bio-binders made from pine wood chips and processed by fast pyrolysis. Biobinders and mixtures manufactured with 20%, 25.5%, 30% and 50% of biobinders content were analyzed. They found that the use of biobinders did not change the PG of the base bitumen used. In addition, regarding mixtures, rutting performance was similar or better than that of the non-modified bitumen; almost all the mixtures passed the moisture susceptibility criteria and showed improved low-temperature performance. However, at intermediate temperatures, mixtures with biobinders exhibited less cracking resistance than the conventional one.

Yang & Suciptan (2016) used local Japanese cedar chips from the residue of the wood processing industry as asphalt binder modifier (2% and 8% blending) and as asphalt binder extender (25% and 50% blending). They showed that 50% blend exhibited phase separation after high heating conditions and was the only blend showing clear differences in the performance of the binder compared to the reference one, increasing the high PG by one grade. All blends showed better rutting performance than the base binder.

2.6.3. Use of biobinders as bitumen modifiers

This section deals with researches that used biobinders as bitumen modifiers, i.e. replacing bitumen with biobinders by less than 20% in the mixture.

Williams et al. (2009) conducted a study using fractioned bio-oil in bitumen from three biomass sources: oak wood, switchgrass and corn stover. These biobinders were blended with base bitumen at 3%, 5% and 9% by the mass of bitumen. Rheological properties showed that the biomodification of the bitumen lead to an improvement of the rutting parameter ($G^*/\sin\delta$) of the base bitumen. However, the biobinder decreased thermal cracking resistance.

Fini et al. (2011) and Fini et al. (2012) carried out a study on the use of biobinder made from swine manure. Swine manure was hydrothermically processed to produce bio-oil. This bio-oil was fractionated to extract water, solid residue, and some of the organic compounds. The residue after fractionation was used as a replacement for bitumen. In order to study biobinder rheological properties, it was blended with a PG 64-22 bitumen by 2%, 5% and 10% of weight of base binder. Biomodified bitumen showed decreased viscosity which could allow the reduction of mixing and compaction temperatures of mixes. In addition, cracking temperatures and complex modulus were lower as biobinder content increased. Reduction in cracking temperature was a sign of low-temperature performance improvement. However, reduction in complex modulus could lead to rutting issues. Improvement in thermal cracking resistance of the biomodified bitumen was further corroborated by You et al. (2011) by means of the Asphalt Binder Cracking Device (ABCD) test. Fini & Buehler (2012) attributed the enhancement of low-temperature properties of the biomodified binder to an extension of amorphous region due to reduced crystallization of bitumen molecules because of the presence of bio-binder. This hypothesis was confirmed by X-ray powder diffraction tests and molecular dynamic simulation.

Seidel & Haddock (2012) investigated high-temperature rheological performance of conventional and reclaimed bitumen modified with 1% and 3% of soy fatty acids (a specific portion of soybean oil). Rotational viscosity and small strain linearity were evaluated for all of them, and just the complex modulus of the reclaimed bitumen. They concluded that the soy fatty acids decreased the viscosity and stiffness of all the binders they could be used to make stiff binders more workable (such as reclaimed asphalts). However, the softening effect decreased as the testing temperature increased.

Zofka & Yut (2012) tried to use waste coffee beans as antioxidant bitumen modifiers by adding 2% and 4% to a PG 64-22 bitumen. This modification did not change temperature susceptibility of the binder but neither reduced oxidation. They concluded that coffee beans added served as a solvent rather than as an antioxidant.

Fini, Oldham, & Abu-Lebdeh (2013) studied the combination of biobinder made from swine manure and crumb rubber technologies. For this purpose, they modified a PG 64-22 bitumen with 5% of biobinders and 5%, 10% and 15% of scrap tires crumb rubber. The researchers found that biomodified rubber binder had comparable properties with the CRM binder. In addition, the introduction of the biobinder to the CRM binder was beneficial in improving the low temperature property of the CRM binder while also reducing the CRM binder overall viscosity.

Mills-Beale et al. (2014) completed the characterization of swine manure biobinders through the study of its ageing behavior. They proved that the addition of 5% by weight of biobinders to a PG 64-22 base bitumen reduced the effect of RTFOT ageing by 28.9% and of PAV-ageing by 62.9%.

Aflaki et al. (2014) compared the modification of bitumen with biobinders made from swine manure with other common modification of binders (such as SBS polymers, Gilsonite, polyphosphoric acid or crumb rubber). A PG 64-22 bitumen was modified with 2%, 5% and 10% by weight of a conventional bitumen. Burger's model was used to characterize low-temperature performance of the binders by calculating dissipated energy ratio and the derivation of creep compliance. Biobinder showed the highest energy dissipation ratio which means an improvement of low-temperature behaviour.

Xue et al. (2014) modified asphalt binder with different percentages ranged from 0-20% of ashes made from rice husk and wood sawdust. This modification showed good storage stability when the modifier content was less than 20%. In addition, both modifications exhibited improved viscosity, complex modulus and rutting resistance in comparison with the base bitumen, as well as similar performance after ageing.

Yang, et al. (2014) conducted an investigation on the blend of bio-oil from waste wood resources (5% and 10% by weight of binders) and conventional binders to produce mixtures with biobinders. They found that this modification improved fatigue resistance of the mixtures without adversely compromising rutting resistance and dynamic modulus but slightly reducing the tensile strength. In this sense, they proposed the further used of bio-oils as bitumen modifiers or extenders. However, recently, Yang et al. (2017) studied the chemical characterisation, oxidative ageing and compatibility of bitumen with this bio-oil, suggesting that low percentages (2%) should be used to ensure the stable performance of the blend.

Yang & You (2015) use three bio-oils to modify a base bitumen at 5% and 10% rate. The first bio-oil came from waste wood fast pyrolysis; they produced the second one by reducing the moisture content of the first; and the third bio-oil by adding 0.4% polymer content to the second. They found an improved high-temperature performance of the three bio-modified binders in comparison to the control one, and higher improvement with increased bio-oil content.

Somé et al. (2016) analysed the effect of vegetable oil additives in asphalt mixtures and binder properties in laboratory and field. The additives consisted of a methyl ester of a fatty acid from sunflower and of a plant resin fluxed with monoalkyl esters from vegetable and animal oils. They were blended with a base bitumen at 0.5% and 5%. They found that the additive rejuvenated the base bitumen which seemed promising to be used with RA. They found that the binders with additive were more sensitive to ageing than non-modified binders. However, the performance of the mixtures was good after five years of service life. Finally, they modelled the LVE properties of binders and mixtures using a modified Huet-Sayegh model. The LVE properties were very sensitive to the additive content. Regarding LVE of mixtures and binders, they did not find exactly the same corresponding parameters as Olard & Di Benedetto (2003) suggested for the 2S2P1D model, but similar ones.

Zhang et al. (2017) studied the viscosity, rutting performance and temperature sensitivity of a SBS-polymer modified binder with bio-oil from biomass pyrolysis added up to 20%. Before RTFOT, the SBS-bio-modified binders exhibited higher viscosity, lower rutting resistance and lower temperature sensitivity (decreasing with increasing bio-oil content)

than the base binder. However, after RTFOT-ageing, the rutting performance of the SBS-bio-modified binder was better than the base binder, and improved with increased bio-oil content. The temperature sensitivity was still lower than the base binder, but increased with increasing bio-oil content. This study highlighted the importance of the characterisation of biobinders before and after ageing.

Sun et al. (2016) used the residue from waste cooking oil refined for biodiesel to modify a base bitumen from 2% to 8%. They found that the addition of the bio-modifier decreased the viscosity of the base binder, decreased the high-temperature performance but improved fatigue and low-temperature features. Finally they recommended to use 4% of this modifier and suggested to use the modified binder for recycling asphalt mixtures.

In addition, Gong et al. (2016) investigated properties of bio-additives from waste cooking oil to rejuvenate aged conventional and SBS-modified binders at 1.5%, 1.75% and 2%. They showed that the bio-modification improved workability and rheology of the aged binders so bio-oil appears to be a suitable rejuvenator for bitumen. However, anti-moisture properties should be improve and they highlighted the need for further ageing and fatigue studies.

In this regard, the use of bio-oils has recently been focused on the recycling of asphalt mixtures as rejuvenators. Hill et al. (2013) continued the study of biobinders made from swine manure by using them in RA mixtures. They used a 5% of biomodification in mixtures with 0%, 15% and 45% of RA by weight of mixture. Low-temperature performance of these mixtures and a reference hot mix asphalt mixture was studied by means of Disk-shaped compact tension, indirect tension, and acoustic emission tests.

They concluded that the presence of biobinders increased fracture energy for all RA levels, being higher than that of the hot mix asphalt. In general, biomodified RA mixtures showed better low-temperature performance than hot mix asphalt mixtures. The authors expanded the study of the low-temperature performance of bio-mixtures by introducing three more bio-oils produced with wood, miscanthus and corn stover (Hill et al. 2016; Fini et al. 2016). The results showed that the bio-mixtures had better fracture performance and the effect of increased RA content was less unfavorable than for reference mixtures.

Nayak & Sahoo (2015) used 5%, 10% and 15% of pongamia oil and a composite rejuvenator made of castor oil and coke oven gas condensate to treat a RA binder. They found great potential for the use of these materials showing improved rutting and fatigue performance as well as adequate thermal stability. However, further research on asphalt mixtures was needed. They extended the study (Nayak & Sahoo 2016) of the rejuvenating effect of these oils by means of infrared spectroscopy to obtain the carbonyl index (which should decrease with rejuvenation) and compare. They found that the pongamia oil had an unexpected effect on the aged binder increasing the carbonyl index due to the presence of ketone groups in the oil, which might not be misunderstood as ageing. Based on all properties studied, they finally selected an optimum content of 5% bio-modifier for further study of RA mixtures.

Mogawer et al. (2016) used 5% of biobinder obtained from swine manure in mixtures with 40% RA. They found that the bio-modified binder improved the fatigue resistance of the mixture, with respect to the one without modifier, without adversely affecting rutting and moisture damage properties. They also found good blending between the RA

binder and biobinders, determined by comparison of predicted and measured values of dynamic modulus.

Zhu et al. (2017), as a continuation of the work of Gong et al. (2016), used 5% and 10% of bio-rejuvenator from waste cooking oil to restore the properties of conventional and SBS-modified binders. They determined that the fatigue properties of the rejuvenated binders were improved with respect to the aged binders but could not be equivalent to those of the virgin one. Rutting resistance slightly decreased due to the addition of the rejuvenators. The effect on low temperature properties depended on the base binder with the rejuvenation being more effective for the SBS-modified binder. In terms of ageing, the asphaltenes content of PAV-aged bitumen could be reduced by the addition of the bio-rejuvenator.

The only study found on the analysis of the adhesion properties of biobinders was recently performed by Gong et al. (2017) using a sessile drop device to determine the contact angle and surface free energy. Biobinders were produced with base bitumen and 1%, 2% and 3% of bio-modifier. They concluded that the adhesion properties of the biobinders depend on the compatibility of the bio-additive and the base bitumen. Therefore, it is greatly importance to characterise these properties for new materials.

2.7.Conclusions

After the literature review undertaken, the following main conclusions can be drawn about each of the topics that have been addressed:

- Asphalt mixtures are viscoelastic materials made of aggregates and binder. Their main function is to provide a comfortable, safe and resilient structure for roads. For this, asphalt mixtures have to resist the loads of traffic and climate changes. The main distresses affecting asphalt mixtures, and partially controlled by their binders, are rutting, fatigue, thermal cracking, moisture damage and ageing.
- RA has shown great potential to be reused in roads. In addition, the use of RA leads to cost and raw material savings which make it being a very environmental friendly solution for the construction or maintenance of pavements. However, their use is still limited due to the current lack of confidence in their performance and therefore research efforts are being made to increase RA content in mixtures.
- Current methodologies used for the design of binders with RA and virgin bitumen assume that full blending occurs between them. However, authors have shown that partial blending may take place. DOB is therefore an important parameter to consider when designing RA mixtures.
- The use of rejuvenators looks promising in order to increase RA content in mixtures. Rejuvenators have shown to improve fatigue and thermal cracking of asphalt mixtures in comparison to mixtures with no rejuvenators.
- Many research studies have been carried out about different biobinders. The review of these studies has revealed that biobinders behaviour is really dependant on their composition. In this sense, there are biobinders that have shown good rutting resistance while others improved bitumen low-temperature performance. The same testing as that used for conventional bitumens can be applied to biobinders. The influence of the different biobinders composition on the main

properties of binders for asphalt mixtures has been summarised in the table in Annex I.

- To be used in asphalt mixtures, as a first characterisation, biobinders are recommended to show similar conventional properties (penetration, softening point, etc.) and LVE properties (stiffness, elastic/viscous components, critical temperatures, etc.) to commonly used binders in order to know what to expect from their performance. Their viscosity must be adequate to be able to manufacture asphalt mixtures in conventional asphalt plants. Next, they should exhibit good or at least comparable resistance to conventional binders in terms of the main distresses they could such as rutting, fatigue, thermal cracking, moisture damage and ageing. Biobinders must be miscible and stable if they are combined with conventional or RA binders. Finally, if they are meant to be used with RA, they should provide the desire rejuvenating effect on the RA binder (lowering stiffness and increasing the viscous component as conventional rejuvenators). These properties should be studied at binder and mixture level to provide total confidence to their performance.
- In this regard, biobinders have shown promising performance in order to reduce bitumen demand by totally or partially replacing bitumen. Extensively research has been conducted on the use of biobinders as bitumen modifiers (i.e. <10% bitumen replacement) but less results are found in terms of total replacement of bitumen.

- Recently, the use of biobinders in combination with RA have shown promising results in terms of improving the performance of RA mixtures and increasing the utilization of recycled material.
- The performance of biobinders and asphalt mixtures containing biobinders have to be fully characterised in terms of rheological, performance-related and ageing properties. The performance should be tested over the whole range of service temperatures of asphalt mixtures, due to the different behaviour provided by different biobinders depending on their nature.

CHAPTER 3. CHARACTERISATION OF BINDERS

3. CHARACTERISATION OF BINDERS

This chapter shows the results of the conventional, rheological and ageing characterisation of the binders described in Section 1.4.

3.1. Conventional characterisation

The RA binder, biobinders and control 50/70 penetration grade bitumen were tested to obtain their conventional properties according to European standards for penetration (EN 1426 2015), softening point (EN 1427 2015) and Fraass breaking point (EN 12593 2015). As established before, the BioBinder made from pine resin and linseed oil is an adaptable material whose composition (proportion of each component) will be defined after the asphalt mixture design to meet certain requirements. Therefore, in order to have initial reference values of the behaviour this material, it was decided to blend the resin and the oil in two percentages by mass:

1. BB 75/25 = 75% Resin + 25% Oil
2. BB 85/15 = 85% Resin + 15% Oil

Figure 52 shows the softening point test performed on these BioBinders.

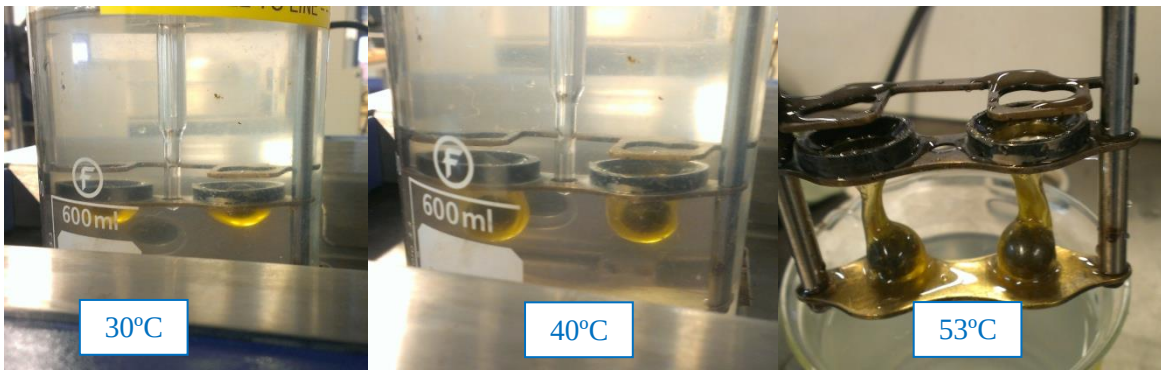


Figure 52. Softening point Ring&Ball test on BB75/25

3.2.Rheological and ageing characterisation

In terms of rheological characterisation, the RA binder, biobinders and control 50/70 penetration grade bitumen were tested to obtain their rotational viscosity and their LVE properties.

A Brookfield viscometer was used to obtain the rotational viscosity from 60 to 200°C depending on the material (hard binders could not be tested at the lower temperatures due to the very high torque needed) keeping the torque as close as possible to 50% of maximum torque (EN 13302 2010).

To obtain the LVE properties of the binders over the whole range of service temperatures of asphalt pavements, they were subjected to temperature and frequency sweeps on a Dynamic Shear Rheometer (DSR) from 0 to 80°C and from 0.1 to 10 Hz. The materials were tested in strain-controlled mode within their LVE range of strain. The LVE range of strain was defined performing strain sweeps from 0.1 to 10% of strain, considering that the LVE range of strain is that for which the norm of the complex modulus decreases up to 5% of the initial value, as shown in Figure 22 in Section 2.4.1.4 of the literature review. To carry out the frequency and temperature sweeps, two parallel-plate geometries were used: 25mm and 8mm diameter (Figure 53). The 25mm geometry was used with a 1mm gap from 30 to 80°C, while the 8mm geometry was used with 2mm gap from 0 to 40°C. In this way, two temperatures were overlapped to later choose the correct one using the Black diagram (Airey 2002). Next, the master curves of the norm of the complex modulus and phase angle of the binders were obtained at a reference temperature of 20°C.

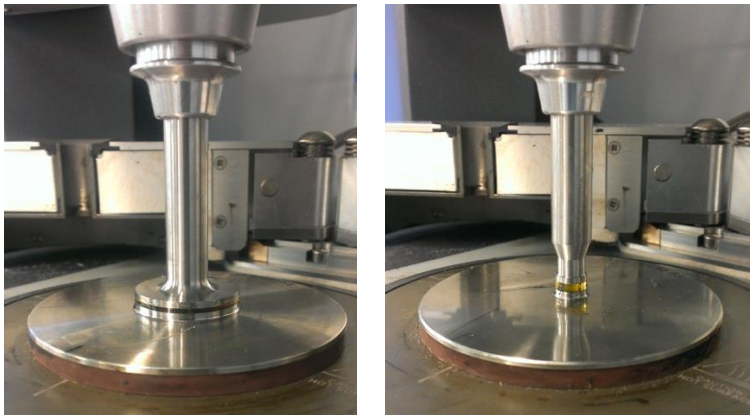


Figure 53. Parallel-plate geometries on a DSR for biobinders testing: 25mm (left) and 8mm (right)

For the study of the ageing properties of the binders and blends, they were subjected to short and long term ageing. Short term ageing, which aims at simulating the ageing that the binders suffer during the manufacturing of the mixture in an asphalt plant, was performed by RTFOT (EN 12607-1, 2014). Long term ageing, which aims at simulating the ageing that the binders suffer after a number of years of service of the pavement, was carried out by means of RTFOT and consecutive PAV test (EN 14769 2012) during 20h at 100°C and 2.1MPa of pressure. The aged binders were then rheologically characterised following the same procedure described above for the unaged binder for comparison. In addition, the RTFOT+PAV aged binders were tested at low temperatures (<0ºC) in the BBR to obtain their stiffness and m-value.

This characterisation of the unaged and aged binders allowed their high, intermediate and low critical temperatures according to Superpave (SHRP 1994) as described in Section 2.3.5.1 of the literature review to be obtained. These critical temperatures are performance-related parameters which provide an initial idea of the performance of the binders for some of the main distresses occurring in asphalt pavements: rutting, fatigue and thermal cracking.

3.3.Results and discussion

3.3.1. Conventional properties

Table 8 shows the conventional properties of the binders. Taking the results of the 50/70 penetration grade bitumen as a reference for a standard virgin binder in asphalt mixtures, it can be observed that the extracted RA binder comes from an aged source showing low penetration, high softening point and high Fraass breaking point. On the other hand, BP shows a high penetration value while keeping high softening point and low Fraass breaking point. This fact reflects the SBS polymer modification, which allows a soft binder to have high softening point. In the case of the BioBinders, the two proportions selected seem to be extreme points for its composition and show the strong dependency of the BioBinder consistency on resin and oil proportions (i.e. only varying by 10% the resin content significantly changes the binder properties). Thereby, BB75/25 is a very soft material with high penetration, low softening point and low Fraass breaking point. On the contrary, BB85/15 is a harder material with penetration and softening point within the limits of a conventional 20/30 penetration grade bitumen (EN 12591, 2009) but with a very high Fraass breaking point, due to the amount of resin it contains. The resin is a significantly brittle material at low temperatures which produced the relatively high cracking temperature of BB85/15 during the determination of the Fraass breaking point. The extreme properties of BB75/25 and BB85/15 revealed the importance of undertaking a careful design of the resin and oil proportions. This task is described in Section 4.4.

Table 8. Binders' conventional properties

Binder	Name	Penetration at 25°C (x 0.1mm)	Softening point (°C)	Fraass breaking point (°C)
Recovered RA Binder(*)	RA	9	75.8	+4.0
BioPhalt®	BP	146	73.5	-15.0
BioBinder 75/25	BB75/25	444	27.1	-17.0
BioBinder 85/15	BB85/15	26	53.0	+10.0
50/70 Pen bitumen	50/70	68	48	-8.0

(*)This RA binder is a 50-50 blend of the RA binders recovered from the two fractions available, being therefore a first approach before having the mixture design with the percentages of each fraction that the mixtures will have.

3.3.2. Rheological characterisation

Figure 54 displays the results of the viscosity of the binders at different temperatures. The RA binder and BP show high viscosity when compared to the 50/70 penetration grade bitumen. In the case of the RA binder, the high viscosity has to be attributed to its aged state and hard consistency. In the case of BP, the high viscosity is due to its SBS-polymer modification which increases the viscosity of binders. BB75/25 and BB85/15 show very different viscosity values highlighting in this case the importance of the resin and oil content for its rheological properties. Analysing Figure 54 in terms of Superpave specification (SHRP 1994) (3000mPa.s at 135^{0}C – red line in the figure) for the use of binders in the manufacturing of asphalt mixtures, it can be observed that all the binders meet the requirement having viscosity <3000mPa.s at 135^{0}C. In addition, the decrease of the viscosity with temperature of all the materials follow a power law.

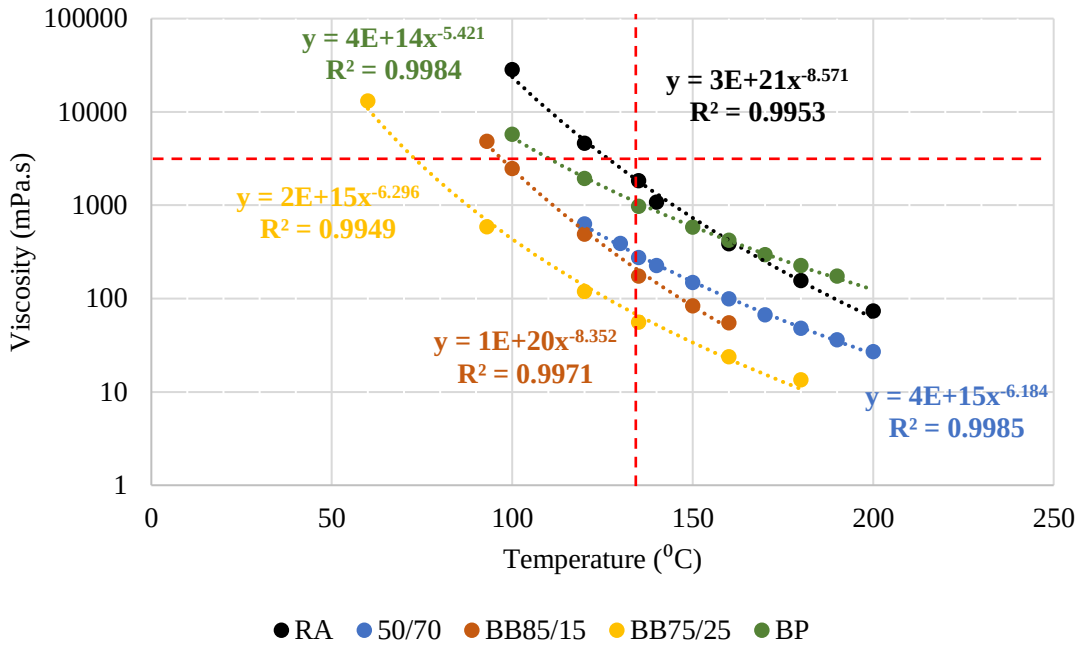


Figure 54. Binders' rotational viscosity

Figure 55 shows the Black diagram of the binders which allows the different viscoelastic behaviour of the materials to be observed. In the Black diagram, high modulus values represent the results at low temperature and vice versa. All binders except BP exhibit thermorheologically simple behaviour over the range of frequencies and temperatures tested since their curves in the Black diagram smoothly overlap for the different temperatures and frequencies. Therefore, the TTSP can be applied to obtain master curves of the binders. The fact that BP does not show this type of curve is probably due to its high polymer content, which is also responsible for the increase of elastic response (i.e. decrease of phase angle) at high temperatures, as indicated in Figure 55. For this binder, at high temperature, the binder becomes soft and the polymer network dominates the behaviour allowing an increased elastic response. However, if temperature keeps increasing, polymers become soft and viscous and consequently the phase angle increases again. Despite these facts, Di Benedetto et al. (2004) showed through their PTTSP that master curves of non-thermorheologically simple materials, such as BP, can still be produced for comparison.

In this regard, Figures 56 and 57 display the master curves of the norm of the shear complex modulus (|G*|) and phase angle (δ) of the binders at a reference temperature of 20ºC respectively.

Figure **56** allows the stiffness of the materials in terms of complex modulus to be compared showing the high value of the RA binder compared to the conventional 50/70 bitumen. This fact, together with the low penetration shown in Table 8, reveals the need for rejuvenation of this source of RA if it is to be used in high amounts in new asphalt mixtures.

Figure 56 shows BB85/15 complex modulus to be significantly dependent on the frequency, being even higher than that of RA at high frequencies. On the contrary, BB75/25 is a soft

material with low complex modulus. Finally, BP shows a different shape of the master curve to the others due to its nature and modification as well as having low complex modulus.

In terms of phase angle (Figure 57), BB85/15 and BB75/25 show a value of 90^0 for a wide range of frequencies compared to the conventional 50/70 revealing therefore their highly viscous component. On the other hand, RA does not reach 90^0 at any frequency and BP presents a high elastic response (component) already observed in the Black space (Figure 55). The complex modulus and phase angle of BP seem to be adequate to be used in high RA content mixtures in the sense that its blend with RA could produce a 50/70 penetration binder. The increased elastic response of BP at high temperatures would help rutting resistance, its lower complex modulus at intermediate temperatures would help fatigue and the low temperature performance can be expected to be the same than the 50/70 (Figure 55). These facts are further discussed with the critical temperatures in Section 3.2.1.1. In the case of BioBinders (resin+oil), the data shows that they are very adaptable by changing the proportion of their components. In this regard, the proportions required to mimic a 50/70 penetration when blended with the RA binder can be worked out. This procedure will be shown in Section 4.4.

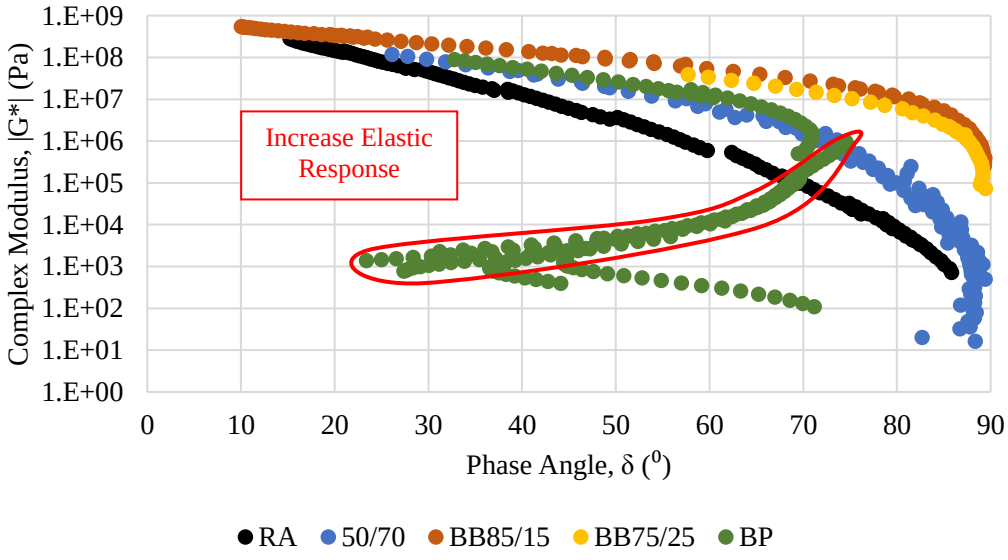


Figure 55. Black diagram of binders

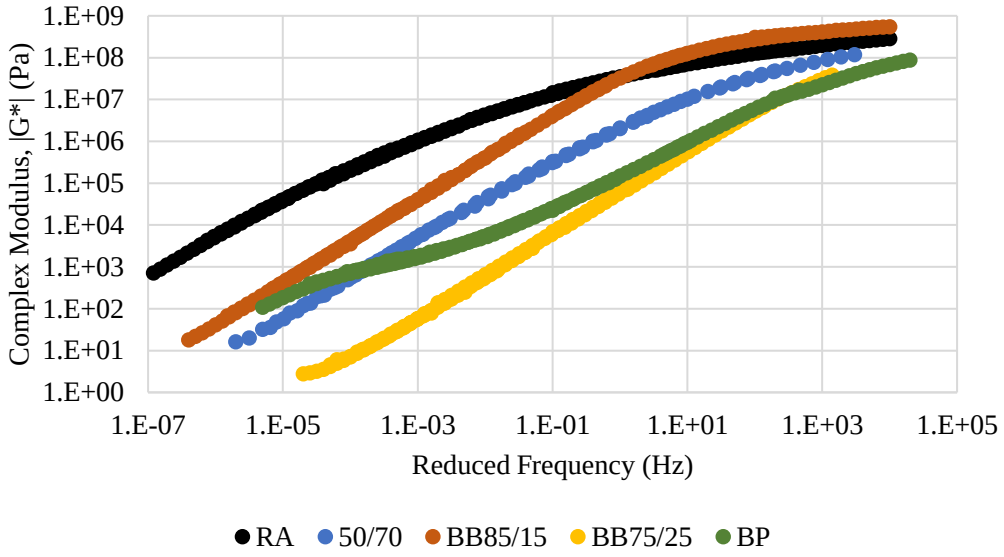


Figure 56. Master curve of the norm of the complex modulus of binders at 20^{o}C

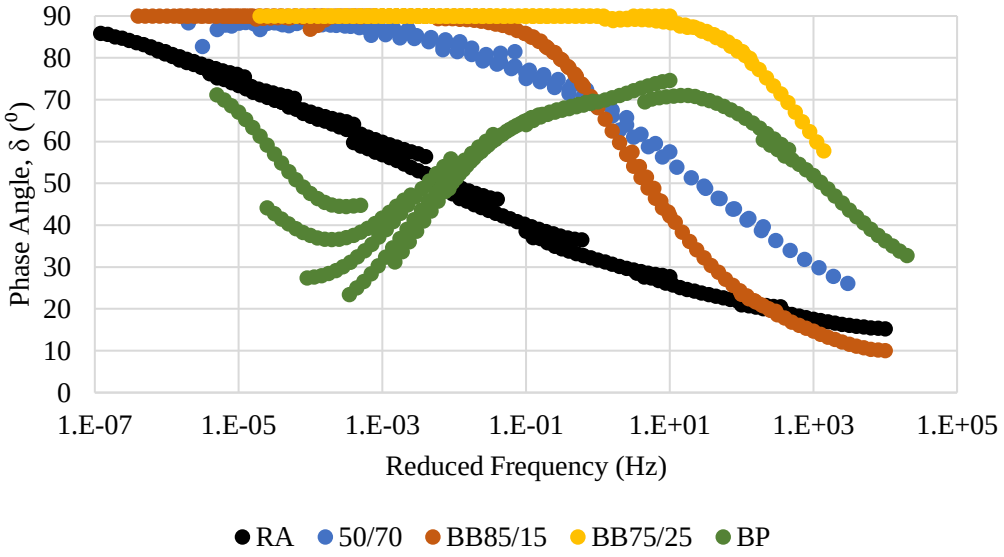


Figure 57. Master curve of phase angle of binders at 20°C

3.3.3. Ageing properties

The results of the frequency and temperature sweeps of the unaged and aged binders are shown in terms of master curves of the norm of the complex modulus and phase angle at a reference temperature of 20ºC in Figures 58, 59, 60 and 61. As reported in Section 2.3.3, in the literature review, the ageing of conventional binders (non-modified) produces an increase in their

complex modulus and decrease of phase angle (Lu & Isacsson 2002). This behaviour is reflected in Figures 59, 60 and 61 for BB75/25, BB85/15 and the 50/70 penetration grade binder respectively which do not contain any polymer modification. On one hand, the 50/70 penetration grade bitumen and BB75/25 gradually change their rheology with the progressive ageing becoming stiffer and more elastic (lower phase angle). On the other hand, BB85/15 seems to be affected by RTFOT ageing but does not show greater changes after PAV. The different ageing behaviour of BB75/25 and BB85/15 has to be attributed to their different resin and oil content and seems to imply that the resin suffers greater ageing during the manufacturing of the asphalt mixture (RTFOT). This fact would lead to the placing of an asphalt mixture on site which is already significantly aged but can also imply some advantages if the ageing rate quickly stabilizes. This fact has specific implications in terms of layer selection where to use this binder in a pavement. Since BB85/15 suffers rapid ageing, it should not be placed in wearing courses, which are the layers most affected by ageing since they are the most exposed to weather conditions.

On the other hand, BP is a SBS-modified binder and its reaction to ageing is different to that of conventional bitumen. Figure 58 shows that the change in complex modulus and phase angle after ageing depends on the frequency range. In this regard, at low frequencies (<0.01Hz), corresponding with higher temperatures in the tests, the complex modulus of BP decreases after ageing and the phase angle increased. This fact indicates a change towards a more viscous rather than more elastic response after ageing and can be attributed to the degradation of the SBS polymer during ageing. Contrary to this, at higher frequencies than 1Hz, BP exhibits increased modulus and decreased phase angle, as occurs for non-modified binders (Airey, 2003). The fact that the degradation of the polymeric network is revealed at lower frequencies/higher temperatures is because at these temperatures the matrix of resin for BP has lost its consistency and the dominant response is that of the polymer network, being able to

reflect its damage. In this regard, BP follows the same tendency for ageing as conventional (non-bio) modified binders (Airey 2003).

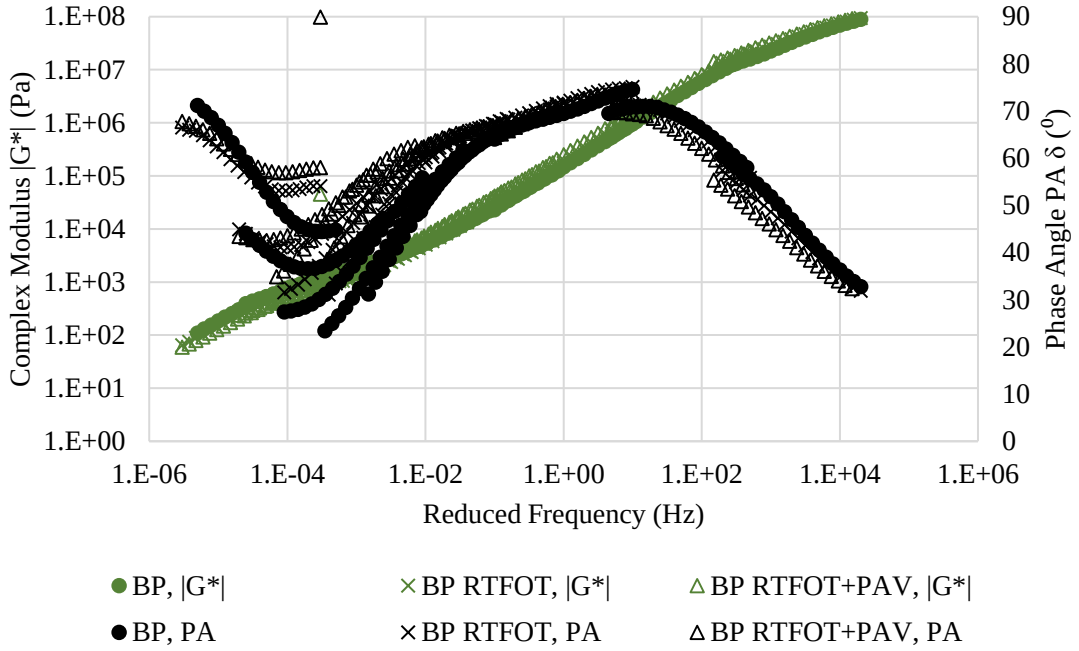


Figure 58. Master curves of the norm of the complex modulus and phase angle of neat and aged BP

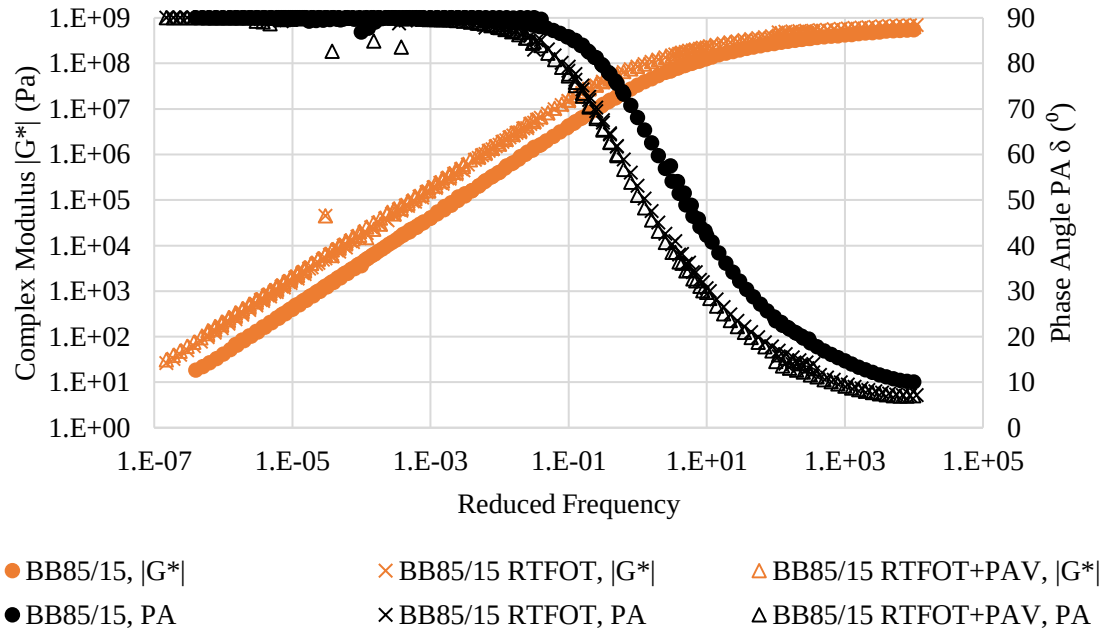


Figure 59. Master curves of the norm of the complex modulus and phase angle of neat and aged BB85/25

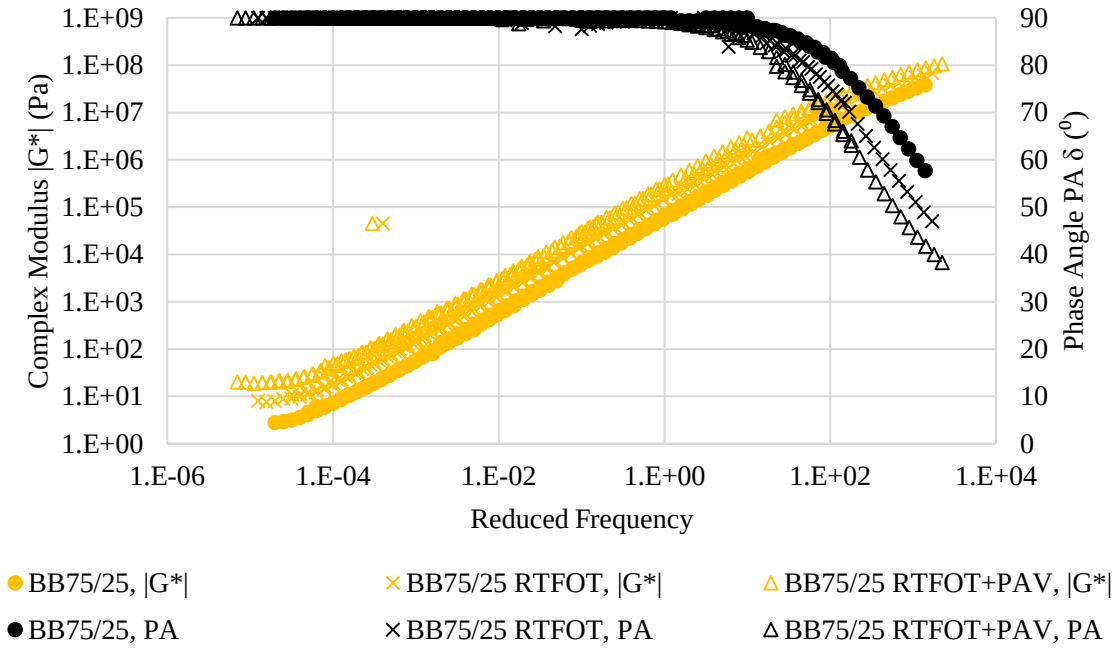


Figure 60. Master curves of the norm of the complex modulus and phase angle of neat and aged BB75/25

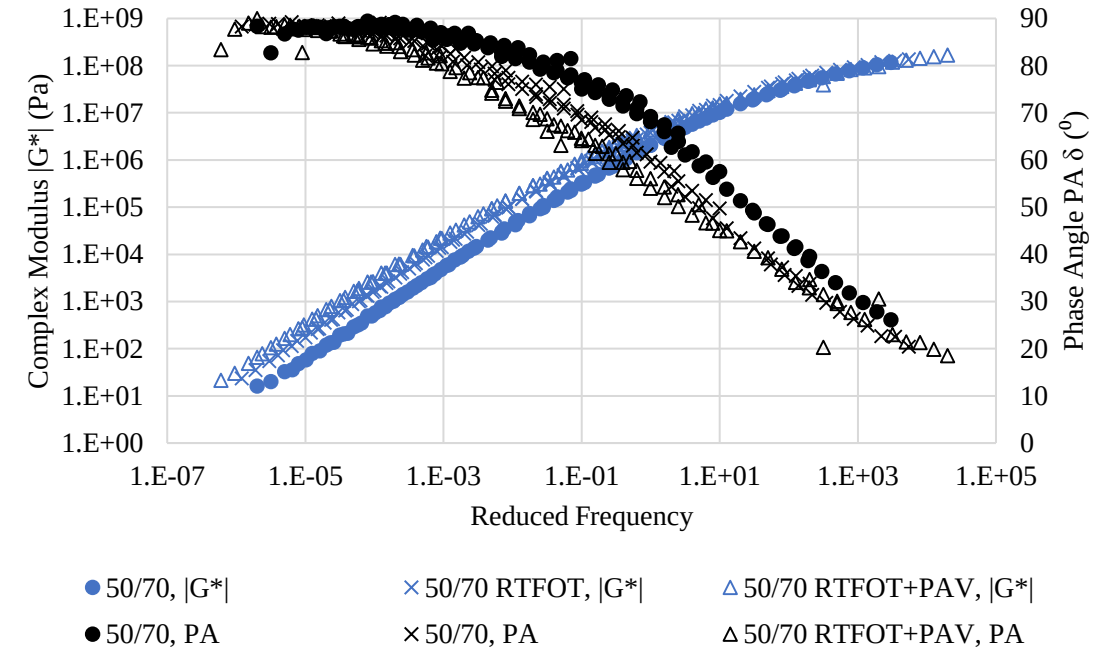


Figure 61. Master curves of the norm of the complex modulus and phase angle of neat and aged 50/70 penetration grade bitumen

BBR tests were conducted on the RTFOT+PAV binders at two different temperatures for each the binder to obtain the critical temperature of stiffness (Tc(S)) and m-value (Tc(m)) according to EN 14771 (2012). Table 9 shows these temperatures and the average results of stiffness (S) and m-value at 60s. The test temperatures were selected according to ASTM D6373-13 (2013) for each material to be close to Superpave low critical temperature thresholds of stiffness and m-value. However, unexpected values of stiffness were obtained for BB75/25 and BP. Due to the soft consistency of these materials, ASTM D6373-13 (2013) recommends to test it at very low temperature (-30ºC and -36ºC). However, BB75/25 and BP are not conventional binders and therefore they do not behave like bitumen, showing greatly increased stiffness at those temperatures probably due to the resin they contain.

The low critical temperatures were obtained by linear extrapolation following the procedure in NCHRP (2001), acknowledging the potential limitation of this extrapolation given the distance between points. ΔT_c was calculated according to Equation (56) in Section 2.4.4 of the literature review. The critical temperatures show the different behaviour of the materials at low temperatures. Firstly, comparing the results of the RA binder and the 50/70 penetration grade binder, the brittle nature of the RA binder can be observed because of its ageing. This fact is also observed in ΔT_c, which becomes negative with ageing indicating a loss of relaxation properties (Hanz & Services 2015). Secondly, the significant difference between the critical temperatures of BB75/25 and BB85/15 is again highlighted with BB85/15 being an extremely brittle material. In addition, the remarkable difference between $T_c(S)$ and $T_c(m)$ of BB75/25 and BP reflected in the high ΔT_c values has to be noticed. Their low $T_c(m)$ indicates that these materials have high ability to relax stresses at low temperatures, however, at the same time, they become very stiff and would fail. This high stiffness is due to the resin they contain, with high amounts in BB85/15. Finally, the RA binder is the only m-controlled binder (i.e. its low critical temperature is $T_c(m)$ and therefore ΔT_c is negative). This means that the biobinders, as

well as the 50/70 penetration grade bitumen, would fail at low temperatures because of the stiffening while the RA binder would fail because of its lack of capability to relax stresses. This fact can be attributed to its ageing state.

Table 9. Binders' BBR results

Binder	Temperature (ºC)	Stiffness, S (MPa)	T_C(S) (ºC)	m-value	T_C(m) (ºC)	ΔT_C (ºC)
RA	-12	446	-7.5	0.243	**-6.1**	-1.4
	-18	758		0.184		
BB75/25	-30	1020	**-5.4**	0.195	-20	13.2
	-36	1375		0.130		
BB85/15	0	394	**+2.0**	0.442	-4.8	6.8
	-6	900		0.263		
BP	-30	763	**-6.1**	0.189	-21	21.7
	-36	965		0.112		
50/70	-24	841	**-10**	0.201	-14	4
	-30	1290		0.139		

3.2.1.1. Critical temperatures

Table 10 shows the high, intermediate and low critical temperatures for the different binders obtained as explained in Section 2.3.5.1 of the literature review. Analysing this table, in terms of performance, the RA binder presents higher critical temperatures compared to those of the conventional 50/70 due to the ageing it has been exposed to. In this regard, it would have good rutting resistance while bad response to fatigue and thermal cracking. On the other hand, BP and BB75/25 high critical temperatures are lower than that of the 50/70 conventional bitumen which could cause some rutting issues if used as fresh binders in virgin mixtures without RA. However, the intermediate ones are also lower, which would imply potentially good fatigue resistance. The high critical temperature of BB85/15 is similar to that of the 50/70, while the intermediate one is higher. All the biobinders' low critical temperatures are high in comparison to the 50/70 penetration grade bitumen which would decrease thermal cracking resistance. From this table, it can be observed that a compromise between the RA properties and the biobinders could be found to obtain closer properties to those of the 50/70 bitumen except for

low critical temperatures. The high critical low temperatures found for biobinders are due to their composition. The resin in the binders become increasingly brittle at low temperatures, causing failure by cracking. Therefore, the higher the content of resin (BB85/15), the more brittle the binder and higher the low critical temperature. The compromise between the RA binder properties and biobinders to mimic as much as possible the 50/70 penetration grade binder is worked out with the blend design.

Table 10. Critical temperatures of the binders

Binder	Name	High critical temperature (°C)	Intermediate critical temperature (°C)	Low critical temperature (°C)
Recovered RA Binder	RA	95.3	36.1	-6.1
BioPhalt®	BP	54.8	11.4	-6.1
BioBinder 75/25	BB75/25	44.1	11.1	-5.4
BioBinder 85/15	BB85/15	67.3	30.4	+2.0
50/70 Pen bitumen	50/70	66.0	19.0	-10.0

In summary in this chapter, the RA binder, biobinders and control binder have been characterised by means of conventional tests, rheology, ageing and critical temperatures. The RA binder has been shown to be a greatly aged binder with hard consistency, high stiffness and high elastic component. It exhibits high values for the three critical temperatures, which is translated into good resistance to rutting while poor performance for fatigue and thermal cracking. These properties reveal the need of rejuvenation of this source of RA if it is to be used in high amounts in new asphalt mixtures.

The biobinders BBs exhibit different properties in terms of consistency and stiffness highly depending on their resin/oil composition. This is an advantageous feature since resin/oil proportions can be worked out and adapted based on the user needs. In any case, the resin/oil combination produce materials with a high viscous component. In terms of critical

temperatures, BB75/25 and BB85/15 show contrasting performance for rutting and fatigue: BB75/25 would exhibit good fatigue resistance while failing because of rutting and BB85/25 would be do the opposite. At low temperatures, the resin seems to have a great effect making them very brittle even if the consistency was soft at room temperature (high penetration value), as contrary to what is usually expected with conventional bitumen. With ageing, BBs become stiffer and increase their elastic component. It is worth noting that BB85/25 seems to rapidly age after RTFOT and then is not affected by PAV. This would have important implications in pavement design in terms of layer selection, or the consideration of placing an already aged material in the field. Since BB75/25 does not show the same tendency, this fact may be attributed to the composition and resin content.

BP is a soft and highly SBS-modified binder showing the same characteristic features of conventional PMBs: high softening point while soft consistency, high elastic component increase at high temperatures and deterioration with ageing of its polymeric network showed at low frequencies. Regarding critical temperatures, BP would have acceptable/low rutting resistance, good performance in terms of fatigue and low thermal cracking resistance (which may be attributed to its resin content in the same way than BBs).

Finally, it can be said that both type of biobinders (BP and BBs) show adequate properties to be used as virgin binders in high RA content asphalt mixtures with the RA source selected at high and intermediate temperatures. This is because the high amount of RA binder would contribute to rutting resistance while the biobinders would help for fatigue. Low temperatures properties may be the main handicap.

CHAPTER 4. BINDERS' BLEND AND ASPHALT MIXTURE DESIGN

4. BINDERS' BLEND AND ASPHALT MIXTURE DESIGN

Once the conventional and rheological properties of the binders were obtained, the blend design for the blend of the RA binder and BP could be carried out. This chapter shows the process and results of such blend design. Next, its outcomes are used as inputs to fix the asphalt mixture design. Following this, the formulation of the adaptable biobinder BB containing resin and oil was undertaken and the blend design was validated.

4.1. Binders' blend design

The first step to perform the blend design of RA binder and BP was to obtain the Replaced Virgin Binder (RVB) percentages. For this, Equation (6) was used with the following variables:

1. **Binder content in the RA**. Since two fractions of RA with different binder contents will be used, the binder content in the RA depends on the percentage of each fraction to be added in the final asphalt mixture. However, this fact depends on the final gradation, which depends on the total RA percentage in the asphalt mixture, which will be an output from the blend design. Therefore, a first hypothesis was needed to have a single binder content in the RA. This hypothesis was that each fraction would be 50% of the total RA. Considering the binder content of each fraction given in Table 2. Characteristics of RA fractions, the binder content to be used is 4%.
2. **Total percentage of RA to be added in the asphalt mixture**. Since the asphalt mixtures should have high RA content for the purpose of this thesis, three high percentages were chosen to perform the blend design: 50%, 70% and 90%.

3. **Final binder content of the asphalt mixture**. From previous experiences with this type of asphalt mixture, two binder contents were chosen to perform the blend design: 4 and 5%.
4. **DOB**. Given that the real percentage of blending that will occur in the asphalt mixture is unknown, the possibility of 100, 80 and 60% of blending were considered. This hypothesis is based on previous studies which show that for hot mix asphalt with high RA content, high blending may take place (Soleymani et al. 2000; Shirodkar et al. 2011).

Having established these variables, 18 RVB percentages (3 RA % x 3 DOB x 2 binder contents) were calculated. Next, the values of penetration, softening point, Fraass breaking point and critical temperatures of BP and the RA binder were introduced in Equations (1) to (5) to obtain the blend design (Table 11). According to Table 11, higher RA contents and higher degree of blending (DOB) would produce harder blends, due to the higher content of RA binder. In this regard, Table 11 is important in order to be able to assess what would happen if full blending does not take place, and whether this risk can be assumed or not.

Figures 62 to 65 show the blending charts and laws for penetration, softening point, Fraass breaking and critical temperatures for 5% and 4% final binder contents. Having these charts, if a specific RVB is entered, it is possible to know the property that the final blend would have in the asphalt mixture. It should be noticed that the maximum RVB in Figures 62 and 63 is 80%. This is due to the fact that the RA binder content (4%) is lower than the desirable final binder content in the mixture (5%) and therefore, for a 100% RA mixture, we would always need to add fresh binder (i.e. the replaced virgin binder cannot be 100%). On the contrary, in Figures 64 and 65, the maximum RVB is 100% since the RA binder content and the final binder

content are the same. In this regard, if full blending took place, there would be no need for fresh binder addition.

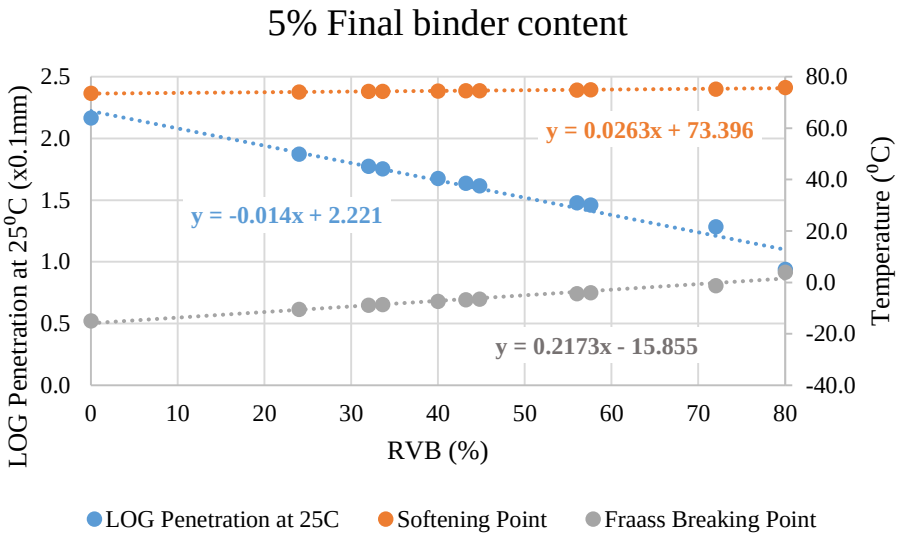


Figure 62. Blending chart of Penetration, Softening Point and Fraass Breaking point for mixtures with 5% final binder content

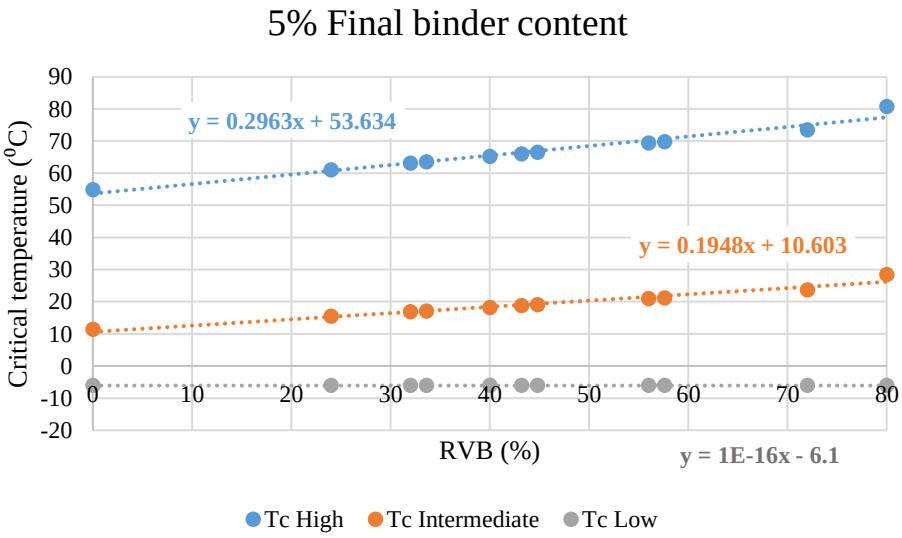


Figure 63. Blending chart of Critical Temperatures for mixtures with 5% final binder content

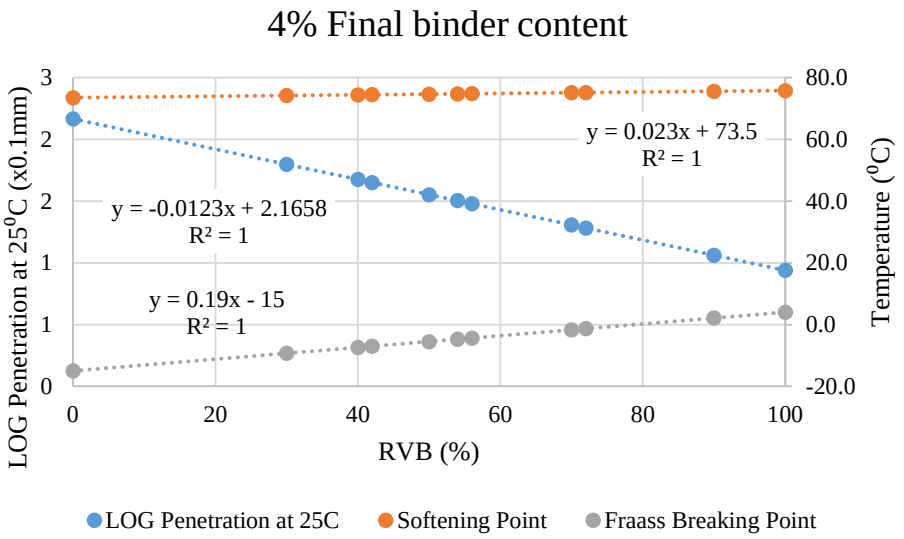


Figure 64. Blending chart of Penetration, Softening Point and Fraass Breaking point for mixtures with 4% final binder content

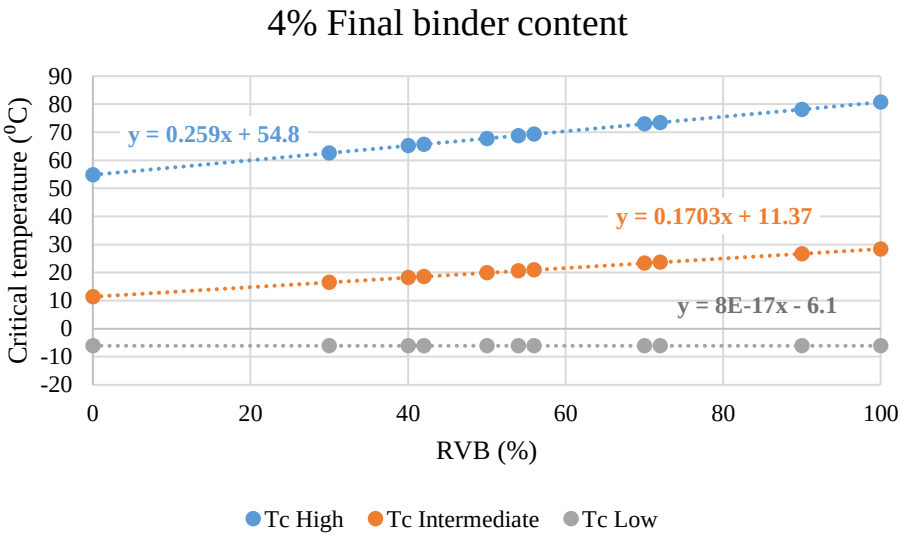


Figure 65. Blending chart of Critical Temperatures for mixtures with 4% final binder content

Table 11. Blend design for 4% binder content in RA

Binder content in the RA (%)	Final binder content in the mix (%)	RA (%)	DOB (%)	RVB (%)	Penetration (x0.1mm)	Softening Point (^{0}C)	Fraass breaking point (^{0}C)	Tc High (^{0}C)	Tc Intermediate (^{0}C)	Tc Low (^{0}C)
			100	**40**	**47**	**74.4**	**-7.4**	**65.2**	**18.2**	**-6.1**
		50	**80**	**32**	**59**	**74.2**	**-8.9**	**63.1**	**16.8**	**-6.1**
			60	**24**	**74**	**74.1**	**-10.4**	**61.0**	**15.5**	**-6.1**
			100	56	30	74.8	-4.4	69.3	20.9	-6.1
4	5	70	80	44.8	41	74.5	-6.5	66.4	19.0	-6.1
			60	33.6	56	74.3	-8.6	63.5	17.1	-6.1
			100	72	19	75.2	-1.3	73.4	23.6	-6.1
		90	80	57.6	28	74.8	-4.1	69.7	21.2	-6.1
			60	43.2	43	74.5	-6.8	66.0	18.7	-6.1
			100	50	35	74.7	-5.5	67.8	19.9	-6.1
		50	80	40	47	74.4	-7.4	65.2	18.2	-6.1
			60	30	62	74.2	-9.3	62.6	16.5	-6.1
			100	70	20	75.1	-1.7	72.9	23.3	-6.1
4	4	70	80	56	30	74.8	-4.4	69.3	20.9	-6.1
			60	42	44	74.5	-7.0	65.7	18.5	-6.1
			100	90	11	75.6	2.1	78.1	26.7	-6.1
		90	80	72	19	75.2	-1.3	73.4	23.6	-6.1
			60	54	31	74.7	-4.7	68.8	20.6	-6.1
Target: ***50/70 Penetration grade bitumen***					*68*	*48*	*-8*	*66.0*	*19.0*	*-10.0*

4.2. Asphalt mixture design

Once the blend design was performed for BP and the RA binder, the final binder content for the asphalt mixtures and the RA percentages were selected. From Table 11, it can be seen that the configuration for blending that produces a closest approximation to the target 50/70 penetration grade bitumen is "50% RA – 5% total binder content" (in bold in Table 11) keeping a compromise with the uncertainty for the DOB. This means that for the three DOBs considered:

- The penetration would be close to 50/70.
- The softening point would never decrease to 48^0C due to the individual values of BP and RA (Table 8). However, a higher softening point could improve the behaviour of the asphalt mixture at high temperatures. Therefore, it is not considered as a drawback.
- The Fraass breaking points are close to or lower than -8^0C. Therefore, a better low temperature resistance could be expected.
- The high critical temperatures are close to that of the 50/70 penetration grade bitumen.
- The intermediate temperatures are lower, and therefore better in terms of fatigue performance, than that of the 50/70 penetration grade bitumen.
- The low critical temperatures are always the same because BP and RA binder have the same value. This temperature is higher than that of the 50/70 penetration grade bitumen so this fact has to be taken into account if asphalt mixtures would be exposed to cold climates.

Consequently, 50% RA and 5% total binder content were chosen to produce asphalt mixtures and blends with biobinders and the reference binder.

4.2.1. Asphalt mixture gradation

The first step before the manufacturing of asphalt mixtures and blends was to define the gradation for 50% RA content. As stated in the methodology, this procedure was developed in Eiffage (Lyon, France) as a collaboration with this project following the method described in Olard & Pouget (2013) to optimise the mineral skeleton of high modulus asphalt mixtures with RA. The specific procedure will not be described here, since it is beyond the scope of the present thesis. The outcome obtained for the different aggregate and RA fractions is shown in Table 12 and the final gradation is displayed in Figure 66.

Table 12. Percentage of each fraction for 50% RA content mixtures

Fraction	10/14	8/12 RA	0/8 RA	0/2	Filler	Total
Percentage in mass in the mixture (%)	37.0	36.0	14.0	10.0	3.0	100.0

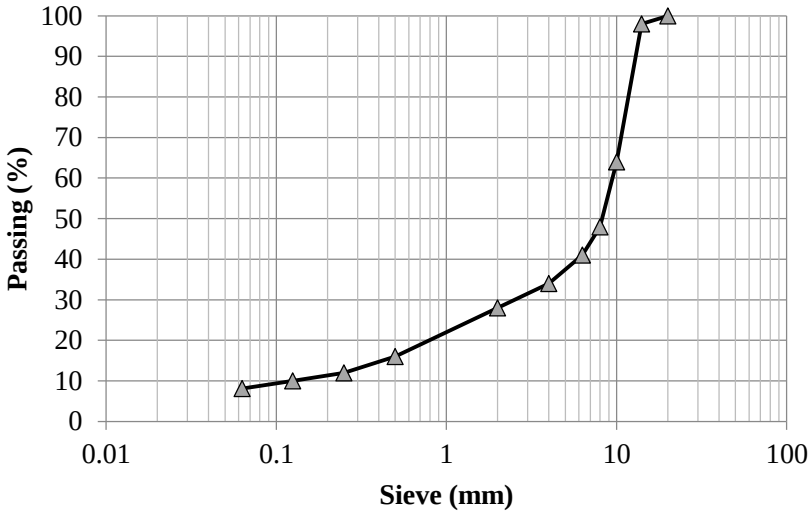


Figure 66. 50% RA mixture gradation

In this regard, the definition of the percentages of each RA fraction gives us two parameters that had been assumed before:

1. **Percentage of each RA fraction binder in the final mixture**. These percentages were calculated on the basis of 100kg of total asphalt mixture according to the asphalt mixture gradation as following:

$$RA\ binder\ from\ fraction\ 0/8\ in\ 100kg\ of\ mixture$$
$$= kg\ of\ 0/8\ \ fraction\ \cdot binder\ content\ of\ \ 0/8\ \ fraction$$
$$= 14kg\ of\ \ 0/8\ \ fraction \cdot 5.38\%\ binder\ content$$
$$\approx 0.8\ kg\ of\ binder\ from\ 0/8\ \ fraction$$

$$RA\ binder\ from\ fraction\ 8/12\ in\ 100kg\ of\ mixture$$
$$= kg\ of\ 8/12\ \ fraction\ \cdot binder\ content\ of\ \ 8/12\ \ fraction$$
$$= 36kg\ of\ \ 8/12\ \ fraction \cdot 2.78\%\ binder\ content$$
$$\approx 1\ kg\ of\ binder\ from\ 8/12\ \ fraction$$

This means that in terms of the RA binder, 44.4% of the binder would come from the 0/8 fraction, while a 55.6% would come from the 8/12 fraction. In Table 8, it was stated that the RA binder tested was a 50%-50% blend of each RA fraction binder. Since these percentages are closed to the ones obtained with the gradation, and the RA binders' properties were not very different, the blend design performed with the first RA blend was considered valid. In further sections of the thesis, the RA binder will be a blend of 44.4% binder from the 0/8 fraction + 55.6% binder from the 8/12 fraction.

2. **Binder content in the RA**. Following the previous maths, in the 50% RA mixtures, if full blending takes place, 1.8% of the binder would come from the 50% RA. This means that the binder content coming from RA is 3.6%. The blend design in Section 3.3.1 was performed assuming a binder content of 4%. Since this variable can significantly affect the

results, the blend design was carried out again to check whether 50% RA mixtures with 5% binder content would still be the best option.

4.3. Binders' blend design reformulation

Table 14 shows the results of the blend design performed for 3.6% binder content in the RA. It can be observed that the configuration that provides a 50/70 penetration binder is "50% RA – 5% binder content". In addition, this configuration provides a good compromise for the three DOBs studied and the rest of the properties. Thereby, these parameters were fixed to produce three asphalt mixtures with the same design, but changing the fresh binder. In Table 14, the design parameter used in the following section for the BioBinder (BB) has also been included and the full comparison for rheology is shown in Section 5.3.

4.4. BioBinder formulation

The BioBinder (BB) produced from pine resin and linseed oil is an adaptable material whose consistency can be tuned in order to obtain a specific target to be blended with the RA binder. Previously, two blends of pine resin and linseed oil were characterised in order to understand their conventional and rheological properties. In this section, the final blend of pine resin and linseed oil is defined, since the asphalt mixture design is fixed and therefore the percentage of BB and RA binder to blend is known.

4.4.1. Methodology

The objective was to obtain a blend of BB and RA binder that provides a 50/70 penetration binder as in the case of BP. For this purpose, DSR rheology was chosen as the design property as it is more performance-related than conventional properties. In this regard, the complex shear modulus of the blend of BB and RA binder at 15ºC and 10Hz was selected as the rheological parameter for design. This choice was based on two facts:

- The French standard for asphalt mixtures characterisation (Delorme et al. 2007) considers this parameter as the reference to classify them into types. Since this standard will be used for asphalt mixtures, it was considered a good reference parameter.
- Due to the tedious task of recovering RA binder, the testing plan was programmed in order to use the smallest possible amount of this material. Complex shear modulus (|G*|) measured using a DSR is known to only need a small amount of material and produces valuable data. Therefore, since different blends had to be tested, the use of DSR rheology was considered the best option.

In this regard, the BioBinders displayed in Table 13 were manufactured according to the procedure described in Section 1.4.2. Frequency and temperature sweeps were carried out from 1 Hz to 25 Hz and from -10°C to 60°C. Two parallel-plate geometries were used: 8 mm diameter parallel-plates from -10°C to 30°C, and 25 mm diameter parallel-plates from 20°C to 60°C. For each binder, the correct geometries were selected at 20°C and 30°C depending on the rheological results in order to achieve a smooth Black diagram (Airey, 2002). Master curves were produced using the mathematical procedure defined by Chailleux et al. (2006).

Table 13. Manufactured BioBinders

BioBinders	Resin (%)	Oil (%)
BB 85/15	85	15
BB 82/18	82	18
BB 80/20	80	20
BB 78/22	78	22
BB 75/25	75	25

Once these results were obtained, in order to predict the behaviour of the blends of RA binder and BioBinders, the log-log traditional blending law for the norm of the complex modulus (|G*|) at 10 Hz and 15°C was applied following Equation (76) (Whiteoak & Read 2003).

Table 14. Blend design for 3.6% binder content in RA

Binder content in the RA (%)	Final binder content in the mix (%)	RA (%)	DOB (%)	RVB (%)	Penetration (x0.1mm)	Softening Point (^{0}C)	Fraass breaking point (^{0}C)	Tc High (^{0}C)	Tc Intermediate (^{0}C)	Tc Low (^{0}C)	|G*|, 10Hz, 15^{o}C (MPa)
3.6	5	**50**	**100**	**36**	**53**	**74.4**	**-7.4**	**65.2**	**18.2**	**-6.1**	**4.0**
			80	**28.8**	**65**	**74.2**	**-9.5**	**62.3**	**16.3**	**-6.1**	**3.0**
			60	**21.6**	**79**	**74.0**	**-10.9**	**60.4**	**15.0**	**-6.1**	**2.2**
		70	100	50.4	35	74.7	-5.4	67.9	20.0	-6.1	7.4
			80	40.3	46	74.4	-7.3	65.2	18.2	-6.1	4.8
			60	30.2	62	74.2	-9.3	62.6	16.5	-6.1	3.2
		90	100	64.8	23	75.0	-2.7	71.6	22.4	-6.1	13.5
			80	51.8	33	74.7	-5.2	68.2	20.2	-6.1	7.8
			60	38.9	49	74.4	-7.6	64.9	18.0	-6.1	4.6
3.6	4	50	100	45	41	74.5	-6.5	66.5	19.0	-6.1	5.9
			80	36	53	74.3	-8.2	64.1	17.5	-6.1	4.0
			60	27	68	74.1	-9.9	61.8	16.0	-6.1	2.8
		70	100	63	25	74.9	-3.0	71.1	22.1	-6.1	12.5
			80	50.4	35	74.7	-5.4	67.9	20.0	-6.1	7.4
			60	37.8	50	74.4	-7.8	64.6	17.8	-6.1	4.4
		90	100	81	15	75.4	0.4	75.8	25.2	-6.1	26.5
			80	64.8	24	75.0	-2.7	71.6	22.4	-6.1	13.5
			60	48.6	37	74.6	-5.8	67.4	19.6	-6.1	6.8
Target: *50/70 Penetration grade bitumen*					*68*	*48*	*-8*	*66.0*	*19.0*	*-10.0*	*11.4*

$$\log(|G^*|_{blend}) = x \cdot \log(|G^*|_{RA}) + (1 - x) \cdot \log(|G^*|_{BB}) \quad (76)$$

where $|G^*|_{blend}$ is the predicted norm of the complex modulus of the RA binder + BioBinder blend, $|G^*|_{RA}$ is the norm of the complex modulus of the RAb and $|G^*|_{BB}$ is the norm of the complex modulus of the BioBinder, all of them at 10 Hz and 15°C, and x is the percentage of the RA binder in the blend expressed in decimals.

In this sense, the BioBinder that could produce a close approximation (± 10%) to the norm of the complex modulus of 50/70 penetration bitumen at 10 Hz and 15°C, together with two additional BioBinders to further study the effect on the RA binder were selected.

The amount of RA binder to have in the blends was given by the blend design and consisted of the RVB (%) for full blend for 50% RA content mixtures with 5% total binder content. This value was taken from Table 14 and is 36%. In this way, blends of 36%RA binder and the three selected BBs were produced and tested in the DSR under the same conditions as the BioBinders themselves.

4.4.2. Analysis of results

Figures 47 and 48 show the master curves of the norm of the complex modulus and phase angle of the five manufactured BioBinders with different resin/oil proportions, compared to the RA binder and 50/70 penetration bitumen. In general, BioBinders' master curves show a different shape than both RA and 50/70 penetration bitumen and high influence of the resin content. Furthermore, their visco-elastic properties seem to be more sensitive to loading conditions: at high frequencies (>10 Hz), BB85/15 and BB82/18 display higher |G*| values than that of the RA binder, while BB78/22 and BB75/25 are even softer than the 50/70 penetration bitumen. In terms of phase angle, the same tendency is observed with BB85/15 and BB82/18 being more elastic than the RA binder, while BB78/22 and BB75/25 are more viscous than the 50/70

penetration bitumen. At low frequencies (<10 Hz), all BioBinders have lower stiffness and higher phase angles than RA binder and their comparison to 50/70 pen bitumen depends on the resin percentage. These properties show the potential of these materials to be able to rejuvenate RA binder to a specific target through their blending, if resin/oil percentages are properly adjusted.

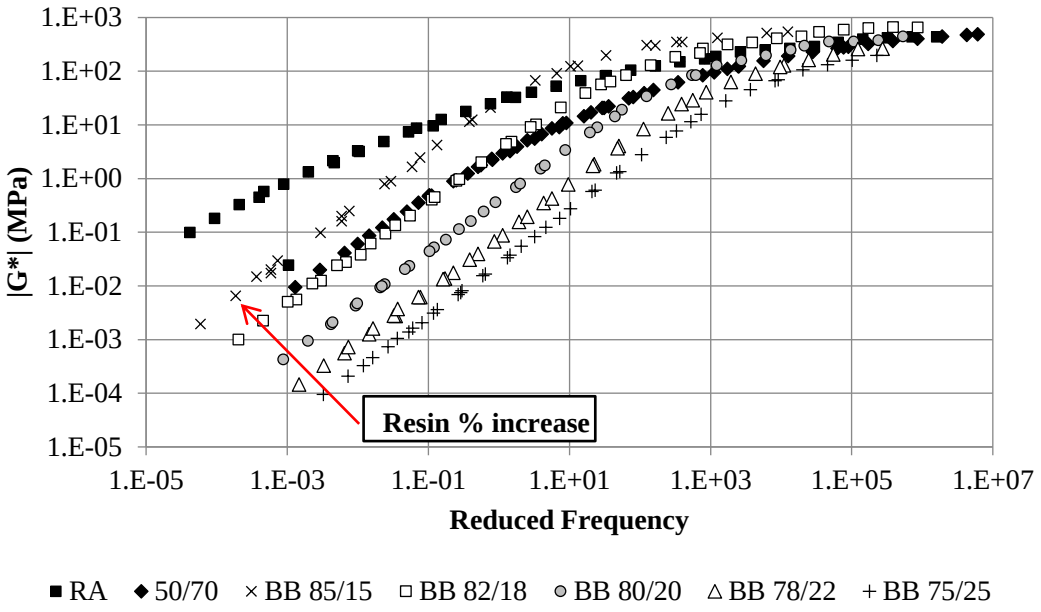


Figure 67. Master curves of norm of complex modulus of binders at T_{ref} = 15°C

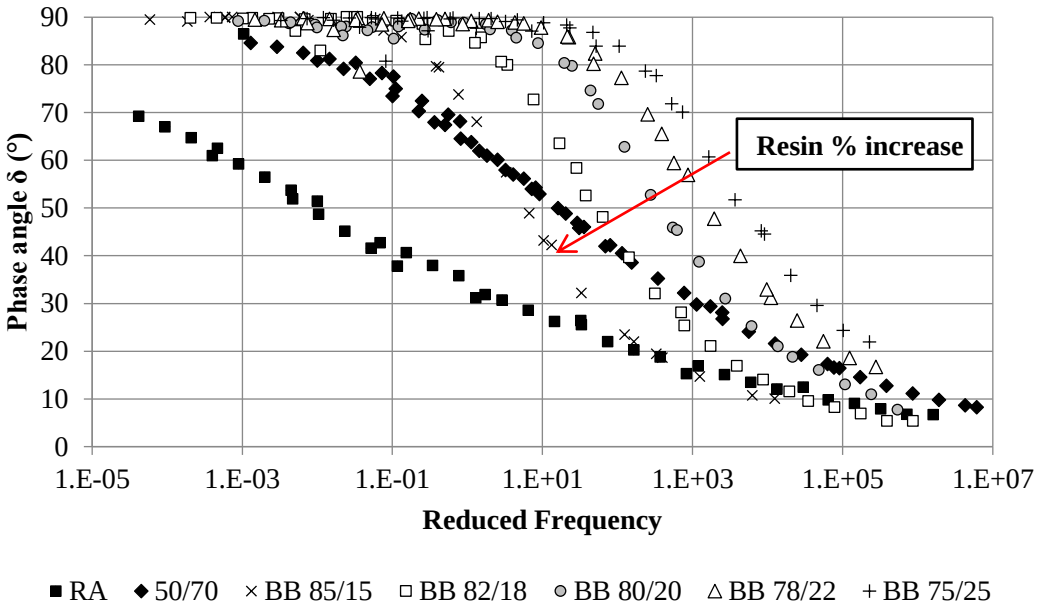


Figure 68. Master curves of the phase angle of binders at T_{ref} = 15°C

In order to determine the precise percentage of resin and oil to be blended with the RA binder, Equation (76) was applied to predict |G*| at 15°C and 10 Hz for the different blends of BioBinder and RA binder and the results compared to that of the 50/70 penetration bitumen. Figure 69 displays the results of this calculation together with the experimental value of |G*| at 15°C and 10 Hz of the various BioBinders and the 50/70 penetration bitumen (dash line).

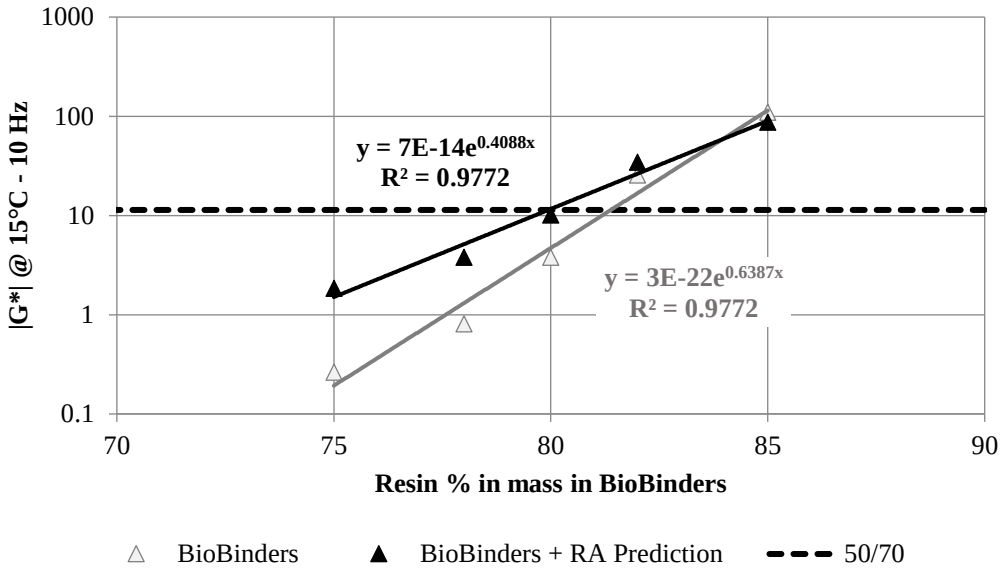


Figure 69. Norm of the complex modulus at 15°C and 10 Hz

Prediction of |G*| at 15°C and 10 Hz for the different blends showed that mixing BB80/20 with the RA binder would produce the binder with the closest value to that of the 50/70 penetration bitumen. In addition, resin percentage in mass in BioBinders versus |G*| at 15°C and 10 Hz fitted a logarithmic law with a high regression coefficient. Thus, it can be deduced that resin increase produces an exponential increase in |G*| for the BioBinders. This fact is related to concentrated suspension theory (Roscoe 2002), which models blends of two materials as a matrix of one with suspension spheres of the other. In our case, the oil would be considered the matrix and the resin the spheres. The concentrated suspension theory states that the properties of the blend would change exponentially with the increase of spheres concentration.

Given these results, BB80/20 was blended with the RA binder. In addition, the RA binder was blended with BB78/22 and BB82/18 in order to further understand the interaction between RA and BioBinders. Master curves of the norm of the complex modulus and phase angle of the three blends, compared to the 50/70 penetration target bitumen and RA are shown in Figures 70 and 71.

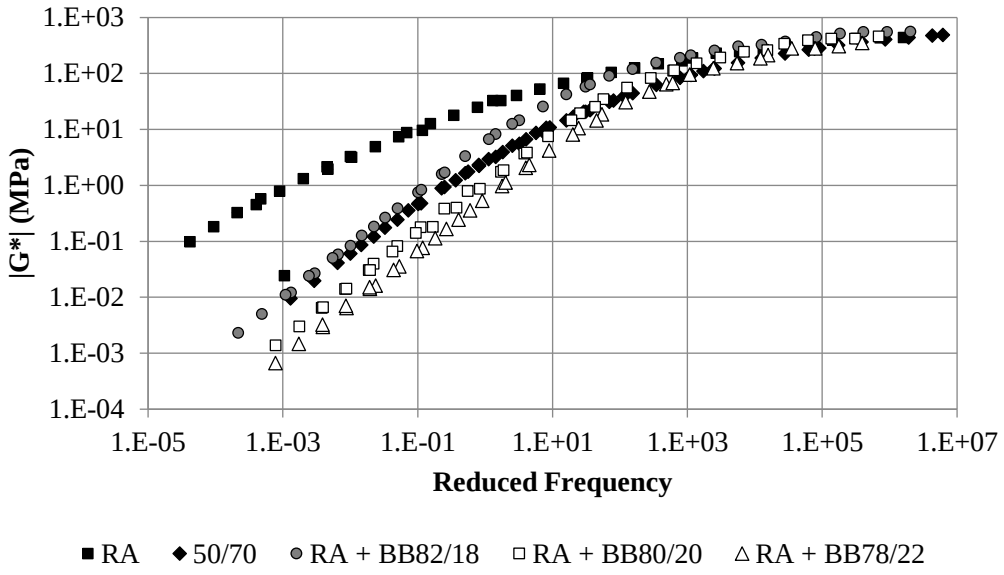


Figure 70. Master curves of norm of complex modulus of blends at T_{ref} = 15°C

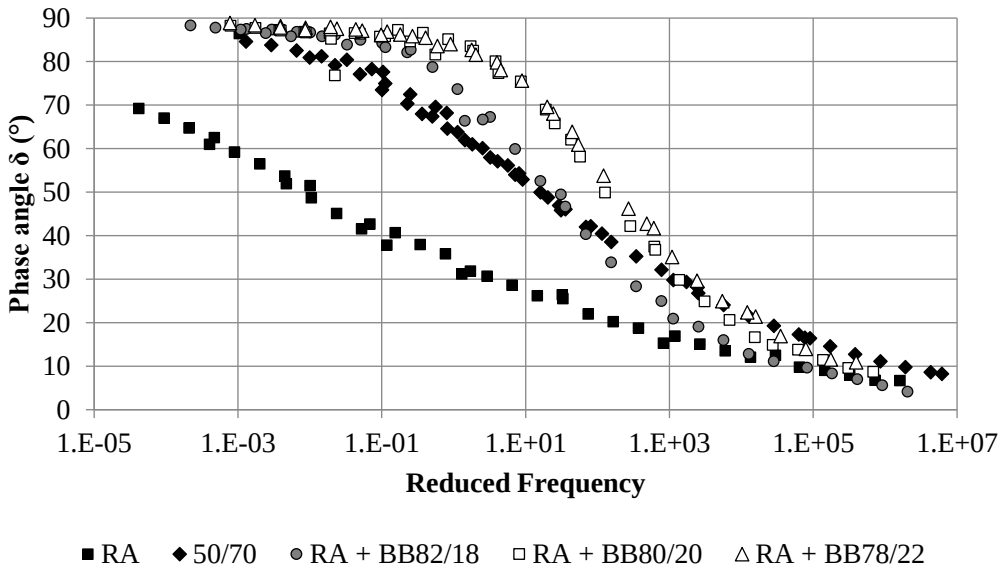


Figure 71. Master curves of the phase angle of blends at T_{ref} = 15°C

The RA + BB80/20 blend behaved as predicted by the traditional logarithmic blending law at 15°C and 10 Hz being very similar to the 50/70 penetration bitumen in terms of complex modulus. However, the shape of the complex modulus master curve is not the same as that of the 50/70 penetration bitumen. At frequencies higher than 10 Hz, the RA + BB80/20 blend presents a slightly stiffer behaviour than that of the 50/70 penetration bitumen, while at frequencies lower than 10 Hz the blend is softer. RA + BB80/20 being stiffer than 50/70 penetration bitumen at high frequencies is translated into RA + BB80/20 being stiffer at low temperatures. This might represent an issue for asphalt mixtures resistance to thermal cracking. On the other hand, RA + BB80/20 is softer than 50/70 penetration bitumen at low frequencies, which correspond to high temperatures and could imply less rutting resistance of the asphalt mixture. Finally, RA + BB80/20 blend phase angle is higher than that of the 50/70 penetration bitumen meaning that its behaviour is more viscous. Depending on the temperature range, this fact can be beneficial or harmful for the asphalt mixture. At high temperature, the viscous component would favour the appearance of ruts, while at low temperatures it would help the resistance to thermal cracking increasing the relaxation capacity of the asphalt mixture. These facts have to be taken into account to further analyse their influence on asphalt mixture performance. BB80/20 will be termed as “BB” for the rest of the thesis.

4.4.3. BioBinder blend design

Having established the composition of BB, their properties could be obtained and the blend design between the RA binder and BB could be performed to predict the properties that the blend would have in the 50% RA content asphalt mixture with 5% binder content for different DOBs. Table 15 shows the conventional properties and critical temperatures of BB and Table 16 displays its blend design with the RA binder. Table 15 shows that BB is a soft binder with high penetration, low softening point and low Fraass breaking point which is able to produce a blend with the RA binder (for 100%DOB) that can be considered a 50/70 penetration grade

binder. The critical temperatures of BB in Table 15 reveal that it has a slightly low Tc(High), acceptable Tc(Intermediate) and high Tc(Low). Table 16 shows that its blend with the RA binder would improve Tc(High) and Tc(Low) while Tc(Intermediate) would slightly increase implying a worse fatigue performance. The design parameter |G*| at 10Hz and 15ºC has also been included in Table 16.

Table 15. Properties of BB

Binder	Penetration (x0.1mm)	Softening Point (^{0}C)	Fraass breaking point (^{0}C)	Tc High (^{0}C)	Tc Intermediate (^{0}C)	Tc Low (^{0}C)
BB	216	33	-10.3	55.7	20.7	-5.5

Table 16. BB blend design with RA binder

DOB (%)	RVB (%)	Penetration (x0.1mm)	Softening Point (^{0}C)	Fraass breaking point (^{0}C)	Tc High (^{0}C)	Tc Int (^{0}C)	Tc Low (^{0}C)	|G*|, 10Hz, 15ºC (MPa)
100	36	68.0	48.4	-5.2	64.7	23.5	-5.7	10.2
80	28.8	85.6	45.3	-6.2	62.9	22.9	-5.7	8.4
60	21.6	107.9	42.2	-7.2	61.1	22.4	-5.6	6.9

4.5. Validation of binders' blend design

The purpose of the blend design was to theoretically assess the properties of the blend of the RA binder and BP and select the RA and binder content of the asphalt mixtures targeting a 50/70 penetration grade bitumen for the blend. Based on that, the composition of the BioBinder BB was also fixed to the same target.

Having done that, the blends of RA binder and biobinders could be manufactured in the laboratory and the actual properties could be obtained to be compared to the theoretical values of the blend design for the validation of the procedure. The blends were manufactured under the full blending assumption (i.e. DOB = 100%) for asphalt mixtures with 50% RA content and 5% binder content. These parameters provide a RVB percentage equal to 36% (see Table 14).

Therefore, blends of 64% biobinder and 36% of RA binder were manufactured following the procedure described in Section 1.5.4.1 of the methodology.

These blends were tested to obtain their values of penetration, softening point and critical temperatures. Table 17 shows the results of penetration, softening point and critical temperatures compared to those of the blend design for BP and the target 50/70 penetration grade bitumen.

Comparing the blends to the target binder, in terms of conventional properties, the penetration of RA+BP and RA+BB meet the requirements of being a 50/70 penetration grade binder and are equivalent to the target binder. The softening point of RA+BB is similar to that of the 50/70 penetration grade bitumen while, as it could be expected, RA+BP exhibits a higher softening point due to its SBS modification. In terms of critical temperatures, the high critical temperatures of the blends are slightly lower than the target but still acceptable. The intermediate temperature of RA+BP is better than that of the 50/70 penetration grade binder and the low critical temperatures are quite similar. With this preliminary assessment, RA+BP appear to be a suitable blend for asphalt mixtures. On the other hand, RA+BB exhibits higher intermediate and low critical temperatures than the target, which may cause some issues in asphalt mixtures. This fact is further analysed in subsequent chapters.

Comparing the laboratory results of RA+BP and RA+BB to the blend design values, it can be observed that RA+BB has a good match for penetration and softening point while RA+BP comparison appears to be less direct. This fact may be attributed to the polymer content of BP, which makes the prediction of the conventional properties of a binder less simple. On the other hand, the critical temperatures show good equivalency for both blends.

Table 17. Laboratory results vs. Target binder and Blend design values

	Laboratory results					Blend design values				
Binder	**PEN (x0.1mm)**	**SP (ºC)**	**T_c (High)**	**T_c (Int)**	**T_c (Low)**	**PEN (x0.1mm)**	**SP (ºC)**	**T_c (High)**	**T_c (Int)**	**T_c (Low)**
RA+BP	63	61.1	61.6	17.8	-8.9	53	74.4	65.2	18.2	-6.1
RA+BB	69	45.8	61.2	27.7	-5.7	68	48.4	64.7	23.5	-5.7
50/70	*68*	*48*	*66.0*	*19.0*	*-10*					

These facts indicate that the blend design performed is able to provide trustworthy information about the properties of the blends of a RA binder and the fresh binder to be used in RA mixtures, and therefore, it is a useful tool to have inputs for the asphalt mixture design.

4.6. Selection of higher RA content

As established in Section 1.5.3 of the methodology, a higher RA content than that obtained for the 50/70 penetration grade bitumen was selected keeping the final binder content fixed for better comparison of asphalt mixtures' properties. Based on the blend design in Table 14, 70% RA content was considered as the best option to produce the second group of asphalt mixtures. This binder would be equivalent to a 35/50 penetration grade binder if full blending takes place, but a 50/70 penetration grade if the DOB is between 60% and 80%.

Next, the gradation of these asphalt mixtures should be as close as possible to the 50% RA content mixtures. To produce this, there were two main considerations:

- To keep the ratio between the two RA fractions in weight as similar as possible, in order to have the same RA binder in the mixtures.
- To pay special attention to sieves 10, 2 and 0.063 mm, as a recommendation from Eiffage.

Taking into account these points, the gradation shown in Table 18 and Figure 72 was defined. It can be observed that the gradations for both RA percentages are equivalent. Consequently,

70% RA content was chosen to be studied in asphalt mixtures with the two biobinders BB and BP and the reference.

Table 18. Percentage of each fraction for 50% RA content mixtures

Fraction	10/14	8/12 RA	0/8 RA	0/2	Filler	Total
Percentage in mass in the mixture (%)	24.0	50.0	17.0	6.0	3.0	100.0

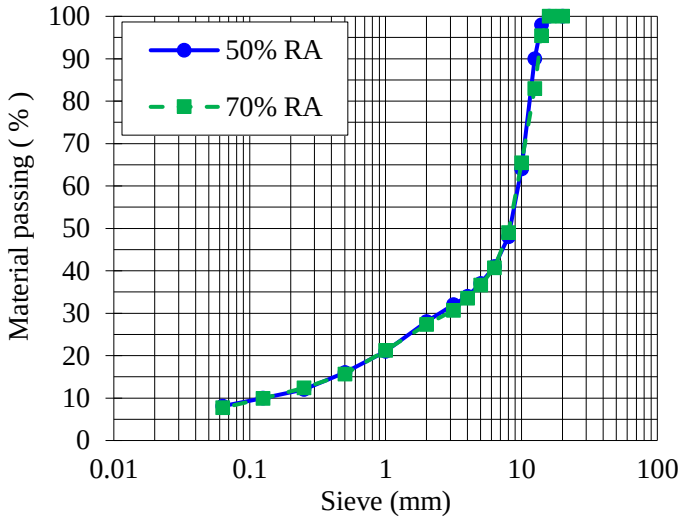


Figure 72. 70% RA mixtures gradation

Thereby, the asphalt mixtures matrix to be studied was finally defined as shown in Table 19.

Table 19. Final mixtures matrix

Mix	Binder	RA (%)	Binder content (%)
50% RA PMB	PMB	50	5
50% RA BB	BB	50	5
50% RA BP	BP	50	5
70% RA PMB	PMB	70	5
70% RA BB	BB	70	5
70% RA BP	BP	70	5

CHAPTER 5. EVALUATION OF BIOBINDERS' REJUVENATING EFFECT

5. EVALUATION OF BIOBINDERS' REJUVENATING EFFECT

The aim of this chapter is to study the rejuvenating effect of the biobinders as total replacement of conventional bitumen for the manufacture of the 50% RA content asphalt mixtures. This effect was assessed using rheology testing and different analysis techniques.

In addition to the materials described in Section 1.4, in this chapter, an additional conventional 70/100 penetration grade bitumen was included as a reference for BB. Table 20 shows the penetration at 25°C and softening point of this bitumen.

Table 20. Conventional properties of 70/100 penetration grade bitumen

BINDER	ROLE in the chapter	NAME	PENETRATION @ 25°C (x0.1mm)	SOFTENING POINT (°C)
70/100 penetration grade bitumen	Reference for BB	70/100	86	46.0

5.2. Methods

5.2.1. Rheology testing

Binders and blends were tested in a DSR. Frequency and temperature sweeps were carried out from 1 Hz to 25 Hz and from -10°C to 60°C. For this purpose, two parallel-plate geometries were used: 8 mm diameter parallel-plates from -10°C to 30°C, and 25 mm diameter parallel-plates from 20°C to 60°C with 1 mm gap. Tests were carried out in strain-controlled mode at 0.06% strain in order to stay within the LVE region of the binders' behaviour. For each binder, correct geometries were selected for 20°C and 30°C depending on results in order to achieve a smooth Black diagram (Airey 2002).

Using these data, master curves of the norm of the complex modulus and phase angle of the different binders were produced at 15°C for comparison following the procedure developed by Chailleux at al. (2006). This procedure minimises errors in the calculation of shift factors for

master curves. Then, cross-over frequencies (ω_0) at 15°C and rheological indexes (R) of RA binder and its blends were determined in order to assess the rejuvenating effect of the different materials. As explained in Section 2.4.1.6, binder's crossover frequency is that frequency at which the binder's phase angle is equal to 45° at a certain temperature (i.e. frequency at which loss and storage moduli are equal). R-value of a binder is the distance between the norm of the complex modulus at the crossover frequency and the glassy modulus (usually taken as 1 GPa in shear loading). Crossover frequencies of binders decrease with ageing while R-values increase. Therefore, according to several researchers (Rowe et al. 2015), crossover frequency versus R-value space can be used to visually evaluate binders' ageing and rejuvenation.

5.2.2. δ-method application

A relationship between rheological properties of bitumen and its molecular weight distribution (MWD) is generally assumed in the literature (Tuminello & Cudré-Mauroux 1991; Wu 1988; Lesueur 2009; Tuminello 1986; Zanzotto et al. 1999). The basic assumption of the δ-method is that for a given frequency, the phase angle of the complex modulus is proportional to the fraction of heavy molecules at this frequency. Therefore, a relationship can be established between the oscillation frequency and the molecular weight. Moreover, phase angle's master curve can be associated with the cumulative molecular weight distribution of the binder. Consequently, from the differentiation of the phase angle master curve, an apparent molecular weight distribution (AMWD) can be obtained. This differentiation requires a continuous curve, so the data has to be fitted with a continuous model. The Huet-Such model (Such 1982; Such 1983; Olard 2003) has been chosen for this purpose as it is well suited for bitumens.

The Huet-Such model is a combination of one spring (G_∞), two parabolic creep elements ($0<h<k<1$) with one coefficient (δ) that regulates the balance between them and a dashpot (β) placed in series with the other elements. This model and its respective equation are represented

in Figure 73. Model parameters were adjusted to the rheological test data obtained on the DSR device after master curves construction at T_{ref}=0°C.

$$G^* = \frac{G_\infty}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}}$$

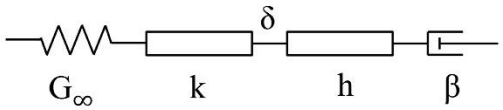


Figure 73. Huet-Such model and equation

A more detailed description of the δ-method can be found in Themeli et al. (2015) and in Section 2.4.1.6 of the literature review. The molecular weight distribution obtained by δ-method is termed "apparent" because the proportionality condition to the phase angle, proved for polymers, is assumed for bitumen in this study. Therefore, the δ-method provides the Apparent Molecular Weight Distribution (AMWD).

5.3. Results and discussion

5.3.1. Rejuvenating effect analysis through rheology results

The blends' rheology is shown in Figure 74 in the Black Space. Figure 74 reveals that the blends of RA and the different materials present thermo-rheologically simple behaviour. This fact allows the Time-Temperature-Superposition-Principle (TTSP) to be applied for the construction of their master curves and further analysis.

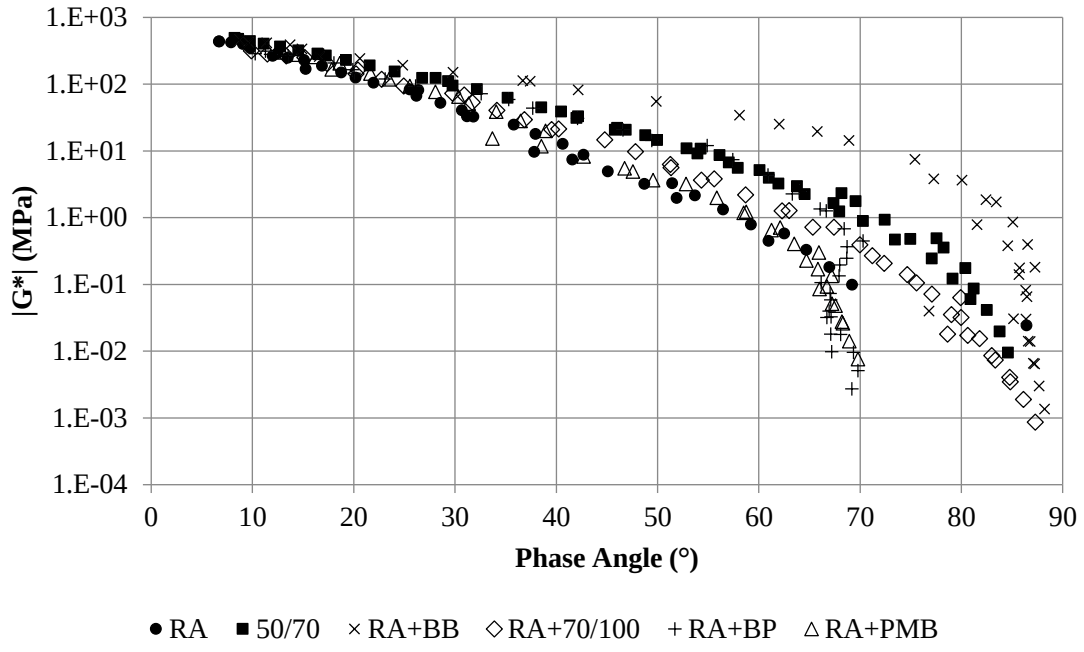


Figure 74. Black diagram of blends

In order to further evaluate the effect of the different binders on the RA binder, cross-over frequencies vs. rheological indexes (R-values) space (Rowe et al., 2015) are displayed in Figure 75. On one hand, cross-over frequencies are related to the elastic/viscous nature of binders, meaning that the higher the crossover frequency the higher the viscous component of the material (due to the fact that the binder reaches 45^0 of phase angle at a higher frequency). Therefore, the materials with higher elastic component can be found at the bottom-middle part of these graphs. On the other hand, R-values are the logarithmic difference between the norm of the complex modulus at the cross frequency of the specific binder and the norm of the glassy modulus. This means that R-values provide a measure of the binders' stiffness in an equi-elastic state and at a given temperature. In this sense, at the same elasticity level, the greater the R-value the stiffer the binder. In this regard, Figure 75 shows that RA point is located at the bottom-right part of the plot, having high R-value and low cross-over frequency. Subsequently to the rejuvenating effect, the blend of RA binder with the different materials produces a shift of this point up and to the left in Figure 75, which is the translation of a change in the shape of

master curves. In this sense, it can be said that biobinders produced less elastic and softer (at the same level of elasticity) rejuvenated RA binder in comparison to the reference binders, since the points are higher and more to the left in the plot.

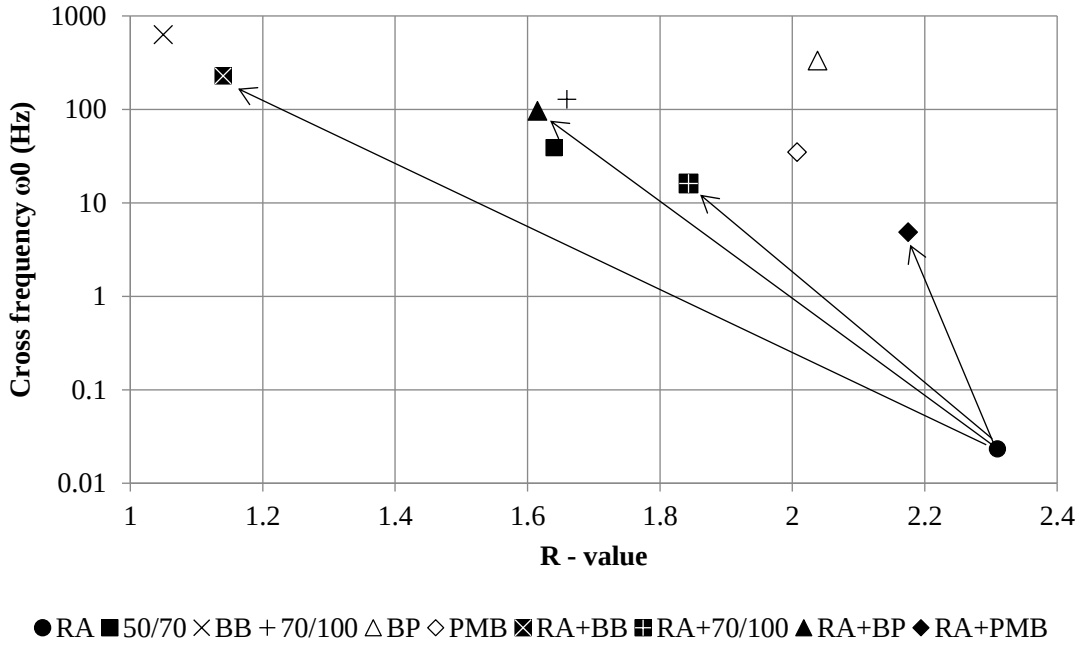


Figure 75. Crossover frequencies vs. R-values

Fatigue (G*sinδ) and rutting (G*/sinδ) parameters were used to evaluate the potential of the rejuvenating effect of biobinders and reference binders on fatigue and rutting resistance on the RA binder. For this purpose, G*sinδ = 5000 kPa and G*/sinδ = 1 kPa at 1.59 Hz were taken as thresholds for obtaining critical temperatures of the different materials for comparison purposes. Figure 76 shows these results with dashed lines representing rutting and fatigue parameters of the 50/70 pen bitumen. It can be seen that rutting critical temperatures of blends of the different binders (conventional and bio-materials) are equal or higher than that of the 50/70 pen bitumen. This means that their rutting behaviour is expected to be equivalent to that of the 50/70 pen bitumen. Regarding fatigue, RA+BB and RA+BP blends present closer critical temperatures to 50/70 pen bitumen, while RA+70/100 and RA+PMB are higher; thus fatigue resistance of the blends with biobinders can be expected to be better than with conventional

binders. In conclusion, blends of RA and biobinders are likely to have a positive rejuvenating effect on RA performance for high-RA content mixtures. This result is in accordance with other investigations about rejuvenating agents (Zaumanis et al. 2014b). However, it is important to note that in this investigation the rejuvenating agents would act as a total virgin bitumen replacement in the asphalt mixtures and not simply as an additive.

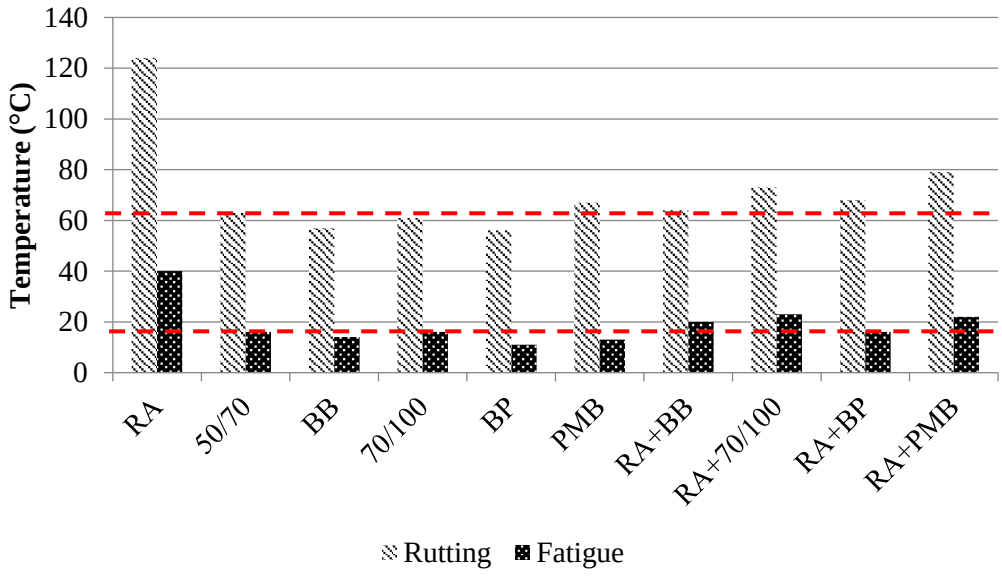


Figure 76. Rutting and fatigue performance temperatures

5.3.2. Rejuvenating effect analysis through AMWD results

In this section, the Apparent Molecular Weight Distribution (AMWD) for all blends is plotted and compared to that of the RA binder. δ-method application is restricted to materials that exhibit a continuous monotonic curve on the Black diagram; therefore, its application was only possible for RA, 50/70 bitumen and blends, and not for the original materials such as BP and PMB. For this purpose, Huet-Such model parameters were determined in order to obtain the required continuous master curves of binders for the δ-method and are displayed in Table 21. Master curves at 0^0C of the norm of the complex modulus and phase angle of RA binder and its blends are shown in Figures 77 and 78 respectively. The master curves show the good accordance of RA+BP and RA+BB with the 50/70 penetration grade binder, providing further

evidence of the validity of the blend design performed in Chapter 4. The glassy modulus G_∞ represents the value of |G*| at infinite frequency and it remains almost constant (~600 MPa) for all the binders.

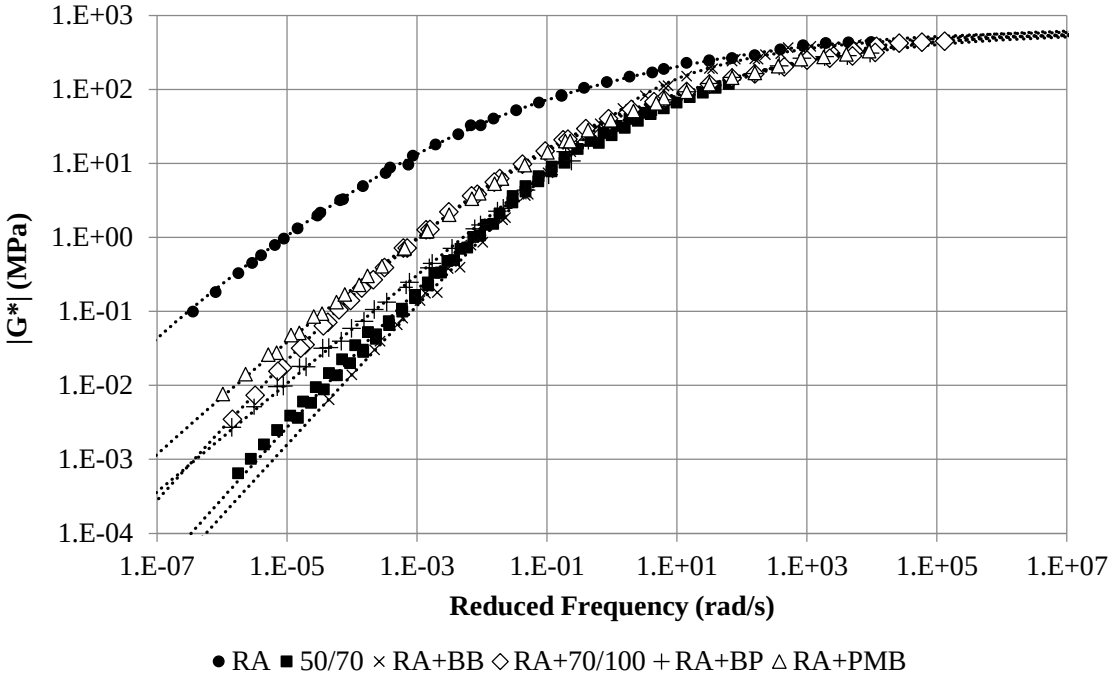


Figure 77. Norm of the complex modulus (|G*|) master curves at 0°C and Huet-Such model fitting

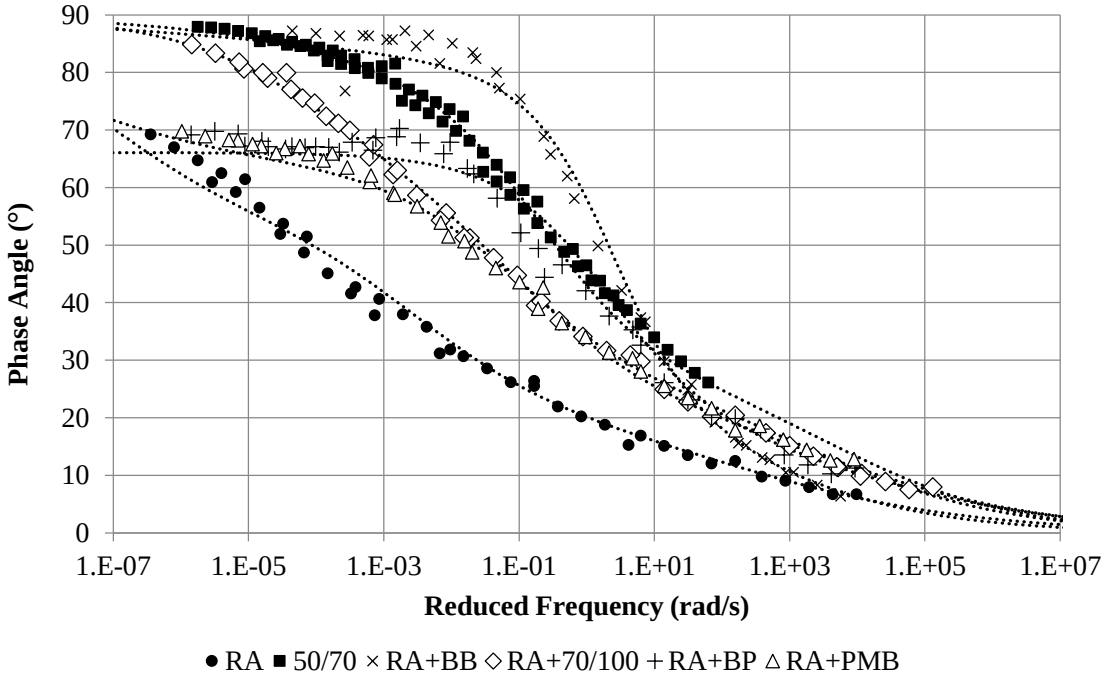


Figure 78. Phase angle (°) master curves at 0°C and Huet-Such model fitting

Table 21. Huet-Such rheological model parameters and WLF coefficients for RA binder and blends at T=0°C

Bitumen / Parameter	G_∞ (MPa)	δ	k	h	β	τ (s)	C1	C2
RA	627.68	5.15	0.24	0.62	348.22	4.25E+00	25.87	154.27
RA+BB	551.71	2.44	0.30	0.85	3.64	1.12E-01	18.22	126.82
RA+BP	581.51	3.50	0.25	0.73	1.53E15	3.526E-02	20.71	126.93
RA+PMB	579.14	6.14	0.30	0.71	422.04	1.51E-01	22.23	136.56
RA+70/100	623.42	5.17	0.26	0.65	53.32	8.93E-02	19.22	113.74
50/70	661.22	6.96	0.32	0.76	6.50	7.61E-02	27.28	195.75

In the case of the RA+BP blend, the modelling is on the limit of δ-method application. The β value seems inconsistent because the increasing accumulative curve for the phase angle achieves a plateau value at 70°, instead of continuously increasing towards 90° as for the other blends. This is due to the high content of polymers of BP, limiting at the same time the calculus of the parameters of the Huet-Such model and the application of the δ-method. Therefore, the RA+BP AMWD curve has to be considered as only indicative for comparison. In this regard, this constraint does not exclude the use of this tool to evaluate the rejuvenating effect induced by the blending between RA and BP.

The AMWDs are plotted with the apparent molecular weight (AMW) in g/mol on the abscise axis and the corresponding probability density f(AMW) on the ordinate axis in Figure 79. The trend between curves is used as a first approach to quantify the rejuvenating effect of the blending through the apparent molecular weight distributions. In addition, cross-over points (w(co)), at which phase angle is equal to 45^0 (i.e. loss and storage moduli are equal), of the different binders have been displayed.

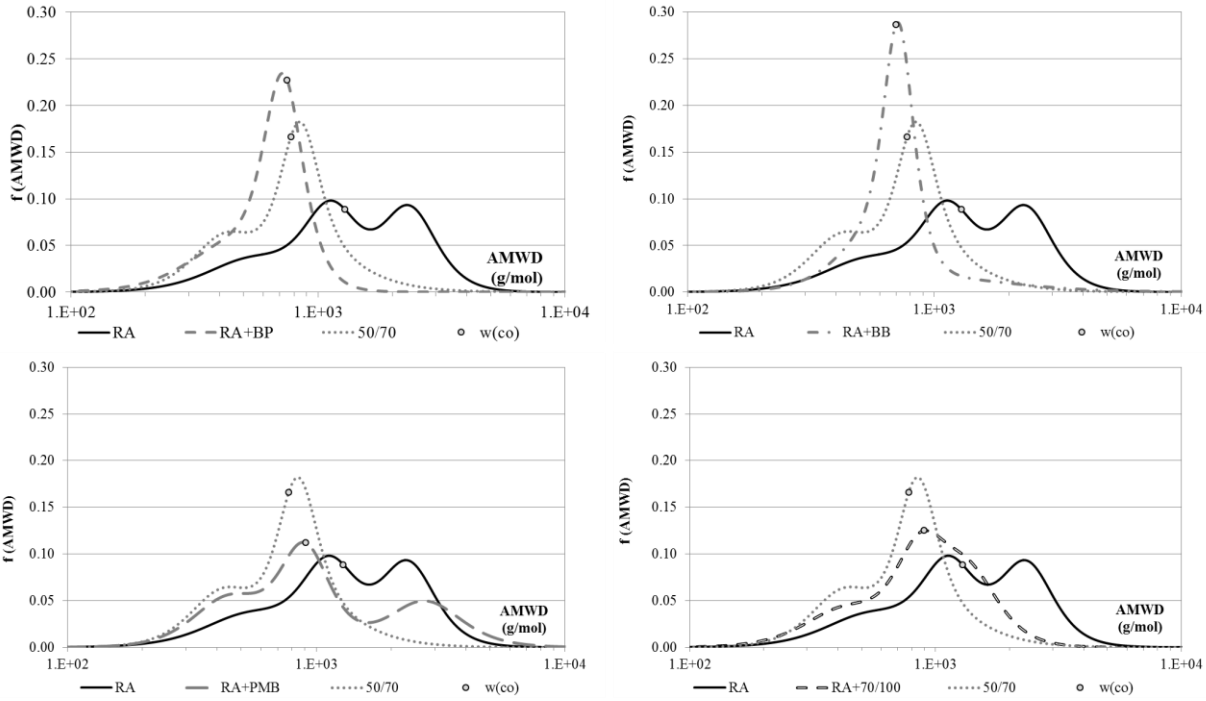


Figure 79. AMWD of RA and its blends

Firstly, Figure 79 reveals the difference between RA, which presents a bi-modal AMWD with one peak around 1000 g/mol and the other at higher molecular weight (as expected for an aged binder) and 50/70 pen bitumen, which possesses a mono-modal AMWD with a peak around 750 g/mol. According to Mullins (2011), asphaltenes have molecular weights between 500-1000 g/mol. Therefore, the fact that RA exhibits heavier molecules than 1000 g/mol could mean that molecular clustering may be taking place, producing high molecular weight molecules up to 2500 g/mol. In this regard, the δ-method shows a great potential to provide new information about bitumen ageing.

Regarding the blends of RA with the different binders, the main effect that can be observed in Figure 79 is the shift of RA's AMWD to the left (i.e. to lighter weights) after blending. In terms of biobinders blends, RA+BB and RA+BP exhibit light AMWD (lighter than 50/70 pen bitumen), both with a unimodal distribution below 1000 g/mol. On the other hand, the RA+PMB blend shows its molecular weight peak at nearly the same point as the 50/70 pen

bitumen with the PMB having a second peak at higher AMW induced by the polymers present in the blend. Lastly, blend RA+70/100 shows a unimodal distribution with a wider base than the other blends.

Nevertheless, rejuvenating effect is clear in all cases. In addition, the movement to the left of the cross-over points from the RA binder to those of the blends can be also seen as a rejuvenation indicator.

In summary, in this chapter, the rheological characterisation of the blends revealed that the biobinders and conventional binders that were studied produced a rejuvenating effect on RA binder that can be easily appreciated in the cross-over frequencies versus rheological indexes space. In this regard, the blend of biobinders with the RA binder generates less elastic and softer binders, having a comparable effect to traditional petroleum-based binders.

In terms of performance prediction, the blends of the RA binder and biobinders show equivalent rutting critical temperatures compared to 50/70 penetration bitumen and RA blends with traditionally used binders, which would lead to similar rutting resistance in the asphalt mixture. Blends of the RA binder and biobinders showed improved fatigue resistance in comparison to the rest of blends. The fact that the RA binder fatigue performance can be enhanced with biobinders without compromising rutting behaviour is a desirable rejuvenating effect.

A more fundamental evaluation was undertaken to assess low-temperature properties of the blends. To this end, the materials response was fitted at 0^{0}C with the Huet-Such model. Parameters obtained for biobinders seem reasonable in comparison with those of conventional binders (except for the RA+BP blend which is at the limit of its application). From these parameters, the δ-method was applied to determine the apparent molecular weight distribution of RA, 50/70 binders and RA blends. This AMWD allowed the rejuvenating effect of binders

on the RA binder to be visualised through the shift of the RA binder distribution to lighter molecular weights. In this regard, it can be highlighted that RA+BB and RA+BP blends show similar AMWD to the 50/70 penetration bitumen, which is not the case for the RA+PMB and RA+70/100 blends having a less pronounced rejuvenation effect.

CHAPTER 6. PERFORMANCE OF RECLAIMED ASPHALT BLENDS AND ASPHALT MIXTURES WITH BIOBINDERS

6. PERFORMANCE OF RECLAIMED ASPHALT BLENDS AND MIXTURES WITH BIOBINDERS

After having analysed the suitability of biobinders to rejuvenate the RA binder, the performance-related properties of the binders' blends and the mechanical performance of the 50% RA content asphalt mixtures were fully characterised over the whole range of service temperatures in asphalt pavements. Therefore, this chapter deals with the characterisation in terms of LVE properties, rutting, fatigue, thermal cracking, moisture damage and ageing of binders' blends and asphalt mixtures. In the following sections, these properties are studied for blends and asphalt mixtures and then related between them to analyse whether there exists a correlation. These correlations between binder blends and asphalt mixtures properties should shed light on the degree of blending of the biobinders and RA binder and the further adequacy of the binders' blend design carried out in Chapter 4 to be used for RA mixtures.

6.2. LVE properties

The LVE properties of binders' blends and asphalt mixtures have been characterised by means of rheological testing and modelling as follows.

6.2.1. Rheological testing

The binders' blends described in Section 4.5 were tested in the Dynamic Shear Rheometer (DSR) to obtain their shear complex modulus (G*) and phase angle (δ). Temperature and frequency sweeps were carried out from -10 to 60ºC and from 1 to 25Hz. Due to the wide range of temperatures used, two parallel-plates geometries were used in the DSR: 8mm (from -10 to 30ºC) and 25mm (from 20 to 60ºC). The correct data for each binder at 20ºC and 30ºC were then selected using their Black diagrams (Airey 2002).

Regarding the testing of the asphalt mixtures, after their manufacturing and compaction into

slabs, trapezoidal specimens were obtained and tested in two-point bending mode to find their complex modulus (E*) and phase angle (δ). Temperature and frequency sweeps were carried out from -10 to 40^0C and from 1 to 40Hz (EN 12697-26:2012 Annex A) as described in detail in Section 2.4.1.3 of the literature review.

6.2.2. Modelling

RA's blends and asphalt mixtures' rheological data were modelled using the 2S2P1D (2 Springs, 2 Parabolic elements, 1 Dashpot) (Di Benedetto et al., 2004; Olard & Di Benedetto, 2003) due to its ability to obtained continuous master curves over a wide range of frequencies. This model is able to reproduce binders' viscoelastic behaviour through a combination of one spring (E_∞), two parabolic creep elements (0<h<k<1) with one coefficient (δ) that regulates the balance between them, a dashpot (β) placed in series with the other elements, and finally a spring in parallel to the previous system (E_0) (Figure 80). Model parameters for the blends were fitted from the rheological tests performed in the DSR, while data from two-point bending tests and relative master curves at T_{ref}=0°C were used to obtain the model's parameters for the asphalt mixtures (Chailleux et al., 2006). Furthermore, in the case of binder blends, G* data from the DSR were converted to E* using Poisson ratio of 0.5 (Whiteoak & Read 2003), which in turns allowed E_∞ to be obtained. This conversion was carried out in order to be able to further relate the binder's parameters with those derived from the asphalt mixtures modelling.

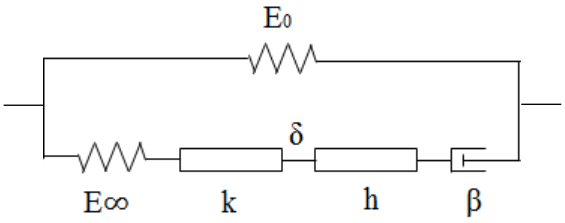


Figure 80. 2S2P1D model

6.2.3. Results and discussion

6.2.3.1. Binders' blends

The rheology of the blends was previously shown in Chapter 5 in the Black space and in the form of master curves. For the purpose of this section, the results of the rheology testing of the blends are presented in terms of Cole-Cole diagrams in Figure 81. As mentioned in Section 2.4.1.4 of the literature review, Cole-Cole diagrams display the balance between the viscous and elastic component of binders and asphalt mixtures. In this regard, Figure 81 reveals that RA+BB maintains a high viscous component even after blending with RA, while RA+BP and RA+PMB exhibit comparable diagrams. This difference between binders' blends LVE properties have to be attributed to the different nature and composition of the biobinders and reference binder. On one hand, BB is a greatly viscous material, since the resin and oil it contains do not provide much elasticity (as shown in Figure 68 with BB80/20 having high phase angle for a large range of reduced frequencies), and therefore its blend with the RA binder remain highly viscous. On the other hand, BP and PMB are SBS-polymer modified binders with a high elastic component providing comparable curves in the Cole-Cole diagram.

In summary, Figure 81 provides two main ideas: firstly, the blend of RA with the three binders produces an increase in RA viscous behaviour, which could be considered as viscoelastic properties' rejuvenation as mentioned in Chapter 5; secondly, under binders' full blending assumption RA+BP and RA+PMB blends show similar Cole-Cole diagrams and therefore asphalt mixtures with BP and PMB can be expected to have similar rheology while the asphalt mixture with BB would be different.

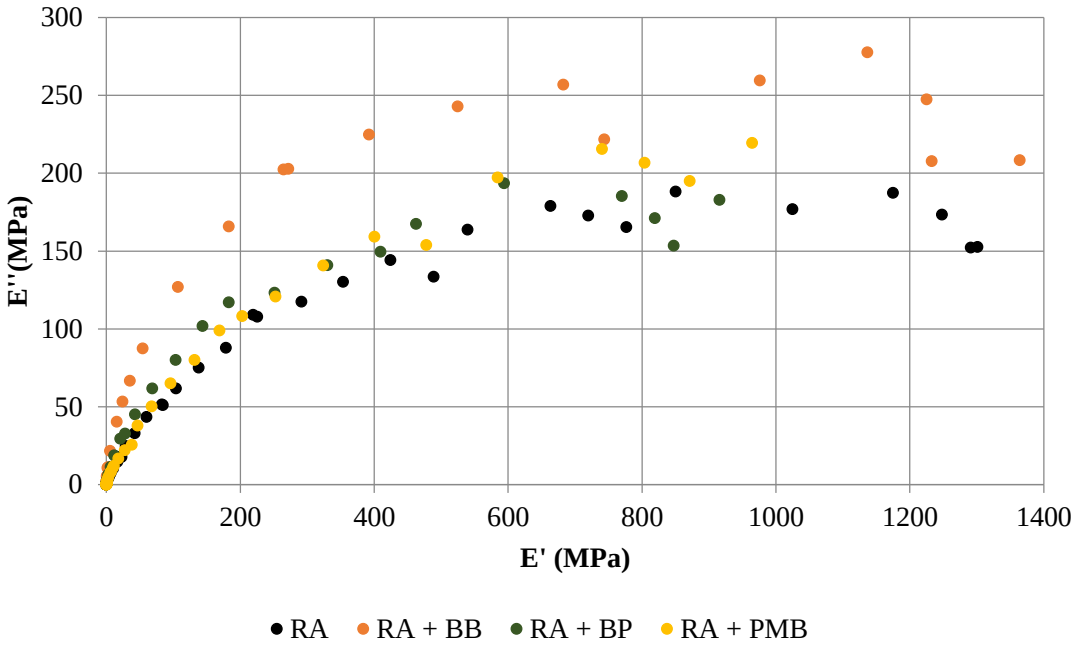


Figure 81. RA and blends' Cole-Cole diagram

6.2.3.2. Asphalt mixtures

Figures 82 and 83 display Black and Cole-Cole diagrams of the three 50% RA content asphalt mixtures after two-point bending tests. These diagrams provide different results to what could be expected from the binder blends' results. Black diagram in Figure 82 shows that 50% RA Mix BB and 50% RA Mix BP have a comparable behaviour at high temperature. Moreover, Cole-Cole diagrams of the three asphalt mixtures are different, with 50% RA Mix BB and 50% RA Mix BP being closer to each other than to 50% RA Mix PMB. These facts are not in accordance to those showed for binders' blends, which means that the binders in the asphalt mixtures are not the same than the blends studied. The fact that there are different results in terms of LVE properties of blends and asphalt mixtures could be explained considering that the binders' blends were manufactures under the assumption of full blending, and this might not be taking place during the manufacturing of the asphalt mixtures. The high viscous component of the asphalt mixtures containing biobinders is also noticeable due to the high phase angles (70º) reached (Figure 82) and viscous component dominating the elastic component up to high values (5000-6000MPa) (Figure 83) in comparison to the asphalt mixture

with PMB. In this regard, biobinders are shown to have an important influence in the LVE properties of the asphalt mixtures.

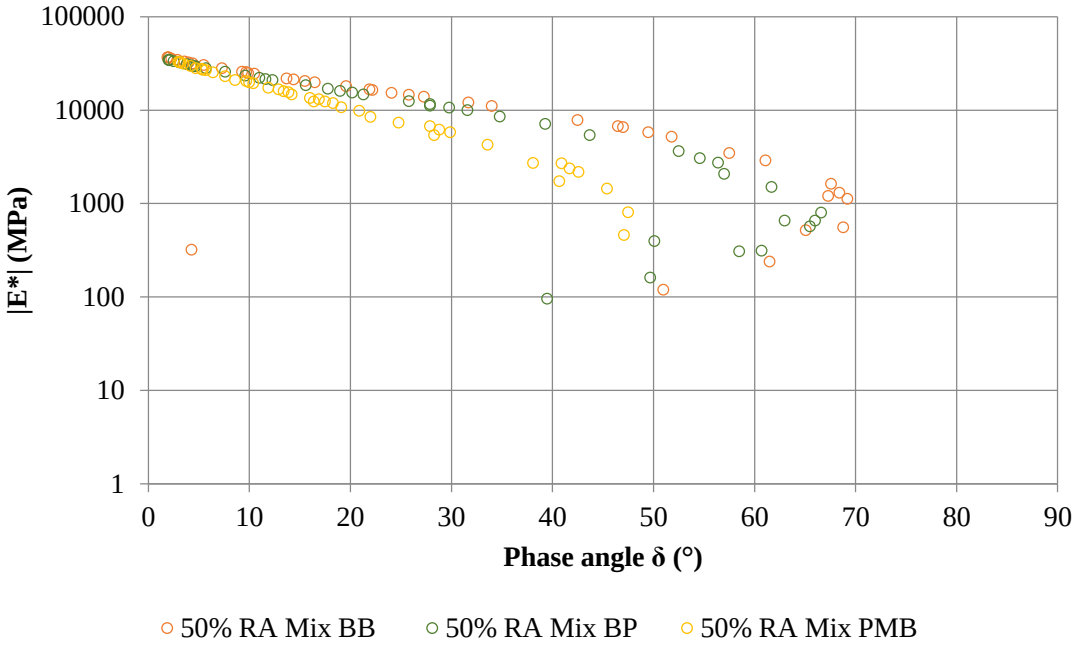


Figure 82. Mixtures' Black diagram

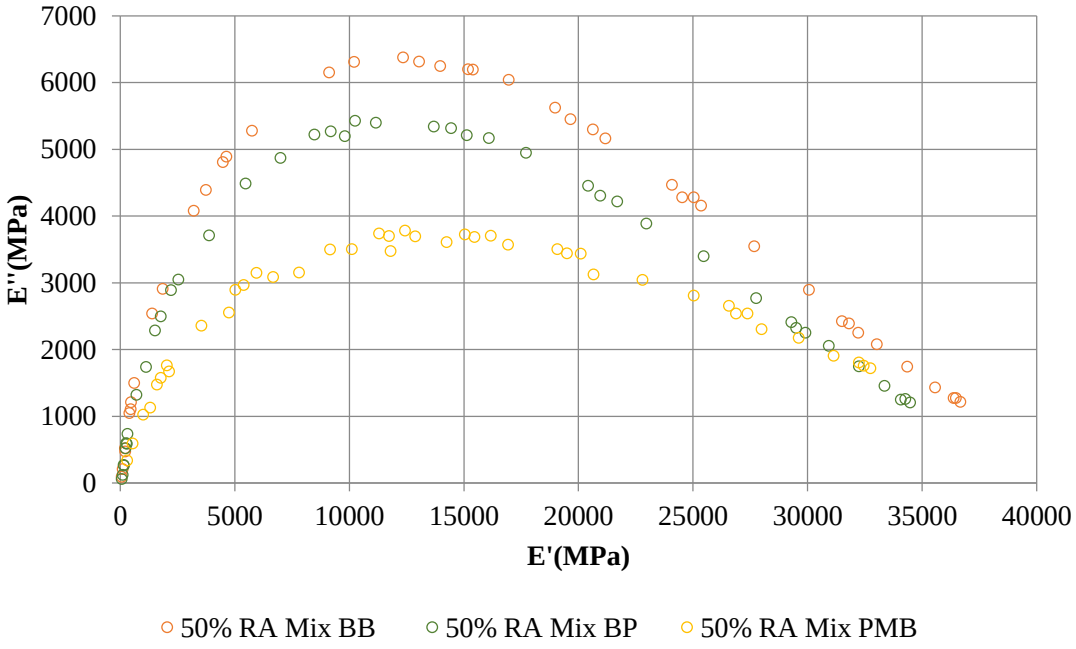


Figure 83. Mixtures' Cole-Cole diagram

Table 22 shows the norm of the complex modulus and phase angle of the three asphalt mixtures at 15°C and 10Hz. This value is used as reference for high-modulus asphalt mixtures in France having to be equal or higher than 14000MPa. It can be observed that bio-mixtures have an acceptable complex modulus to be considered as high-modulus asphalt mixtures, which was the aim of the design using only recycled materials and biobinders. It is also worth noting that 50% RA Mix BB has the highest norm of the complex modulus at 15°C and 10Hz, which was not expected since BB is the softest fresh binder used. This fact reiterates the fact that BB hardens more than conventional binders during the manufacturing of the asphalt mixtures due to its composition as shown in Section 3.3.3.

Table 22. 50% RA mixtures' complex modulus and phase angle at 15°C and 10Hz

Mixture	|E*| @ 15°C, 10Hz (MPa)	δ(°)
50% RA Mix BB	16587	21.9
50% RA Mix BP	12416	25.8
50% RA Mix PMB	13381	16

6.2.3.3. Comparison of binders' blends and asphalt mixtures LVE properties through modelling

Master curves at T_{ref}=0°C were produced for each binders' blend and asphalt mixture and the 2S2P1D model fitted to the data. However, 50% RA Mix BB, RA+BP blend and 50% RA Mix BP reached infinite values of the β parameter during the minimization process. This fact means that the linear dashpot in 2S2P1D model could be removed without influencing the results. The 2S2P1D model without linear dashpot is known as the "Huet-Sayegh" model (Sayegh 1965). This peculiarity for RA+BP is due to its high polymer content and has been already observed by other researchers (Sun, Y. et al. 2016).

Master curves of the norm of the complex modulus and phase angle are displayed in Figures 84 and 85 respectively together with the model results. The model parameters are shown in Table 23. As explained in Section 2.4.1.6 of the literature review, previous research showed

that binders and asphalt mixtures parameters should be related to each other having the same value for δ, k, h and β (Di Benedetto et al., 2004; Olard & Di Benedetto, 2003). However, the materials studied do not show such a relationship and therefore the step of predicting mixtures behaviour from binders seems less direct. This fact could be due to the high RA content in the asphalt mixtures and the hard consistency of the RA binder (low penetration of 9x0.1mm) which could hinder the full blending between RA and fresh binders. This issue was already highlighted by Mangiafico et al. (2013) in a similar study of RA mixtures with conventional binders. If this is the case, the binder present in asphalt mixtures is not the same as the binders' blends studied, and therefore the relationship between them is not possible.

Table 23. 2S2P1D and Huet-Sayegh parameters for blends and mixtures at T=0°C

Binder/Mixture	E_0	E_∞	δ	k	h	β	τ	C1	C2
RA+BB	0	1344	4.7	0.34	0.83	2.7	0.12	17.7	122.0
50% RA Mix BB	42	38033	1.3	0.26	0.80	-	4.87	30.3	211.7
RA+BP	0	1828	3.6	0.24	0.73	-	0.03	20.2	122.4
50% RA Mix BP	40	36395	1.2	0.22	0.71	-	3.33	28.2	172.1
RA+PMB	0	1682	5.9	0.31	0.69	361.0	0.14	22.1	134.0
50% RA Mix PMB	88	39935	2.0	0.18	0.52	100.7	15.31	30.6	180.4

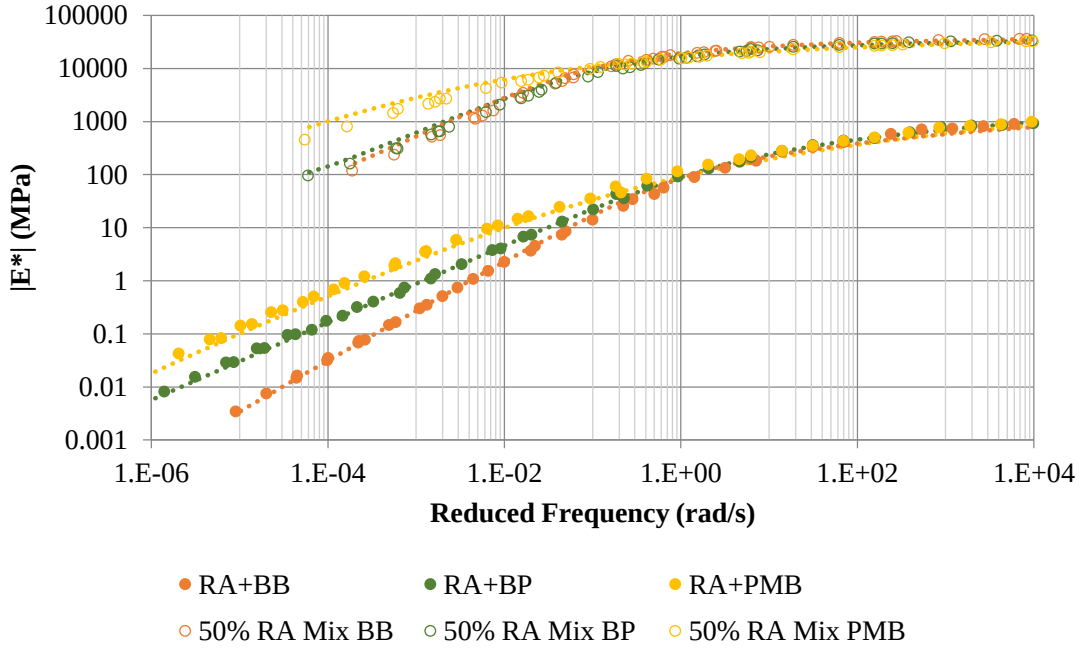


Figure 84. Master curves of the complex modulus and 2S2P1D model (dotted lines) at Tref=0°C for binder blends and asphalt mixtures

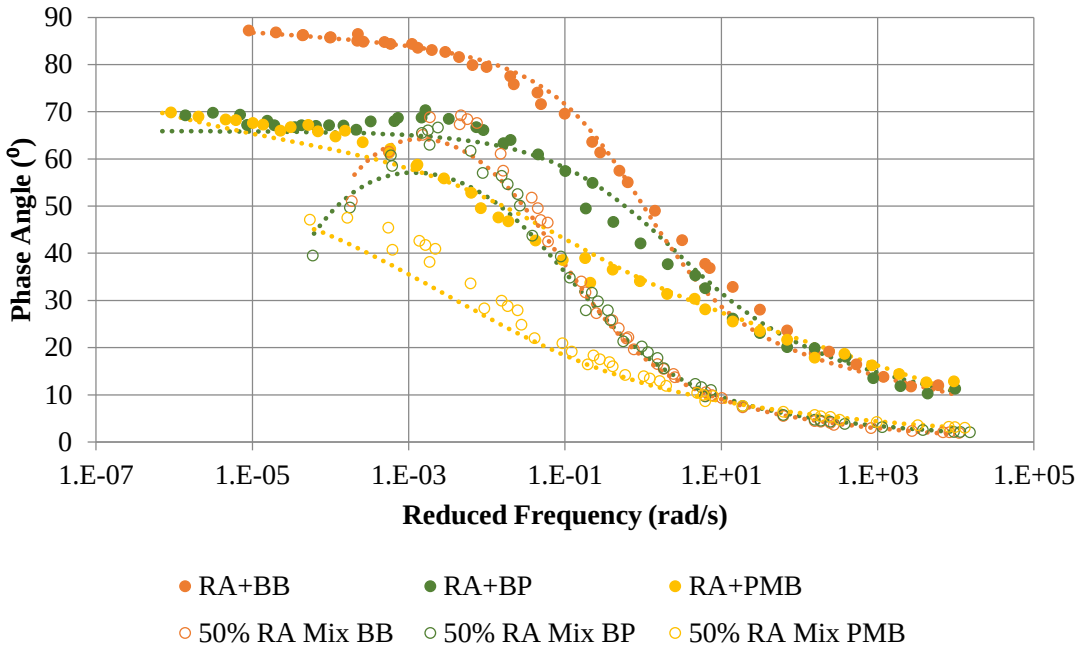


Figure 85. Master curves of the phase angle and 2S2P1D model (dotted lines) at Tref=0°C for binder blends and asphalt mixtures

In order to further assess this issue, the normalised Cole-Cole diagrams of binders' blends and asphalt mixtures were produced. For this purpose, E* is normalised following Equation (77).

$$E^*_{norm} = \frac{E^* - E_0}{E_\infty - E_0} \quad (77)$$

where E_0 and E_∞ are respectively the minimum and the maximum asymptotic values of the norm of the complex modulus obtained with the models (Table 23). The normalised Cole-Cole diagrams display the real part of E^*_{norm} in the x-axis and the imaginary part in the y-axis and are shown in Figure 86. It can be observed that binder blends and asphalt mixtures with the same binder do not completely overlap, especially for BP, which confirms that there is no direct link between binder blends and asphalt mixtures rheological properties (Mangiafico et al. 2013) and supports the hypothesis of partial blending taking place instead of full blending. This is due to the fact that if full blending does not take place, part of the RA binder remains inactive and the binder in the asphalt mixture would contain more biobinder or reference binder than

the blends studied. If this happens, the asphalt mixtures should show higher viscous component than the blends, because of the higher viscous component of the biobinders and reference binder in comparison to the RA binder, as it is the case of BP in Figure 86.

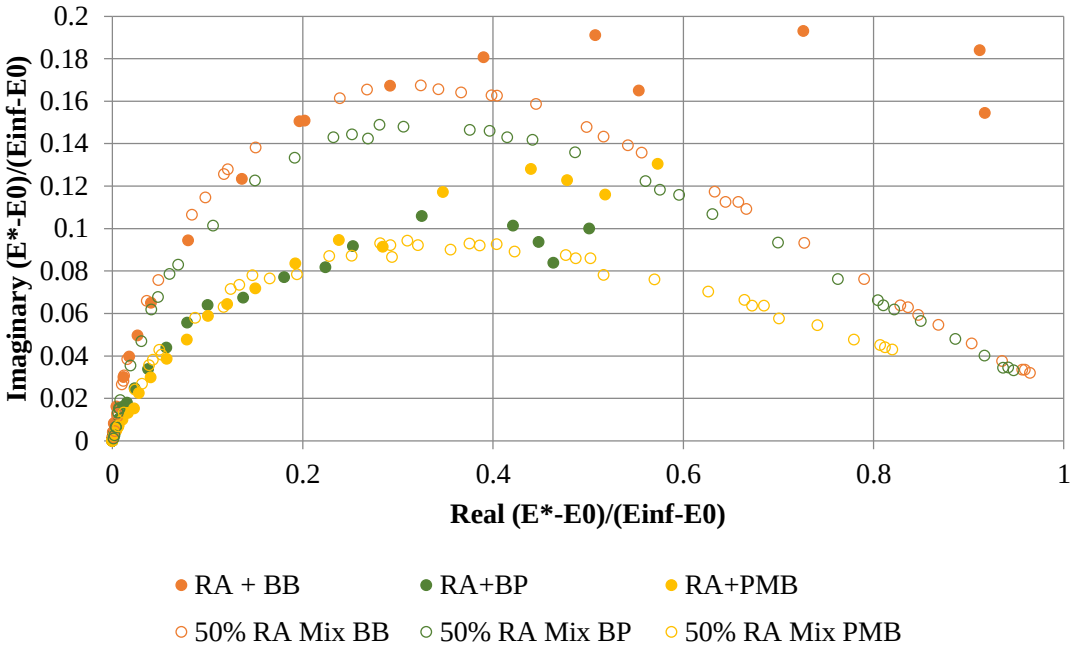


Figure 86. Normalised Cole-Cole diagram for binder blends and asphalt mixtures

Nevertheless, the influence of the binders in asphalt mixtures can be noticed in Figures 84 and 85 where at low frequencies the binder blends and asphalt mixtures provide the same ranking for modulus and phase angle.

In summary, in this section, the LVE properties of binders' blends and asphalt mixtures with 50% RA are shown. Binders' blends were studied by means of DSR while asphalt mixtures were tested in two-point bending mode. Rheological data from both tests was analysed and modelled using 2S2P1D and Huet-Sayegh models. Biobinders have an important effect on asphalt mixtures behaviour providing an increased viscous component in comparison to the reference asphalt mixture. However, no direct links between their LVE properties were found. This fact could possibly be due to the hypothesis of full blending between RA and biobinders

that was made for binder blends and manufactured asphalt mixtures, which may not be taking place.

6.3. Rutting

The main distress that pavements may exhibit at high temperatures (>40ºC) is rutting. The rutting resistance of binders' blends was analysed by means of MSCR tests while the resistance of asphalt mixtures was evaluated using RLAT.

6.3.1. MSCR

In order to study the response of the binders' blends to rutting, Multiple Stress Creep-Recovery Tests (MSCRT) were carried out at 40ºC and 60ºC at different levels of stress in the Dynamic Shear Rheometer (DSR). According to AASHTO T350-14 (2014), these tests should be performed at 0.1kPa and 3.2kPa to obtain data within and outside the LVE response of the binders respectively.

In the DSR, the MSCRT consists of the application of the shear load at the specific stress level to deform the sample during 1 second (creep) loading, and the allowance of strain recovery during 9 seconds (recovery). At each stress level, 10 creep-recovery cycles were applied (AASHTO T350-14 2014). The tests were carried out using the 25mm parallel plate geometry with 1mm gap. Short-term aged binders (RTFOT) were tested for rutting resistance. This test has been found to provide good correlations with the rutting resistance of asphalt mixtures (Bukowski et al. 2011).

From the MSCRT, the main parameters obtained are the percentage of recovered strain R (%), which provides a measurement of the material capability to recover strain, and the non-recoverable compliance J_{nr} (1/kPa), which is the potential of the binder to suffer permanent deformations. Jnr is obtained by dividing the non-recovered strain by the applied stress. In

addition to the recovery capacity, the stress susceptibility of binders can be assessed. For this purpose, a Stress Susceptibility Parameter ($J_{nr,diff}$) was calculated. These parameters were described in Section 2.4.2 of the literature review.

6.3.2. RLAT

The rutting resistance of the asphalt mixtures was assessed by means of Repeated Loading Axial Tests (RLAT) according to the Standard BS DD 226 (1996). This test applies an unconfined axial stress of 100kPa ± 2kPa to cylindrical specimens in cycles of "1s stress application – 1s rest" for a total of 3600 cycles. The tests were performed at 40°C. This test was chosen due to the fact that the asphalt mixtures designed are meant to be used in base or binder layers, and therefore they will not be subjected to wheel passes (as in wheel-tracking or Hamburg-wheel-tracking tests) but to tension-compression cycles in the pavement structure.

6.3.3. Results and discussion

6.3.3.1. Binders' blends

The results of the MSCRT at 40^0C and 60^0C in terms of recovery R(%) and J_{nr} are shown in Figures 87 and 88 respectively. The first noticeable result is the high recovery and low J_{nr} that the RA binder exhibits in comparison to a conventional 50/70 penetration grade binder. This fact may lead to the conclusion that the RA binder is highly flexible and elastic. However, if the strain that the binders suffered during the test is analysed (Figures 89 and 90), the significant difference in deformation between the RA binder and the 50/70 reveals the RA binder's high recovery is due to the low strain that it suffers because of its hard consistency. Hence, a small amount of strain recovered may be translated into a high percentage of recovery. On the contrary, the 50/70 binder presents high strains and it is not able to recover more than 15%. These results are in accordance with the high critical temperatures of the binders shown in

Table 10 which revealed the greater high critical temperature of the RA binder and therefore its higher resistance to rutting.

When it comes to the blends of RA with the biobinders and the reference binder, Figures 87 and 88 show that RA+BP and RA+PMB are able to keep their recovery close or even higher than that of the RA binder. However, while the blend with the PMB keeps a low J_{nr}, the blend with BP has an increased value compared to that of the RA binder. This occurs because the blend of RA and BP is a softer binder with a higher deformation (Figure 89b), Figure 90b)); however, it is still able to recover 40-50% at 40°C and 15-55% at 60°C. The good performance shown by RA+BP and RA+PMB is due to the polymers content of BP and PMB that increases the elasticity of the RA binder when blended with it allowing high recovery values in comparison to the conventional 50/70 penetration grade bitumen.

Regarding RA+BB, its recovery is lower than that of the RA binder but still comparable to the 50/70 conventional bitumen. Moreover, the J_{nr} of RA+BB is lower than that of the 50/70 at 40°C due to its lower strain during the test (Figure 89a)) while at 60°C it becomes higher (Figure 90a)).

This fact reveals the importance of the temperature for MSCRT. Table 24 shows the sensitivity of the recovery R (%) of the binders to temperature in percentage. The binders whose recovery is more affected by temperature (from 40°C to 60°C) are those whose softening point is lower than 60°C: RA+BB and 50/70. This occurs because of the change in the consistency of binders when they are tested at temperatures higher than their softening point. In addition, these changes are more perceptible at the highest stress.

Finally, the susceptibility of the binders to the stress level is assessed using $J_{nr,diff}$ in Table 24. The binder' susceptibility to the stress level at 40°C is much lower than 75%, which is the limit

established for this parameter (Golalipour 2011). However, at 60°C, this susceptibility significantly increases. This is particularly true for RA+BP, 50/70 and the RA binder.

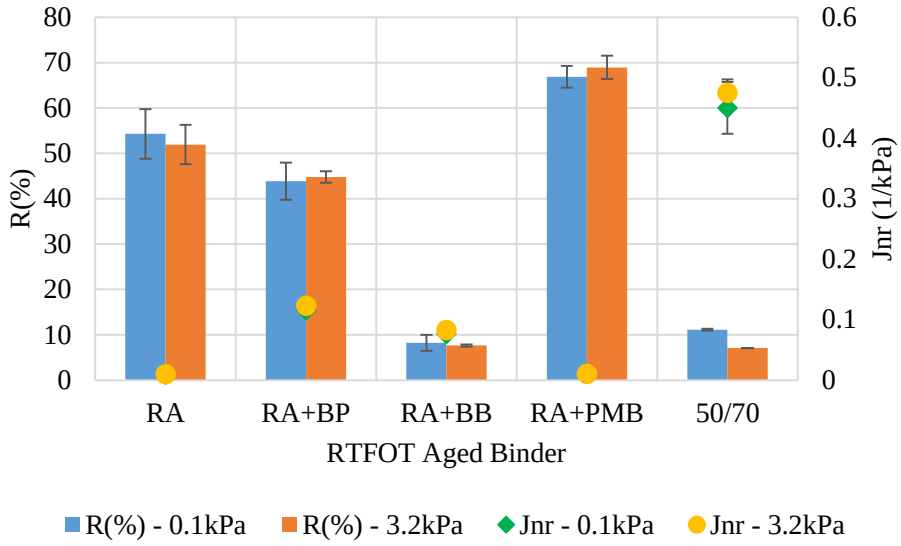


Figure 87. R (%) and Jnr at 40°C of binders

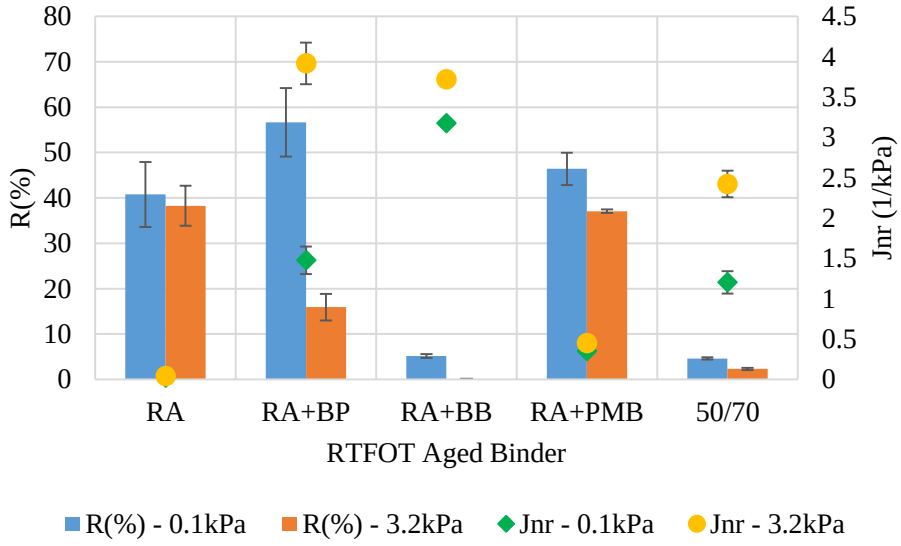
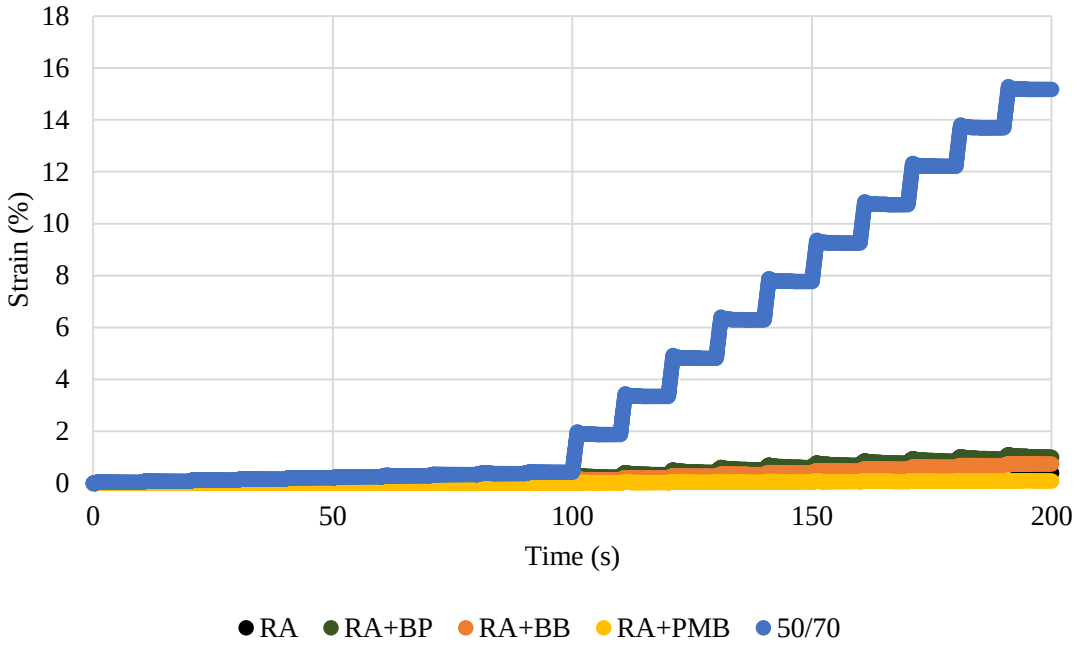
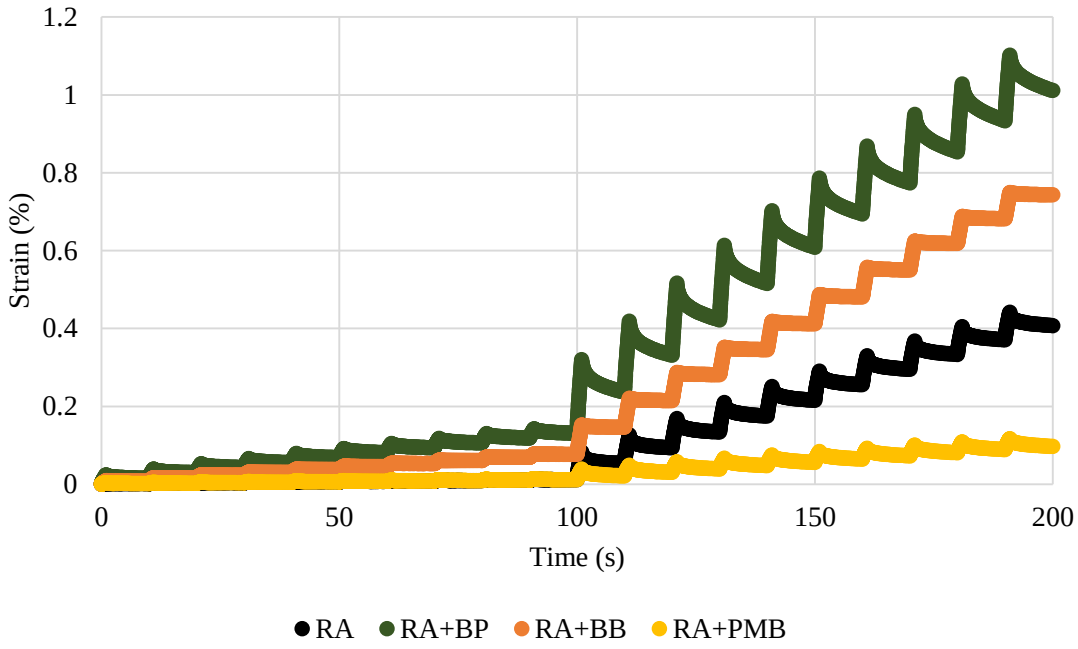


Figure 88. R(%) and Jnr at 60°C of binders

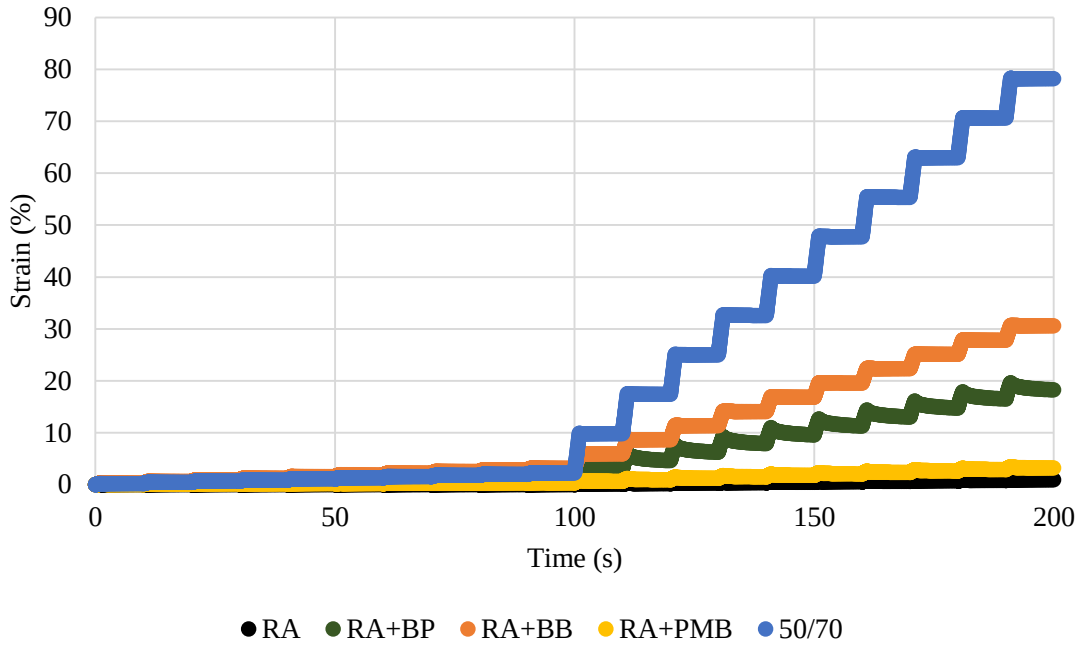


a)

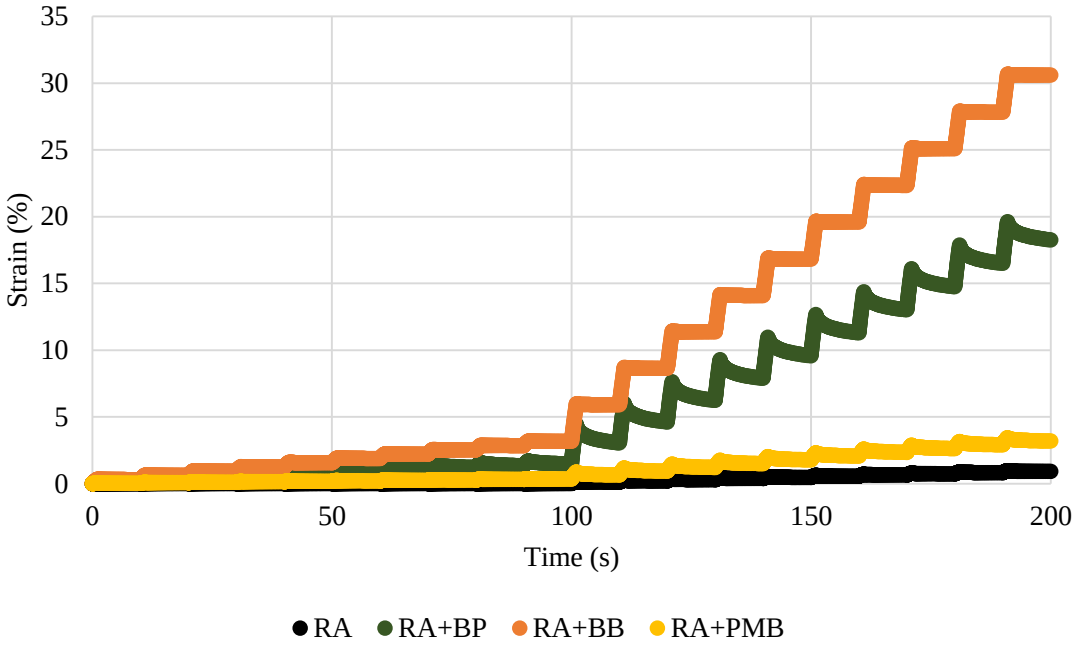


b)

Figure 89. Strain during MSCRT at 40^{0}C of: a) all binders; b) RA binder and blends



a)



b)

Figure 90. Strain during MSCRT at 60^{0}C of: a) all binders; b) RA binder and blends

Table 24. Parameters in MSCRT

Binder	Change of R(%) due to temperature at 0.1kPa	Change of R(%) due to temperature at 3.2kPa	$J_{nr,diff}$ at 40°C	$J_{nr,diff}$ at 60°C
RA	25%	26%	6%	90%
RA+BP	-29%	64%	6%	165%
RA+BB	**38%**	**99%**	8%	17%
RA+PMB	31%	46%	-4%	28%
50/70	**59%**	**67%**	5%	101%

Given these results, in summary, BP is able to maintain RA rutting resistance at a high level, being comparable to the effect of a high-performance PMB. On the other hand, the blend of RA with BB provides similar rutting resistance to a 50/70 bitumen commonly used in conventional asphalt mixtures.

6.3.3.2. Asphalt mixtures

The rutting resistance of the asphalt mixture was characterised by means of RLAT at 40°C. This test provides as the main outcome the axial permanent deformation of the asphalt mixture after the loading cycles. The average of two specimens tested is shown in Table 25. A standard asphalt mixture is considered to have a good rutting resistance if its axial deformation is lower than 2% (Widyatmoko 2008). According to Table 25, the three asphalt mixtures pass this threshold so could be considered suitable in terms of rutting resistance.

Table 25. Axial deformation of asphalt mixtures after RLAT

Mix	Axial deformation after RLAT (%)	Threshold for axial deformation (%)
50% RA PMB	0.39	2
50% RA BP	0.71	
50% RA BB	0.54	

6.3.3.3. Relationship of rutting resistance of binders' blends and asphalt mixtures

The axial permanent deformation of the asphalt mixtures after RLAT can be related to the Non-Recoverable Compliance (J_{nr}) of the blends obtained in the MSCRT, which is the potential of the material to suffer permanent deformation. The relationship between these two parameters

is displayed in Figure 91 showing good correlation coefficient (R^2) for linear laws (>0.85) for both MSCRT temperatures. However, the correlation seems better at 40°C, which is possibly due to the temperature being the same as in RLAT. This correlation means that the results for the asphalt mixtures and the blends are in accordance in terms of rutting resistance and the MSCRT provided a good first idea of what to expect using these biobinders in a pavement as shown by previous researchers for this test (Golalipour 2011).

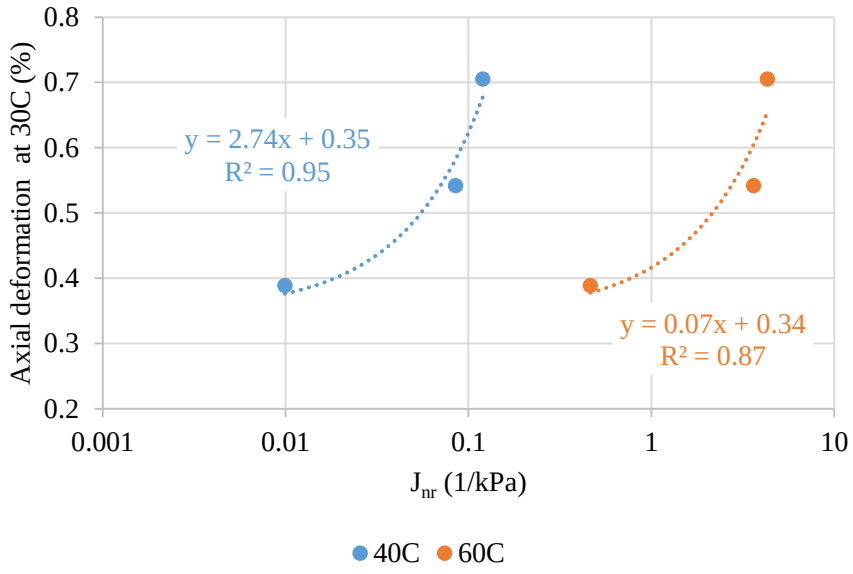


Figure 91. Axial deformation of asphalt mixtures versus Jnr of blends

In summary, both biobinders' blends and bio-asphalt mixtures showed acceptable resistance to rutting when compared to conventional materials and a strong correlation between them was found.

6.4. Fatigue

The main distress that pavements may exhibit at intermediate temperatures (10-40ºC) is fatigue cracking. The resistance of binders' blends to fatigue cracking was assessed by means of Time Sweep tests. Asphalt mixtures were tested using ITFT to obtain their fatigue performance.

6.4.1. Time sweep tests

According to several studies (Shen et al. 2006; Bonnetti et al. 2002), the characterisation of the fatigue resistance can be carried out by performing Time Sweep Tests using the DSR in the classical configuration of parallel plates of 8 mm diameter and 2 mm gap. The following procedure was applied: stress-controlled cyclic loading tests at 20°C and 10 Hz (Table 26). In this case, the samples tested were long-term aged (RTFOT+PAV) due to fatigue cracking usually appearing after years of service life of pavements. The initial norm of the shear complex modulus shown in Table 26 is the average of the different samples tested. The applied stresses were selected depending on the stiffness (complex modulus) of the material. Stiff materials which have a brittle cracking, suddenly fail after a number of cycles even if the initial strain is low (~0.5%), while soft and flexible materials need a higher initial strain to develop fatigue in a measurable number of cycles. Fatigue lines were produced for a range of approximately 1,000 to 100,000 cycles.

Table 26. Initial complex modulus of the binders and Time Sweep Tests stress levels

Binder	Initial norm of the shear complex modulus, |G*| (Pa)	Applied stress (e5 Pa)
RA	83013750	7.5;8.0;8.5;9.0;10.0;11.0;12.0;15.0
RA+BP	14190000	1.5;2.0;2.5;3.0;5.0;6.0;7.0
RA+BB	94471429	4.0;6.0;8.0;9.0;10.0
RA+PMB	20323333	3.8;4.0;5.0;6.0;7.0;8.0
50/70	23638750	3.0;3.5;4.0;5.0;7.0;8.0

Since the definition of the fatigue failure during laboratory testing is still challenging, the fatigue life was measured in accordance to two different failure criteria: N_{f50} and N_{p20}, as defined in Section 2.4.3 of the literature review.

6.4.2. ITFT

Regarding the fatigue resistance of asphalt mixtures, they were subjected to Indirect Tensile Fatigue Tests (ITFT) according to the Standard BS DD ABF (2003). Before being subjected to ITFT, the cylindrical specimens have to be tested to determine their modulus in stress-

controlled mode using the Indirect Tensile Strength Tests (ITST) on one diameter. Then, the specimens were tested for ITFT at 20°C ± 0.5°C and different stress levels (depending on the asphalt mixture) at a frequency of 40 ± 1 load repetitions per minute. The stress levels were selected to obtain fatigue laws over a range of approximately 1,000 to 100,000 cycles to failure. During ITFT, the vertical deformation of the specimen is measured by embedded LVDTs and recorded (Figure 41). The test is set to stop when the deformation if larger than 10mm. The main outcome of ITFT is the fatigue law of the asphalt mixtures for comparison.

6.4.3. Results and discussion

6.4.3.1. Binders' blends

Figures 92 and 93 show the fatigue laws of the RA binder, binders' blends and the 50/70 conventional binder after RTFOT+PAV ageing according to N_{f50} and N_{p20} failure criteria respectively. The first noticeable result is that the two criteria provide different outcomes. In the case of N_{f50}, the RA binder shows lower fatigue life than RA+BP, RA+PMB and the 50/70 binder. This result could be expected due to the high stiffness and therefore low flexibility of the RA binder which does not allow the material to bear high deformations and initiates its cracking and failure (Shah et al. 2007; Mogawer et al. 2012). In this regard, the blend of the RA binder with BP seems to improve that fatigue life and makes it comparable to the 50/70 conventional binder. The blend of RA with the PMB generates the best system in terms of fatigue resistance at low strain levels. Finally, the blend of the RA binder with BB produced a material with lower fatigue life than the RA binder which is related to its high initial complex modulus (stiffness) (Table 26) - even higher than that of the RA binder – due to the ageing of BB, which was shown to be significant because of its nature (Section 3.3.3).

When analysing fatigue life of materials as shown in Figure 92, it is important to consider the strain level that the pavement would be exposed to. In this regard, if a pavement layer is

designed to suffer low strain levels (0.1-1%), in Figure 92 it is clear that the most convenient binder to use would be RA+PMB, since it shows the highest resistance to fatigue as such strain level. Furthermore, it is worth noting that at low strain levels, the improvement that BP could provide to the RA binder disappears. On the other hand, if the pavement layer is meant to bear greater strain levels (>4%), RA+PMB, RA+BP and 50/70 show clear advantages in comparison to the RA binder. This reflects the importance of the slope of fatigue laws when selecting a binder for specific traffic conditions and pavement design, since the convenience of using one material or another may completely change.

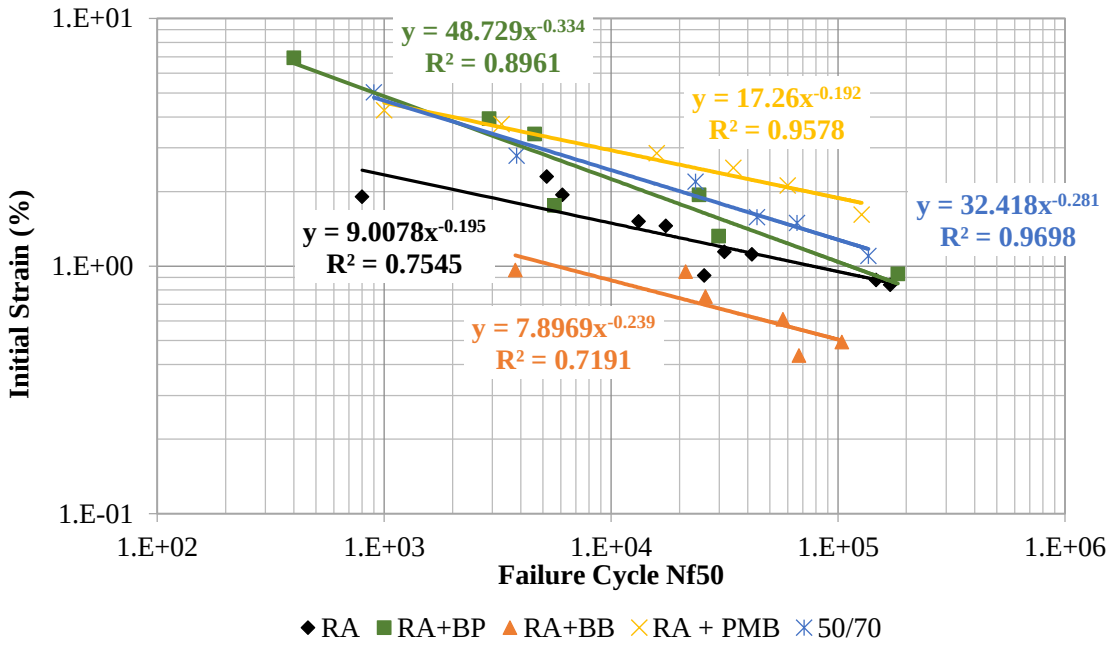


Figure 92. Fatigue laws of binders and blends according to N_{f50} criteria

Regarding the raking of materials according to the failure criteria, a different outcome is shown in Figure 93 according to the N_{p20} criteria. In this case, the RA binder seems to have an equivalent fatigue resistance to the 50/70 conventional binder; the RA+BB and RA+PMB blends show intermediate values and the RA+BP blend exhibits the lowest fatigue life.

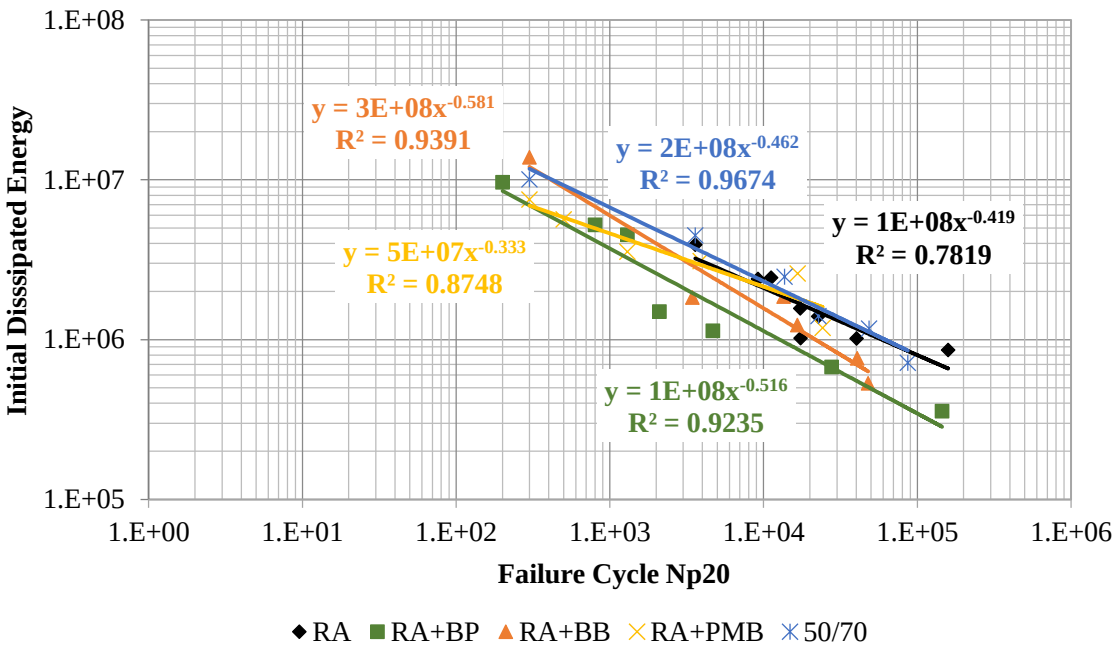


Figure 93. Fatigue laws of binders and blends according to N_{p20} criteria

In order to further understand this discrepancy, Figure 94 shows the evolution of the complex modulus of the binders at a similar level of initial strain (0.9-1.5%). RA+BP, RA+PMB and the 50/70 conventional binder are able to maintain the level of deformation and slowly fail showing a ductile cracking. On the other hand, RA and RA+BB reach the level of strain and quickly fail showing a brittle fracture because of their lack of flexibility and high stiffness. In terms of dissipated energy, Figure 95 displays the evolution of the Dissipated Energy Ratio (DER) of the binders for a similar level of initial dissipated energy (≈1150000 Pa). It reveals how RA+BP rapidly deviates from the "No damage" line producing its early failure according to N_{p20} while the rest of the binders and blends exhibit a slower deviation.

Therefore, the failure criteria used strongly influenced the results. In terms of fatigue resistance, the RA binder is a brittle binder which cannot maintain a strain for a large number of cycles and fails; however, if the dissipated energy is the criterion, it can be comparable to a 50/70 binder. Its blend with the biobinder BB did not decrease that brittleness and consequently RA+BB showed poorer fatigue resistance than the RA binder. On the other hand, BP was able

to provide the RA with flexibility to maintain strain for a longer number of cycles and therefore showed an enhanced fatigue resistance in Figure 92, which was not shown if the dissipated energy is considered.

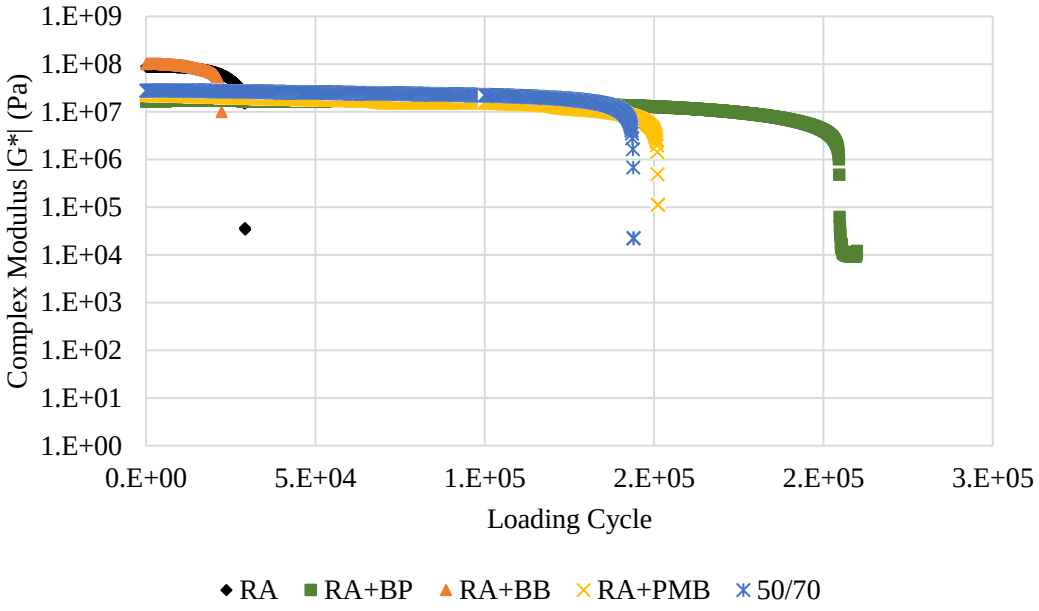


Figure 94. Evolution of the complex modulus during fatigue tests

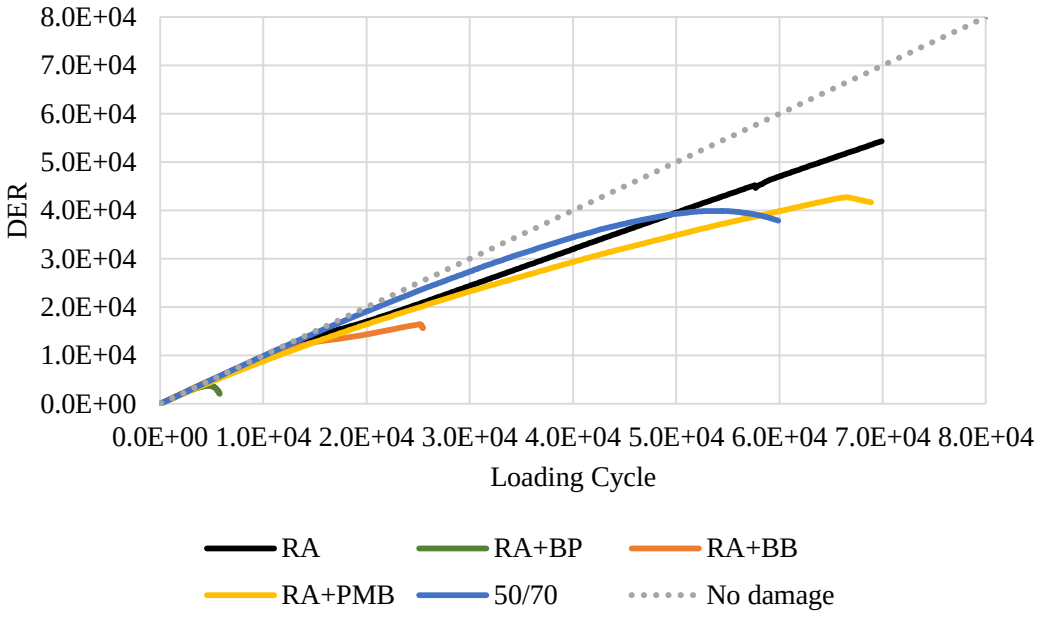


Figure 95. Evolution of the dissipated energy ratio (DER) during fatigue tests

In this regard, the fatigue study of binders' blends provides insight into the behaviour of the materials but does not allow decisive conclusions about their fatigue resistance to be obtained.

6.4.3.2. Asphalt mixtures

The fatigue laws of the three asphalt mixtures at 20°C are shown in Figure 96. The 50% RA mixtures with PMB and BP show equivalent fatigue life while the 50% RA mixture with BB exhibited a slightly lower resistance to fatigue. This fact is probably due to the SBS polymer content of PMB and BP which provides the asphalt mixtures with an enhanced fatigue life (Airey 2004). These fatigue results of the asphalt mixtures are in accordance to those showed in Figure 92 for the fatigue performance of the blends using N_{f50} as failure criteria. Regarding this accordance, it can be seen that the three asphalt mixtures have nearly parallel fatigue laws. This could imply that their slope is dominated by the aggregate gradation, which is the same for the three of them, while the relative position is dominated by the binder.

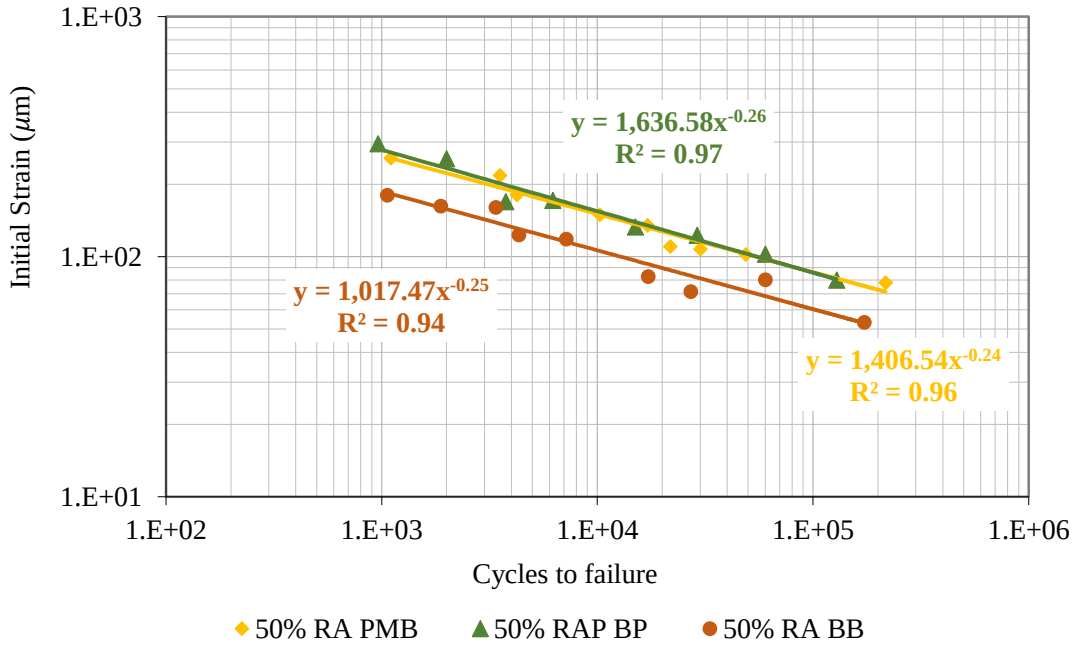


Figure 96. 50% RA mixtures fatigue laws

6.4.3.3. Relationship of fatigue resistance of binders' blends and asphalt mixtures

In order to further analyse the relationship between binders' blends and asphalt mixtures, the failure strain of the asphalt mixtures in ITFT has been related to the failure strain of the blends in time sweep tests at several number of cycles showing good linear relationships (R^2>0.97) (Figure 97). This strong correlation means that the strain in the asphalt mixture linearly increases with an increase of the strain in the blend. This fact was highlighted by Moreno-Navarro et al. (2015) for non-recycled asphalt mixtures with modified and conventional binders and it still holds for RA mixtures with biobinders. In this regard, even if the blends were manufactured in the laboratory under the full blending assumption which then may not occur in asphalt mixtures, their study can still provide valuable information about the performance of the asphalt mixture.

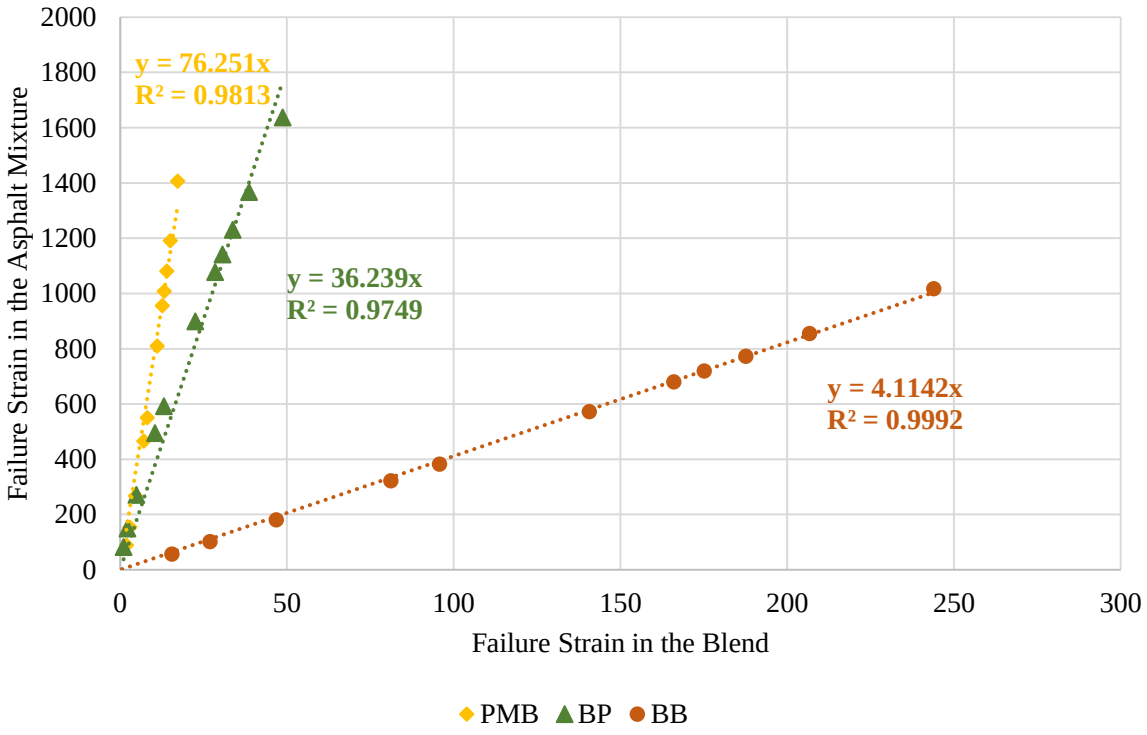


Figure 97. Relationship between initial strain of asphalt mixtures and blends

In summary, the fatigue characterisation of the 50% RA content asphalt mixture with BP has comparable resistance to a 50% RA content asphalt mixture with a conventional PMB probably

due to the polymer content while the 50% RA content asphalt mixture with BB showed poorer performance. The results of asphalt mixtures and binders' blends can be linearly related showing a strong correlation and reinforcing the use of binders' blends testing of RA and binders to obtain information before asphalt mixtures testing.

6.5. Thermal cracking

The main distress affecting pavements at low temperatures (<10ºC) is thermal cracking. The resistance of binders' blends to this distress was assessed by means of Bending Beam Rheometer (BBR) tests while TSRST were used for asphalt mixtures.

6.5.1. BBR tests

Thermal cracking phenomenon is related to the relaxation capability of binders which is usually studied by means of BBR tests in the to obtain their Creep Stiffness S (MPa) and the m-value (EN 14771 2012). Each binder was tested at two different temperatures depending on their properties in order to determine the low critical Superpave temperatures T_c (AASHTO MP1 1998) which correspond to S=300MPa and m=0.300 after 60s of loading. The test temperatures are shown in Table 27. The binders tested were long-term (RTFOT+PAV) aged. In addition to S and m, ΔTcr was calculated as a measure of the cracking potential of the binders following Equation (56) (Anderson et al. 2011) as described in Section 2.4.4 of the literature review.

Table 27. BBR testing temperatures

Binder	Temperatures
RA	-12; -18
RA+BP	-12; -18
RA+BB	0; -6
RA+PMB	0; -6
50/70	-24; -30

6.5.2. TSRST

The thermal cracking performance of the asphalt mixtures was assessed by means of Thermal Stress Restrained Specimen Tests (TSRST) according to EN 12697-46 (2012). In this test, prismatic specimens with section 50x50mm and 160mm length are subjected to a temperature decrease at a constant temperature rate (10K/h) starting at 20ºC. During the test, the length of the specimen is held fixed which prevents the shrinkage that the specimen would naturally experiment due to the temperature decrease. Consequently to the prohibited thermal shrinkage, a cryogenic stress is built up in the specimens which leads to their fracture. Two vertical LVDTs control the position of the specimen (Figure 46). The results of the test are the evolution of the cryogenic stress with the decrease in temperature, the failure stress and the failure temperature.

6.5.3. Results and discussion

6.5.3.1. Binders' blends

Table 28 shows the low critical temperatures for stiffness (S), relaxation criteria (m) and the consequent ΔTc obtained after BBR testing. ΔTc is the difference between the critical low temperature determined by stiffness and relaxation criteria. Analysing Table 28, it can be observed that RA binder and RA+PMB are m-controlled (ΔTc>0). This fact means that the thermal cracking of the binder would be driven by the failure of its relaxation capability. On the other hand, RA+BP, RA+BB and the 50/70 bitumen are S-controlled (ΔTc<0), which implies that its thermal cracking would be controlled by their high stiffness.

Table 28. Low critical temperatures and ΔTc of binders

Binder	Tc (S)	Tc (m)	ΔTc
RA	-7.5	**-6.1**	-1.4
RA+BP	**-8.9**	-17.9	9.0
RA+BB	**-5.7**	-8.8	3.1
RA+PMB	-16.9	**-10.4**	-6.5
50/70	**-10.0**	-14.0	4.0

Figure 98 displays the values of ΔTc of the different binders and the crack warning (dash red line) and limit (red line) provided by Anderson et al. (2011). In this regard, the conventional 50/70 binder stays away from the thresholds, while the RA binder's value is negative and becomes closer to the warning limit. This is in accordance to what researchers have previously shown (Hanz & Services 2015; Anderson 2016): as an asphalt binder ages, ΔTc value becomes more negative, indicating a loss of relaxation properties, which indicates that ΔTc is an important parameter related to asphalt binder durability. In this respect, in Figure 98, it is highly noticeable how BP and BB are able to bring the RA binder's ΔTc to positive values, which might be a sign of rejuvenation but also means that the blends would fail because of their high stiffness (high Tc(S) in Table 28). This fact indicates that the use of these biobinders with RA would be more advisable in warm places, according to binder results. Regarding the reference PMB, it produced the opposite effect to both biobinders having that the blend with the RA binder exceeds the cracking limit. This result may be due to the ageing of the PMB, which damages the polymeric network of the binder reducing its advantages and providing a brittle binder with lower relaxation capacity. However, it significantly improves the low critical temperature of the RA binder.

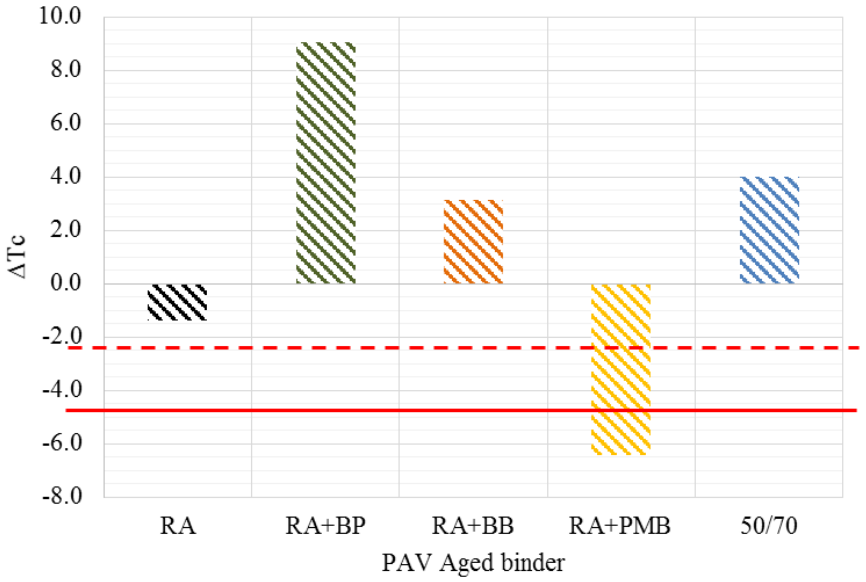


Figure 98. ΔTc of binders and cracking warning and limit

6.5.3.2. Asphalt mixtures

The thermal cracking resistance of the asphalt mixtures was measured by means of TSRST. Four specimens of each mixture were tested. The results of tests are shown in Figure 99 in terms of the cryogenic stress generated in the specimens due to the prohibition of the natural shrinkage because of the temperature decrease. Table 29 displays the average failure temperature and stress for the three RA mixtures together with their standard deviation.

In Figure 99 the RA mixtures with biobinders exhibit similar development and evolution of the cryogenic stress, lower than that of the reference mixture which may be due to the nature of the biobinders containing resin that may shrink in a similar manner. However, the failure temperatures in Table 29 reveal that 50% RA PMB and 50% RA BP fail at the same temperature while 50% RA BB has a slightly higher value. The equivalence between 50% RA PMB and 50% RA BP is possibly due to the SBS polymer content, which help the asphalt mixture to become being less brittle than 50% RA BB. In order to further compare these results, independent (unpaired) two-sample T-tests were performed to check whether the results are significantly different from each other. As result, p-values are presented in Table 29 revealing

that the three asphalt mixtures' failure temperatures are not significantly different, using a threshold of statistical significance of 0.05, and therefore similar thermal cracking performance might be expected. In addition, the results of the two bio-mixtures are very satisfactory if compared to results of conventional mixtures (with RA or bio-materials) in literature which fail at -27.6ºC (Pouget & Loup 2013).

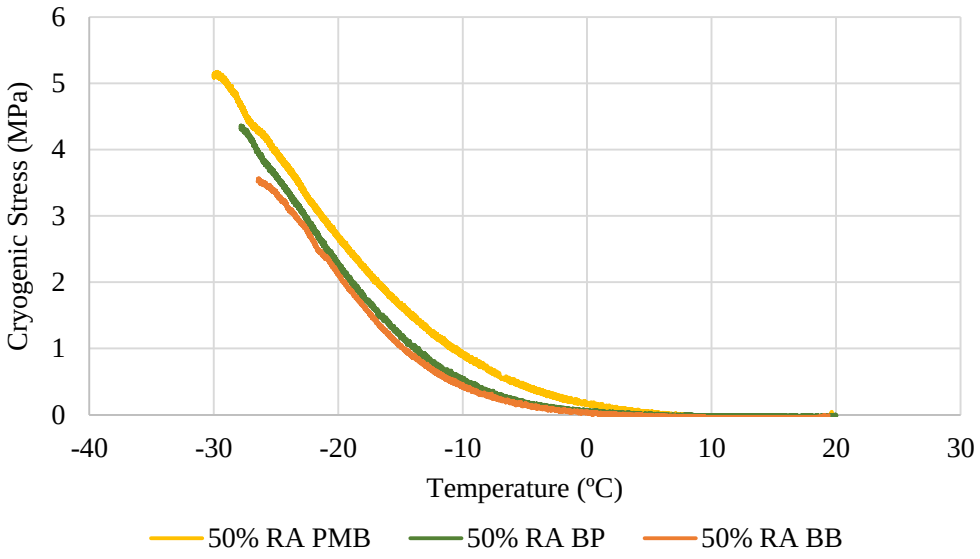


Figure 99. Cryogenic stress in TSRST for 50% RA mixtures

Table 29. Failure temperature and stress of 50% RA mixtures

Mix	Failure Temp. (ºC)	Std Deviation of Failure Temp.	Failure Stress (MPa)	Std Deviation of Failure Stress	p-value		
					50% RA PMB	50% RA BP	50% RA BB
50% RA PMB	-28.8	1.0	5.4	0.2	-	0.98	0.10
50% RA BP	-28.8	1.5	4.4	0.0	0.98	-	0.15
50% RA BB	-26.4	1.2	3.8	0.4	0.10	0.15	-

6.5.3.3. Relationship of thermal cracking resistance of binders' blends and asphalt mixtures

The thermal cracking resistance of the bio-asphalt mixtures was found surprising considering the results of the binders' blends at low temperatures. The critical low temperature for RA+BP was -8.8ºC and -5.7ºC for RA+BB. These critical temperatures are high in comparison to conventional bitumens such as a 50/70 conventional penetration grade binder which has a low critical temperature of -14ºC. Given these data, the bio-mixtures were expected to have an early failure. The fact that it did not occur could be attributed to the asphalt mixtures optimised aggregate packing and binder content, which allow bio-asphalt mixtures with 50% RA content to have equivalent thermal cracking resistance to conventional asphalt mixtures.

6.6. Moisture damage

Moisture damage is one of the main distresses causing the failure of asphalt pavements. The moisture damage of binders' blends was analysed using Bitumen Bond Strength (BBS) tests in dry and after wet conditioning. Asphalt mixtures' moisture damage resistance was assessed by means of ITS before and after wet conditioning.

6.6.1. BBS tests

The Binder Bond Strength properties of the binders and blends with aggregates were studied by means of BBS tests, evaluated with the upgraded PATTI device (Pneumatic Adhesive Testing Instrument) as explained in Section 2.4.5 of the literature review.

To prepare the samples for testing, the aggregate and pull-stub are placed in an oven and heated to a temperature of 70°C for one hour. The binders were heated to 150°C for 1 h to allow them to be fluid enough to coat the aggregate plate. The liquid binder is then poured onto a prepared aggregate plate (with the dimension of 100 mm by 100 mm by 20 mm) which is pressed

immediately by a metal pull-stub to establish a good bitumen–aggregate bond. In this process the film thickness of bitumen was controlled by the pull-stub itself to make sure all specimens have a 0.8 mm bitumen film. Finally, the excess binder at the edge of pull-stub is trimmed by using a heated trimmer.

After the preparation of the samples, they were conditioned for 2h in a temperature-controlled chamber at 5°C to perform the tests at this temperature. This temperature was chosen because of the soft and flexible nature of some of the binders tested, such as BP, which prevented the failure during the test at higher temperatures (before choosing 5°C, tests trials were carried out at 25°C, 15°C and 10°C). Although the standard temperature for this test is 20-25°C, some researchers have reported that a reduced temperature is also valid (Jenkins et al. 2013). Two aggregates types were selected as substrate: granite and limestone. Three replicates were measured for each binder, blend, aggregate type and conditioning.

The binders' blends were subjected to wet conditioning to be later compared with the water sensitivity results of the asphalt mixtures. For this purpose, the moisture conditioning was chosen to be coherent with EN 12697-12 (2008) – Method A. Consequently, the specimens were placed in a bath for 72h at 40°C to induce moisture damage (Figure 100). Next, they were conditioned at 5°C for 2h in a temperature-controlled chamber to carry out the tests under the same conditions as the dry ones.



Figure 100. Moisture conditioning of BBS samples

After the dry and wet conditioning, the ratio between the dry and wet Pull-Off Tensile Strength (POTS) was obtained according to Equation (78) for each blend and aggregate as a measure of the moisture damage suffered.

$$POTSR(\%) = \frac{POTS_w}{POTS_d} \cdot 100 \quad (78)$$

where POTSR is the ratio between the wet and dry POTS, $POTS_w$ is the POTS after wet conditioning and $POTS_d$ is the POTS after dry conditioning.

6.6.2. ITS tests

The moisture damage of the asphalt mixtures was studied according to EN 12697-12 (2008) – Method A for the determination of water sensitivity as described in Section 2.4.5 of the literature review. For the conditioning of the wet set of specimens, they were first placed on a perforated shelf in a vacuum container filled with distilled water at 20°C ± 5°C and subjected to vacuum at a pressure of 6.7kPa ± 0.3kPa for 30min ± 1min. Next, they are located in a water bath at 40°C ± 1°C for a period of 68h to 72h. Finally, the specimens were removed from the water bath and conditioned in a temperature-controlled chamber at 25°C for at least 2h before being tested for ITS. The dry set of specimens were conditioned on a flat surface at room

temperature in the laboratory, within 20°C ± 5°C and then placed together with the wet set at 25°C for at least 2h before being tested.

6.6.3. Results and discussion

6.6.3.1. Binders' blends

Table 30 shows the results of all the tests undertaken in dry and wet conditioned states. Firstly, some general observations can be made on the results in Table 30:

- No purely adhesive (A) failure was observed.
- Granite substrate always produced purely cohesive failure (C).
- Mixed failure (M) only appeared with limestone and after wet conditioning.

Table 30. BBS tests results

Binder/ Blend	Conditioning	Aggregate type	Failure	POTS - Average (kPa)	Std Dev (kPa)
RA	Dry	Granite	C	1994	164
		Limestone	C	1723	127
50/70	Dry	Granite	C	2641	1007
		Limestone	C	2731	952
RA+BB	Dry	Granite	C	1250	176
		Limestone	C	2526	1396
	Wet	Granite	C	2053	1053
		Limestone	M	1527	429
RA+BP	Dry	Granite	C	5277	498
		Limestone	C	4056	775
	Wet	Granite	C	5849	801
		Limestone	M	2962	644
RA+PMB	Dry	Granite	C	4450	311
		Limestone	M	3517	257
	Wet	Granite	C	4225	759
		Limestone	M	1606	567

The results of the dry BBS tests are graphically represented in Figure 101. The RA binder show lower POTS than that of the conventional 50/70 penetration grade. Since all failures are cohesive, this means that the inner cohesion of the RA is lower than that of the 50/70

penetration grade bitumen, which could be due to its ageing state. Next, the effect of the blend of biobinders with the RA binder is clear. On one hand, the blend of the RA binder with BB seems to reduce its POTS with granite while increasing the one with limestone . On the other hand, RA+BP shows a greatly improved pull-off tensile strength being even higher than that of the blend of the RA binder with the conventional PMB (RA+PMB). Therefore, RA+BP can be said to have a great inner cohesion which may represent a great advantage for the performance of the asphalt mixtures.

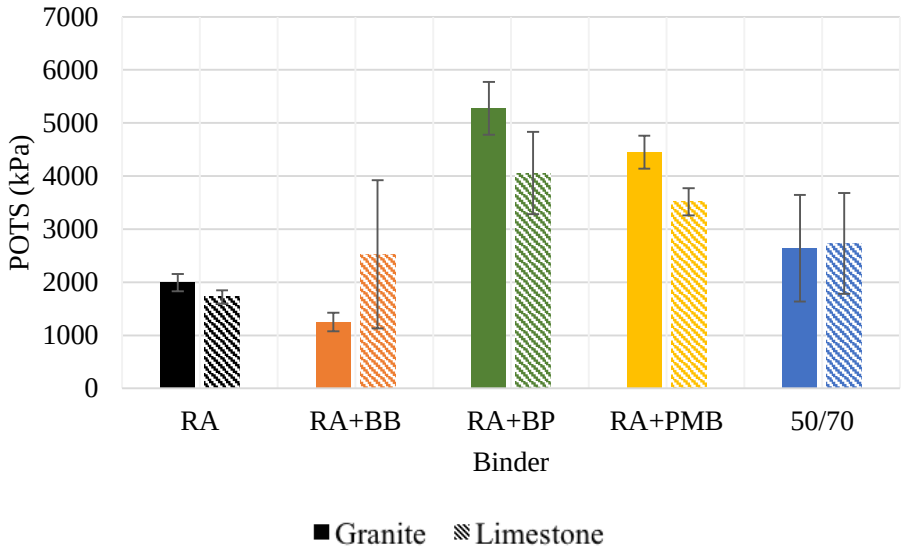


Figure 101. Blends dry POTS for granite and limestone

Table 31 shows the Pull-Off Tensile Strength Ratio between the wet and the dry conditioned samples as described in Equation (78). Combining results in Table 30 and Table 31, a strong dependency on the aggregate type and blend tested is observed. On one hand, regarding the granite substrate, all the blends maintained the purely cohesive failure after 72h in water at 40°C. In fact, the two blends with biobinders show an improved POTS. This fact means that the water did not damage the bond between the biobinders and the granite, but also could have slightly increase the cohesion of the biobinders or have produced some ageing increasing their stiffness and therefore their POTS.

On the other hand, the failure of the three blends became mixed after the wet conditioning with limestone. This means that the water conditioning damaged the bond and therefore POTS decreased as shown by several authors (Moraes et al. 2011; Bahia et al. 2012; Jenkins et al. 2013; Zhang et al. 2015).

In this sense, the wet conditioning revealed the better performance of granite to resist moisture damage in comparison to limestone for the blends tested. The performance of aggregate-binder bonds after water conditioning has been shown to be strongly dependent on the interaction between the type of binder and type of aggregate. However, in most cases in literature, granite has shown less resistance to moisture damage than limestone (Moraes et al. 2011; Zhang et al. 2015). The opposite tendency found with the blends of RA binder and biobinders could be due to a better affinity between granite composition and biobinders' components but further chemical testing (such as surface energy tests) to support this fact would be needed.

Finally, in all cases the blends with biobinders exhibit higher POTSR, which implies better resistance to moisture damage in comparison to the use of a conventional PMB. This may represent an important feature of these bio-materials in combination with RA.

Table 31. POTSR (%)

Blend	Aggregate type	POTSR (%)
RA+BB	Granite	164
RA+BP		111
RA+PMB		95
RA+BB	Limestone	60
RA+BP		73
RA+PMB		46

6.6.3.2. Asphalt mixtures

The moisture damage of the asphalt mixtures was assessed by means of the Indirect Tensile Strength Retained (ITSR). The values of the ITS_d, ITS_w and ITSR are displayed in Figure 102. The values of ITS are the average of three specimens and the bars represent the standard

deviation. Binder and base courses in pavements are usually required to have an ITSR>80% (Ministerio de Fomento, 2004). This requirement is met by the three 50% RA mixtures with the asphalt mixture with BP having the highest ITSR. These results imply that the two mixtures with biobinders would be suitable for a pavement in terms of resistance to moisture damage.

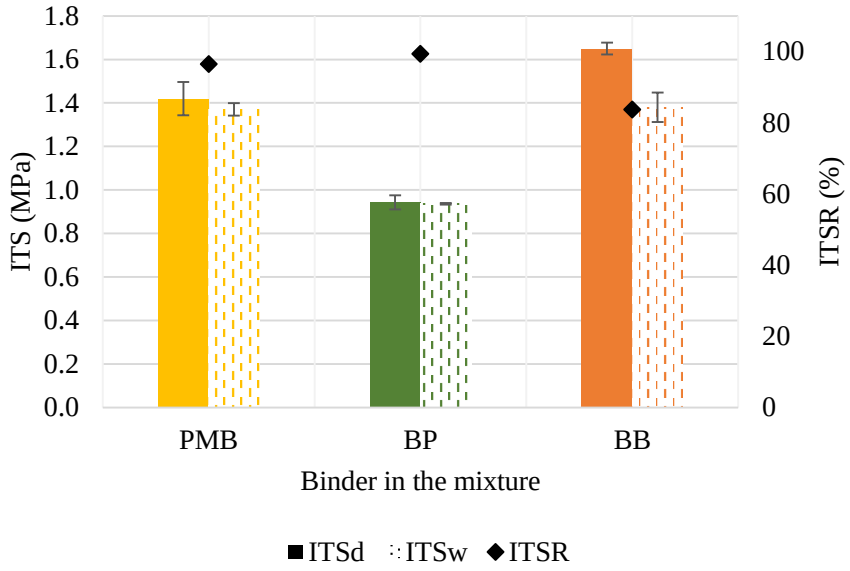


Figure 102. Moisture damage results of 50% RA mixtures

6.6.3.3. Relationship of moisture damage resistance of binders' blends and asphalt mixtures

The ITS of the asphalt mixtures after dry and wet conditioning can be related to the POTS determined for the corresponding blends after the same conditioning. Figures 103 and 104 show the relationships found after dry and wet conditioning respectively for granite and limestone. The linear relationships obtained with acceptable correlation coefficients ($R \geq 0.7$) indicate that the cohesion of the asphalt mixtures and the BBS of the binder-aggregate systems are strictly related, regardless of the type of aggregate. The inverse relationship between these parameters was reported by Kim et al. (2012) but only for dry conditions, since their water conditioning for PATTI tests did not match the water conditioning for asphalt mixtures water

sensitivity. The results here show that this relationship can be found for both dry and water conditioning.

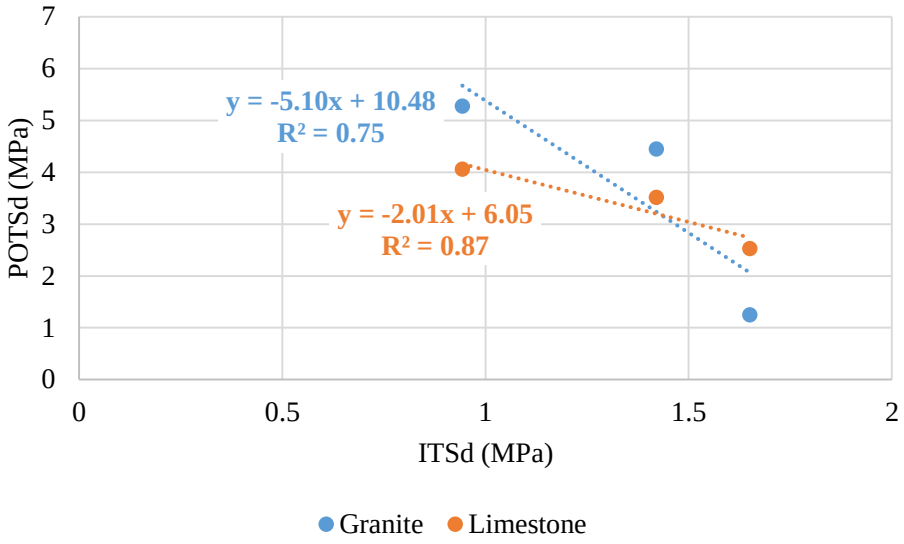


Figure 103. Relationship between POTS and ITS after dry conditioning

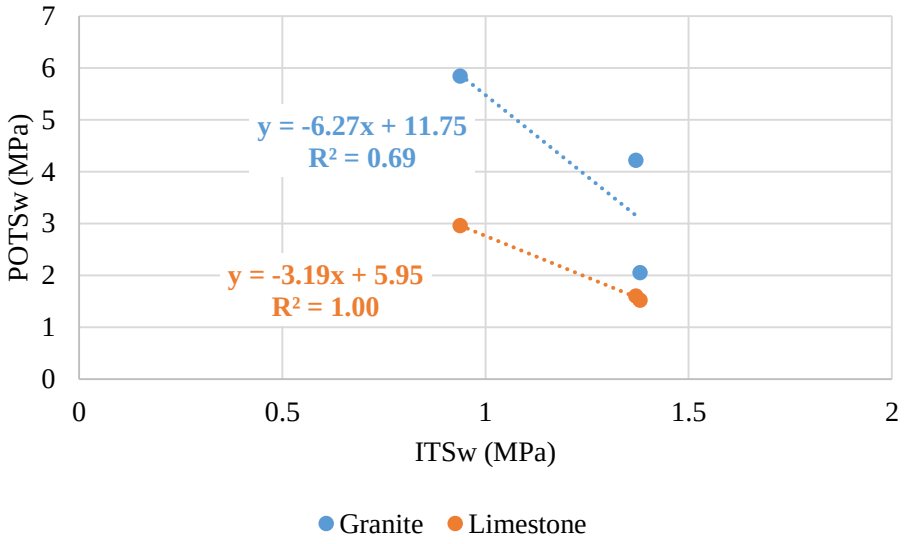


Figure 104. Relationship between POTS and ITS after wet conditioning

In summary, the results of water sensitivity tests showed that biobinders' blends and bio-asphalt mixtures have suitable resistance to moisture damage being comparable or better than conventional RA blends and asphalt mixtures. In addition, the properties of blends and asphalt

mixtures showed good correlations supporting the use of PATTI tests for a preliminary study of the water sensitivity of RA mixtures using binders' blends under full blending assumption.

6.7. Ageing

Binders' blends and asphalt mixtures ageing were studied by means of the change in their LVE properties after ageing. In this regard, different ageing techniques and type of analysis were used for binders' blends and asphalt mixtures as follows.

6.7.1. Ageing of binders' blends

For the study of the ageing properties of the binders' blends, they were subjected to short and long term ageing in the laboratory. Short term ageing, which aims at simulating the ageing that the binders suffer during the manufacturing of the asphalt mixture in an asphalt plant, was performed by RTFOT (EN 12607-1 2014). Long term ageing, which aims at simulating the ageing that the binders suffer after a number of years of service of the pavement, was carried out by means of RTFOT and consecutive PAV test (EN 14769 2012) for 20h at 100°C and 2.1MPa of pressure. In addition, the binders' blends were recovered after the manufacturing of the asphalt mixtures (EN 12697-4 2005) in the laboratory to be analysed and compared with the artificial short-term ageing.

The LVE properties of the unaged and aged blends were analysed by means of frequency and temperature sweeps using the DSR from 1 to 10Hz and from 0°C to 80°C. Two parallel-plate geometries were used to cover the range of temperatures: 8mm diameter and 25mm diameter. The tests at 30°C and 40°C were performed with the two geometries to then select the correct data to produce a smooth Black curve according to Airey (2002). Next, the master curves of the norm of the complex modulus and phase angle were produced using the methodology in

Chailleux et al. (2006) at a reference temperature of 15ºC and with manual shifting at a reference temperature of 20ºC.

Finally, the LVE properties of the binders were used to further analyse their ageing by plotting the R-value versus cross-over frequencies (Rowe et al., 2015) and determining the Glover-Rowe parameter (G-R) for fatigue cracking (Rowe, 2011). On one hand, binder's crossover frequency is the frequency at which the binder's phase angle is equal to 45° at a certain temperature (i.e. frequency at which loss and storage moduli are equal). On the other hand, R-value of a binder is the distance between the norm of the complex modulus at the crossover frequency and the glassy modulus (usually taken as 1 GPa in shear loading). Crossover frequencies of binders decrease with ageing while R-values increase. Therefore, according to several researchers (Rowe et al. 2015), crossover frequency versus R-value space can be used to visually evaluate binders' ageing. On the other hand, G-R parameter (see Section 2.4.3 of the literature review) for the evaluation of fatigue cracking potential of binders considers the complex modulus and phase angle at 15°C at a frequency of 0.005rad/s. The G-R parameter gives a boundary value of 0.18 MPa, which is considered as cracking warning, while a value of 0.45 MPa or more is suggested as cracking limit. These values at this temperature-frequency combination were developed for a PG 58-28 climate region; current work is ongoing to determine how these should be adjusted to other climactic conditions (Rowe, 2011).

6.7.2. Ageing of asphalt mixtures

Two ageing procedures were carried out for the asphalt mixtures:

1. **Ageing of trapezoidal specimens (conventional ageing)**. After compaction, the slabs were cut into trapezoidal specimens to allow two-point bending testing. The specimens were first tested in their unaged stage and then subjected to ageing in a water bath at

60°C and testing after different conditioning times for a total period of 45 days. The inclusion of water was meant to increase the ageing damage in the specimens.

In this regard, the specimens had to be aged already attached (glued) to the two-point bending bases and care was needed to avoid any possible deformation due to the temperature and water effect. Therefore, the specimens were placed on a specially designed support which held the bases and guaranteed their shape stability during ageing (Figure 105).

The specimens were tested in two-point bending mode after 4 days, 8 days and 45 days ageing to obtain their linear-viscoelastic properties to assess their ageing. The tests were performed from -10°C to 40°C from 40Hz to 1Hz according to EN 12697-26 (2012) Annex A.

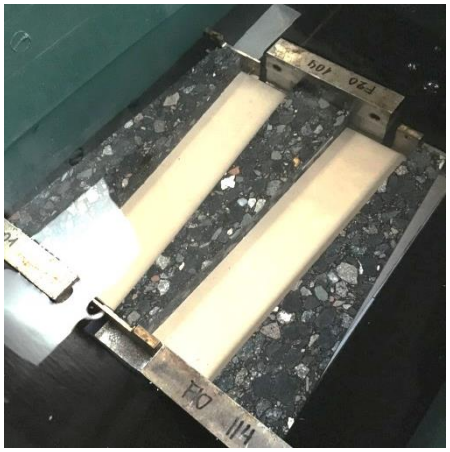


Figure 105. Trapezoidal specimens attached to the two-point bending bases inside the water bath

2. **Ageing of thin specimens (accelerated ageing)**. After compaction, the slabs were cut into rectangular specimens with dimensions 15mm x 100mm and 5mm thick to be tested using the Metravib® (Figure 106) in three-point bending mode. The specimens were first tested in their unaged stage and then subjected to dry and wet ageing using a water bath and an oven at 60°C. They were then tested after different conditioning (ageing) times: 2, 7, 13, 33, 39 and 45 days. Specimens not subjected to ageing were

stored at room temperature and tested at the same time as the aged specimens to be used as control specimens for the ageing of the materials.



Figure 106. Thin specimens for accelerated ageing

The Metravib® is a device which applies tension-compression loading to specimens in a temperature-controlled environment (Figure 107) providing complex modulus and phase angle data for the samples. The tests were carried out at 15°C at 10Hz.

This ageing procedure was considered to be accelerated due to the small size of the samples, which could allow faster evolution of the materials' properties. If this accelerated ageing occurs, then the conditioning time needed to observe ageing in asphalt mixtures could be reduced.

However, due to the size of the samples, the complex modulus of each specimen will be strongly influenced by the aggregates that it contains. This means that the modulus of the samples cannot be considered as an absolute value. Nonetheless, since the phase angle is always a value between 0º and 90º, it can be taken into account as its change would represent the change in the viscoelastic properties of the asphalt mixture due to the ageing process.

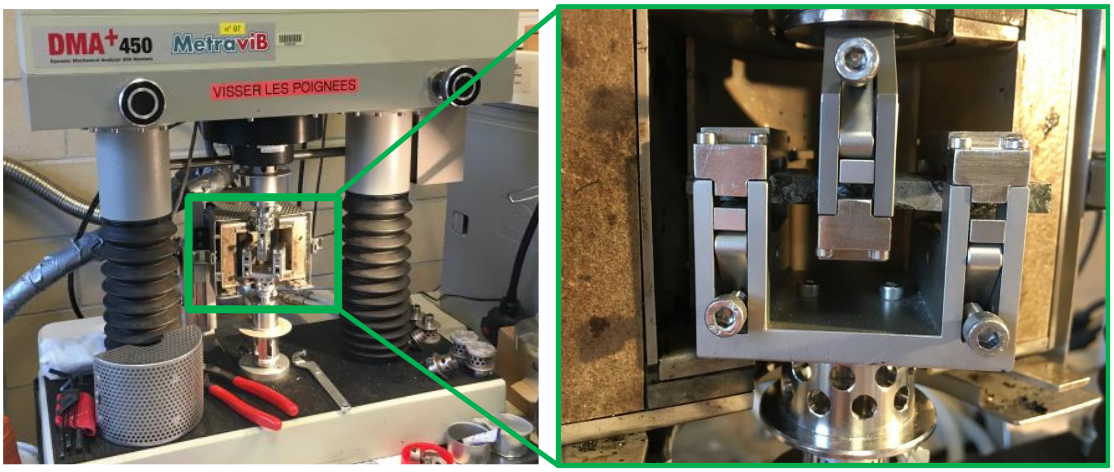


Figure 107. Metravib® with three-point bending device

As explained in Section 2.4.1.6, in order to study the ageing of the mixtures, Mensching et al. (2017) recently discussed the effect of the β and γ parameters - from the fitting of a sigmoidal function to asphalt mixtures' master curve - on the shape of master curves. To perform this analysis for the conventional ageing, the master curves of the asphalt mixtures were obtained after the different ageing conditioning times following the procedure described in Chailleux et al. (2006) at a reference temperature of 15°C. Next, the master curves were fitted with a standard sigmoidal function. Finally, the $(-\beta/\gamma)$ versus γ plot was produced to evaluate the relative position of the points after ageing.

6.7.3. Results and discussion

6.7.3.1. Binders' blends

Figures 108, 109 and 110 show the master curves of the unaged and aged blends of the RA and different binders together with the ones recovered from the asphalt mixtures and the RA binder for comparison. In terms of laboratory ageing, the first remarkable result is that none of the blends reached the aged state of the RA binder after PAV. This could mean that the blends of biobinders with the RA binder would be in a less aged state after years of service life of the pavement than the RA itself in the moment of placing it in a road. This fact is especially true

for RA+BP, whose master curves are significantly different to that of the RA binder compared to RA+BB and RA+PMB blends.

RA+BP present the same type of ageing as BP as shown in Section 3.3.3, where, depending on the range of frequency the complex modulus and the phase either increase or decrease with ageing. However, while for BP this was a unique frequency for BP, for RA+BP two threshold frequencies can be identified, one for the complex modulus and one for the phase angle. This provides three areas in Figure 108. Firstly, at lower frequencies than 0.01 rad/s (Area 1), RA+BP moves toward a more viscous response after ageing having lower complex modulus and higher phase angle. Next, between 0.01 and 1 rad/s (Area 2), the ageing produces an increase in both complex modulus and phase angle meaning that the binder is stiffer but has a more viscous response. Finally, at higher frequencies than 1 rad/s (Area 3), RA+BP exhibit higher modulus and lower phase angle. This complex behaviour after ageing may be due to the combination of BP, which is highly modified, and the RA binder, creating a gap in the change of phase angle and complex modulus with ageing. Finally, RA+BP after RTFOT and after its recovery from the asphalt mixture appear to have equivalent master curves meaning that RTFOT would effectively simulate the manufacturing of the asphalt mixture in the laboratory.

In Figure 109, RA+BB seems to be the blend most affected by ageing in comparison with Figures 108 and 110. Conversely to what happened to RA+BP, the recovered RA+BB from the asphalt mixture does not match the RTFOT master curve and exhibits even greater ageing than RA+BB with the binder after RTFOT+PAV reaching the level of stiffness of the RA binder at frequencies higher than 0.1 rad/s, although maintaining a more viscous response (higher phase angles). This fact means that RA+BB suffers significant ageing during the manufacture of the asphalt mixture which could be due to its composition (resin and oil) and could result in performance issues. Therefore, its ageing in the laboratory should be taken only as a reference

for comparison with the rest of binders and the asphalt mixture has to be carefully studied separately. This fact stresses the importance of comparing the traditional ageing methods to the actual ageing during the asphalt mixture manufacturing for new materials. The ageing study of binders by means of protocols that are not able to reproduce the actual ageing conditions in the field may lead to erroneous conclusions with important consequences such as the selection of the pavement layer in which to use these materials. It should be also highlighted that RA+BP contains a similar resin to RA+BB but the presence of SBS polymers seems to greatly improve its resistance to ageing.

Regarding RA+PMB in Figure 110, its ageing behaviour is comparable to RA+BP due to their similar SBS polymer modification but only shows Areas 2 and 3 divided at 0.001 rad/s. In addition, the RTFOT curve and the recovered curve are equivalent revealing the equivalency of RTFOT ageing and the ageing after laboratory manufacture of asphalt mixtures with petroleum-based binders.

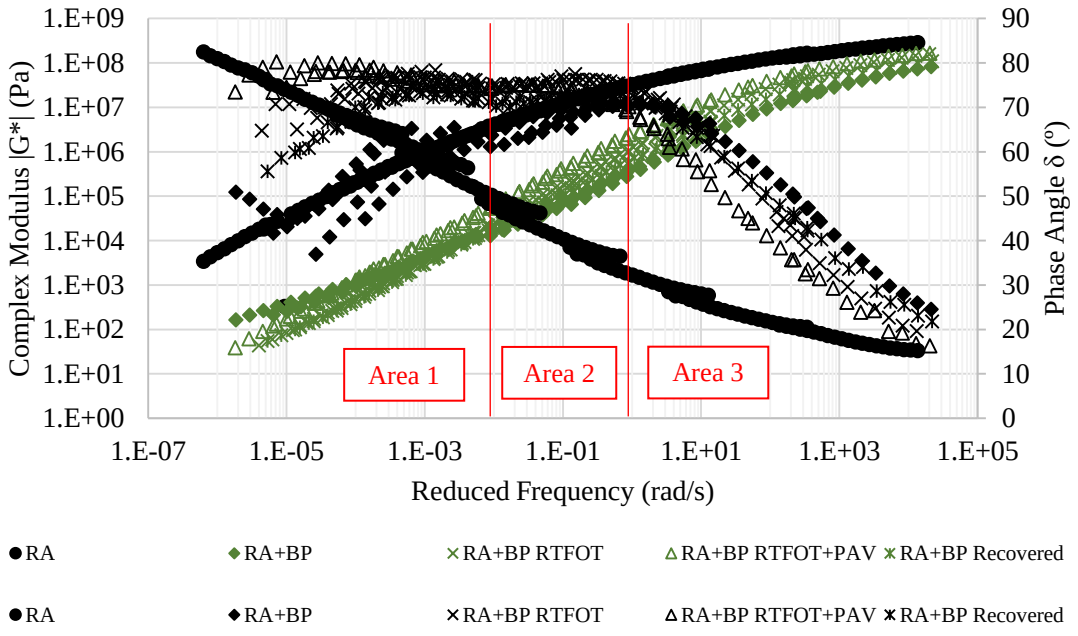


Figure 108. Master curves of the norm of the complex modulus and phase angle of unaged and aged RA+BP, RA and RA+BP recovered at Tref=15ºC

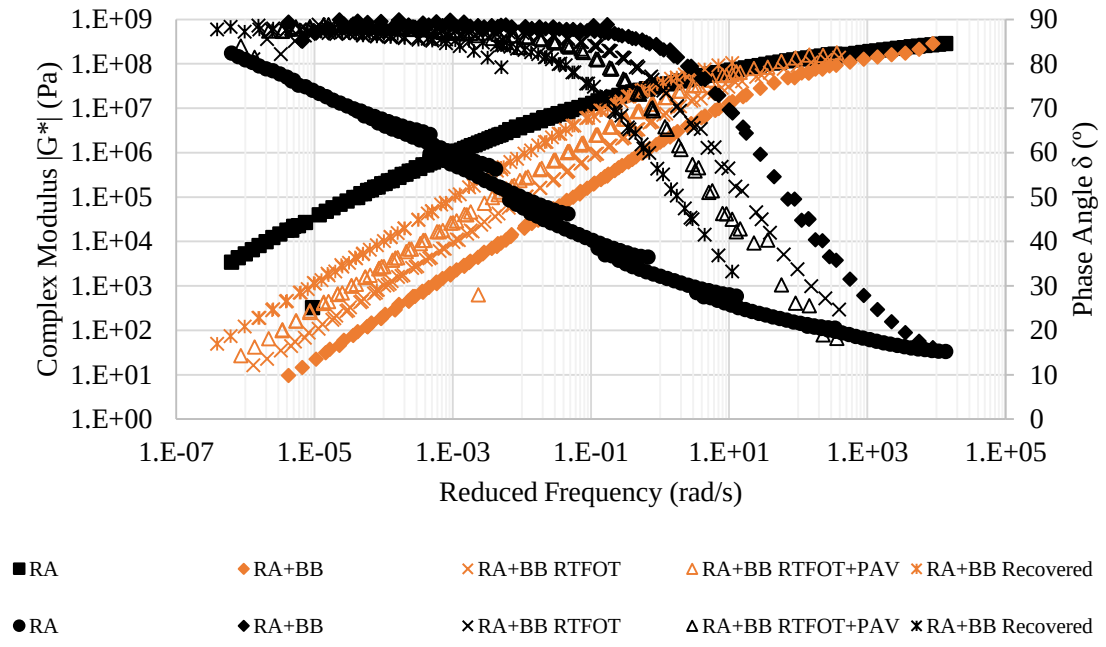


Figure 109. Master curves of the norm of the complex modulus and phase angle of unaged and aged RA+BB, RA and RA+BB recovered at Tref=15ºC

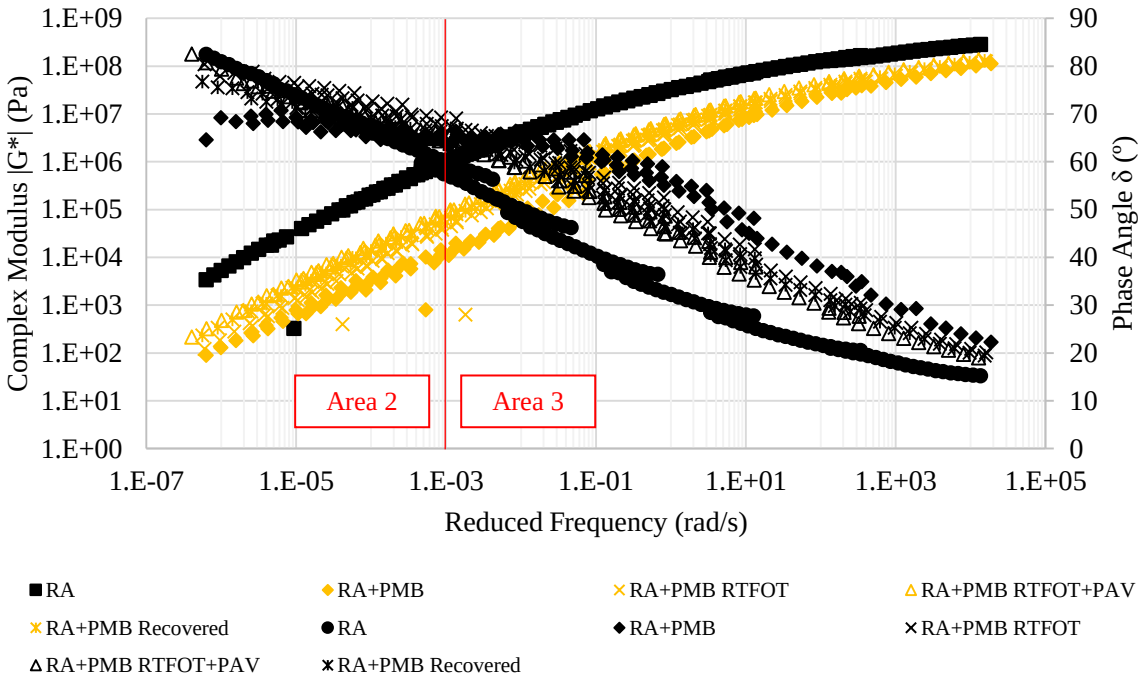


Figure 110. Master curves of the norm of the complex modulus and phase angle of unaged and aged RA+PMB, RA and RA+PMB recovered at Tref=15ºC

In order to put together the results of all the materials, their rheological data were simplified in terms of R-values and crossover frequencies to be plotted in one figure and visually used to assess the relative ageing. As described by Rowe et al. (2009), the ageing of binders produces

a change in the shape of their master curves that can be translated into the change of their R-value and crossover frequency. For conventional binders, the crossover frequency moves to lower values and the master curve of the complex modulus becomes flatter. In this regard, ageing reduces crossover frequencies and increases R-values while rejuvenation should have the opposite effect, as could be observed in Figure 61 for the 50/70 conventional bitumen. According to this, in Figure 111 the RA binder appears as the most aged binder being in the lowest and further right position. The effect of the blend of the RA binder with the biobinders and PMB is interpreted as rejuvenation and was previously shown in Chapter 5. After the ageing of the blends, RA+BB and RA+PMB move down and to the right. However, all the aged RA+BP and the recovered RA+BB have a different relative movement with respect to the unaged binder in the plot, reducing their crossover frequencies but also decreasing the R-values. This may occur because the ageing of the blends is not only changing the shape of the master curves making them flatter, but also producing an upward displacement of the master curve of the complex modulus which may be changing the glassy modulus of these binders. In the case of RA+BP and recovered RA+BP blends, this could also be due to a possible modification in the biobinders because of the solvent used in their recovery from asphalt mixtures. If this happens and the glassy modulus is not 1GPa but higher, the calculation of the R-value should be different and the use of this plot is not directly applicable with the blends of RA and biobinders.

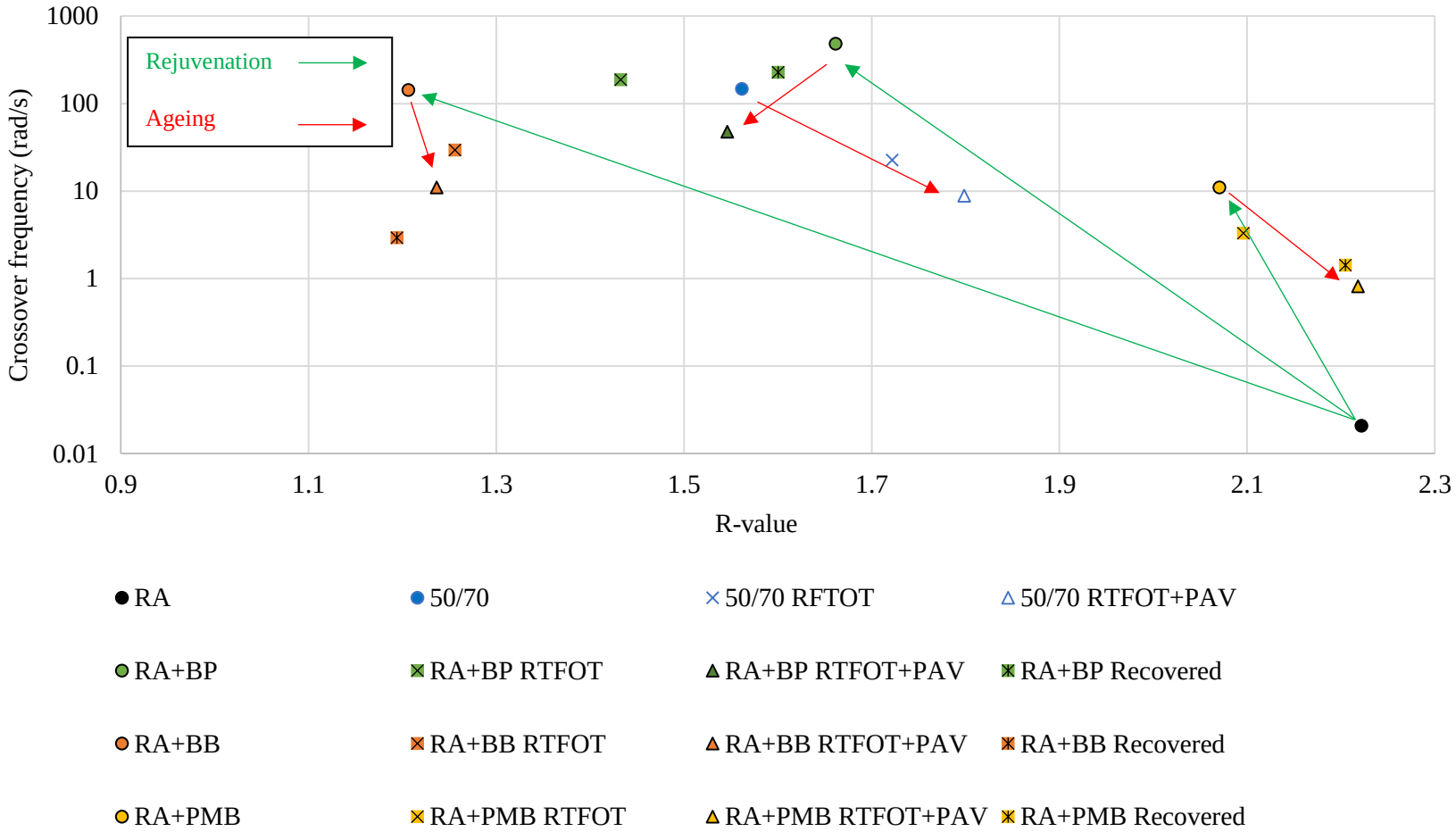


Figure 111. R-value versus crossover frequency of unaged and aged binders and blends

Finally, the cracking potential of the materials was analysed using the G-R parameter to further understand the influence that ageing could have in their performance-related properties. G-R parameters comprise the complex modulus and phase angle at 0.005 rad/s and 15ºC and are compared to the crack warning and limit values. In this regard, different researchers (Rahbar-Rastegar et al. 2017; Mensching et al. 2016) have shown that the ageing of binders should produce a movement of the initial point towards the cracking warning and limit boundary. In the same way, rejuvenation should produce the opposite effect. These movements are displayed with red and green arrows respectively in Figure 112. The RA binder is the only material in the Fail area and its blend with the other binders clearly move it to the Pass area improving therefore the expected cracking performance. The ageing of the materials, with the exception of those containing BP, produced their translation towards the cracking criteria but do not exceed them. In the case of RA+BP, the movement of the points is different because of its different ageing behaviour. The frequency at which the G-R parameter is calculated (0.005rad/s) is lower than 0.01rad/s in Figure 108; therefore the calculation of the parameter is done in the areas in which the ageing of this binder show increased phase angle and decreased modulus, which is opposite to conventional ageing tendency. Consequently, the movement of the points in the graph must be different and is contrary to the rest. This fact means that the cracking thresholds is not valid for RA+BP.

In summary, RA+BP ages in a similar way to conventional PMB binder, having different behaviour which depending on the range of frequencies they becoming stiffer with greater elastic response or less stiff with increased elastic response. RA+BB has the same ageing tendency as conventional non-modified binders becoming always stiffer and having increased elastic response but appears to be more susceptible to ageing. The ageing of the materials has been displayed in R-value versus crossover frequency plot showing the change in the shape of their master curves after ageing. Finally, the cracking potential of the biobinders and RA blends

was assessed by means of the G-R parameter with all of them in the “pass” area even after long-term ageing.

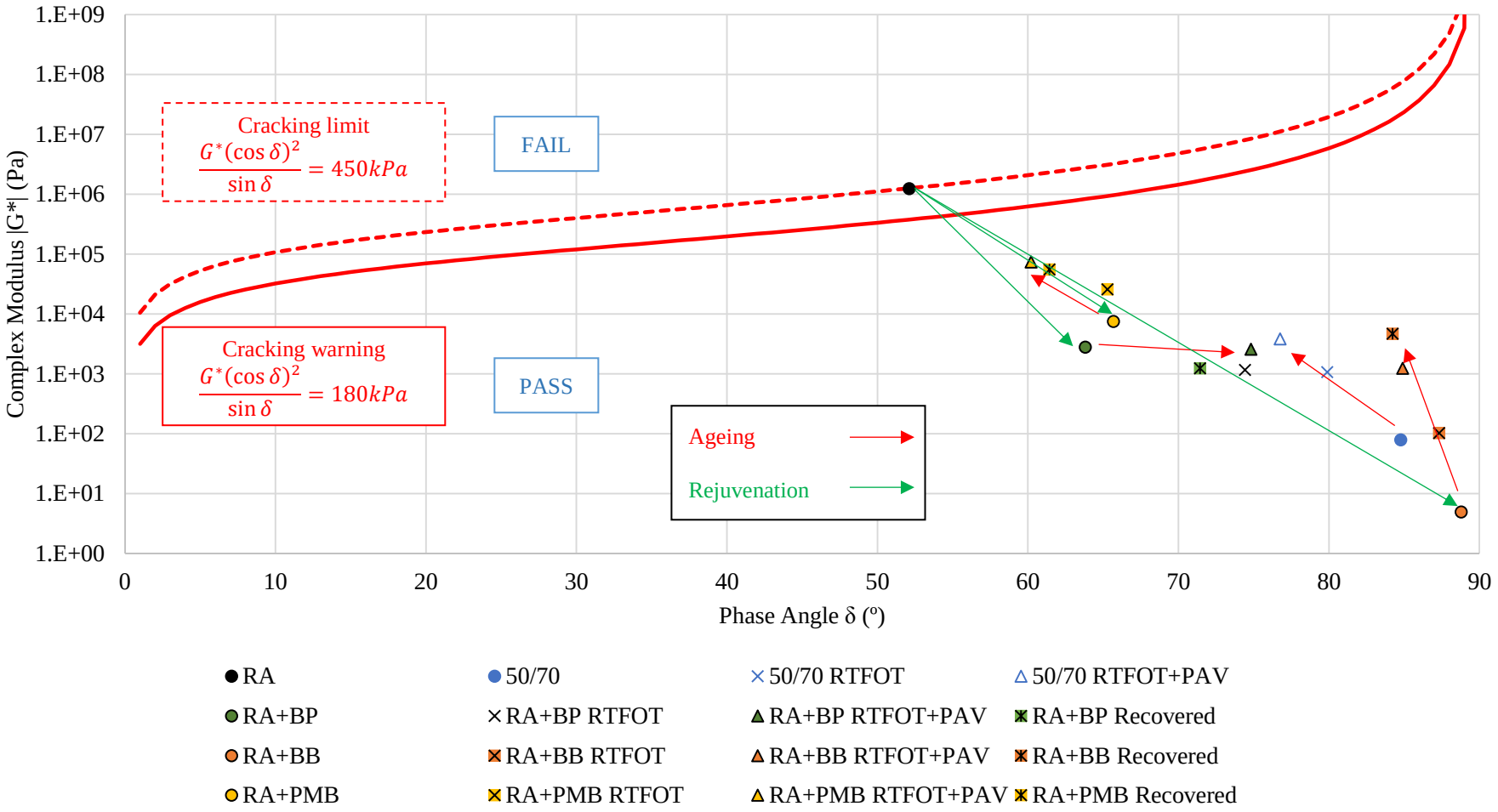


Figure 112. G-R parameter

6.7.3.2. Asphalt mixtures

6.7.3.2.1. Conventional ageing

Figures 113, 114 and 115 show the evolution of the Black diagrams of the asphalt mixtures with 50% RA content and BB, BP and PMB respectively after different ageing conditioning times. Black diagrams are used to highlight differences between the LVE properties of bituminous materials at high temperatures (>50°C) (Mangiafico 2014). It can be observed that for the mixture with BB, every step of ageing produced changes in its rheology so the evolution of the Black diagram is progressive. On the other hand, for the mixture with BP, the Black diagram reveals that only after 45 days of ageing the mixture suffered a noticeable change in its LVE properties. In this regard, the two mixtures with biobinders decreased their phase angle with ageing. On the contrary, the mixture with PMB did not exhibit significant changes. In the three Black diagrams, the points measured at 40°C and 3Hz have been highlighted in red to better appreciate their movement through the Black space.

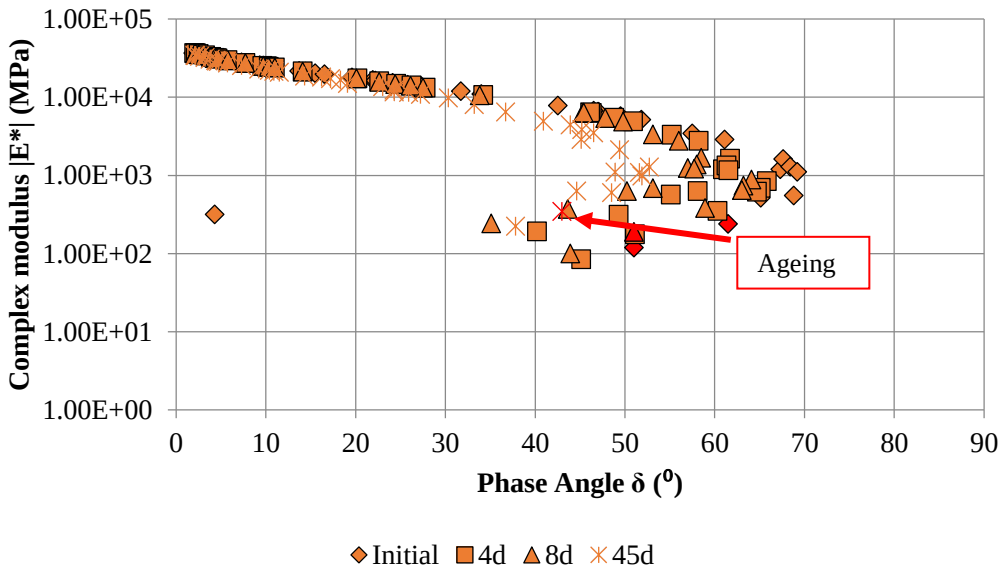


Figure 113. Black diagram of aged 50% RA Mix BB



Figure 114. Black diagram of aged 50% RA Mix BP

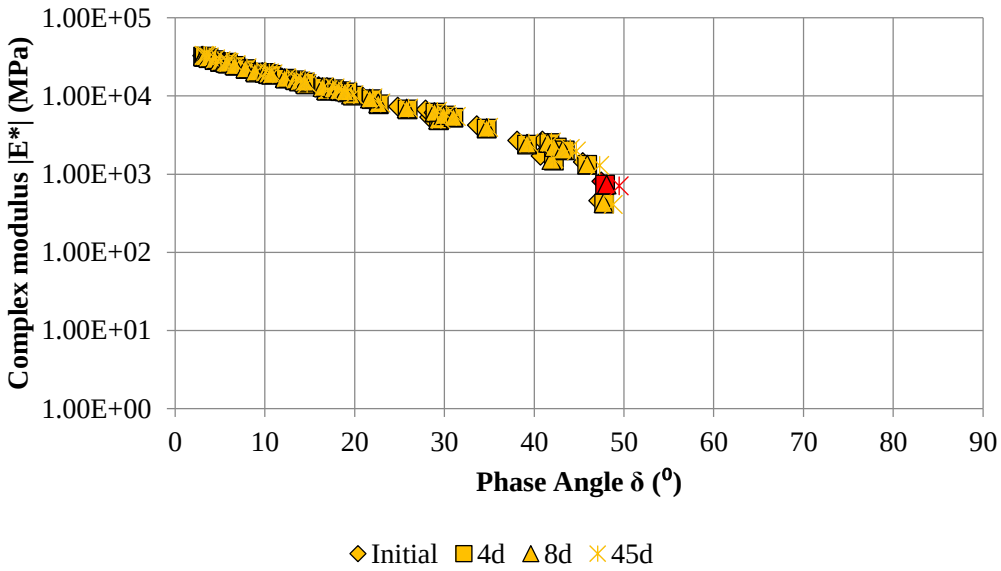


Figure 115. Black diagram of aged 50% RA Mix PMB

In order to highlight the effect of ageing at low temperatures, the Cole-Cole diagrams of the three mixtures have been represented in Figures 116, 117 and 118 respectively. In the case of the mixture with BB, the Cole-Cole diagram shows that the balance between the elastic and viscous component of the asphalt mixture changed after 45 days of ageing. Conversely, the mixtures with BP and PMB did not change this balance.

Given these results, it can be said that the mixtures with biobinders experience a faster rate of ageing than the mixture with the conventional PMB exhibiting changes in their rheology after 45 days of conditioning in water at 60°C.

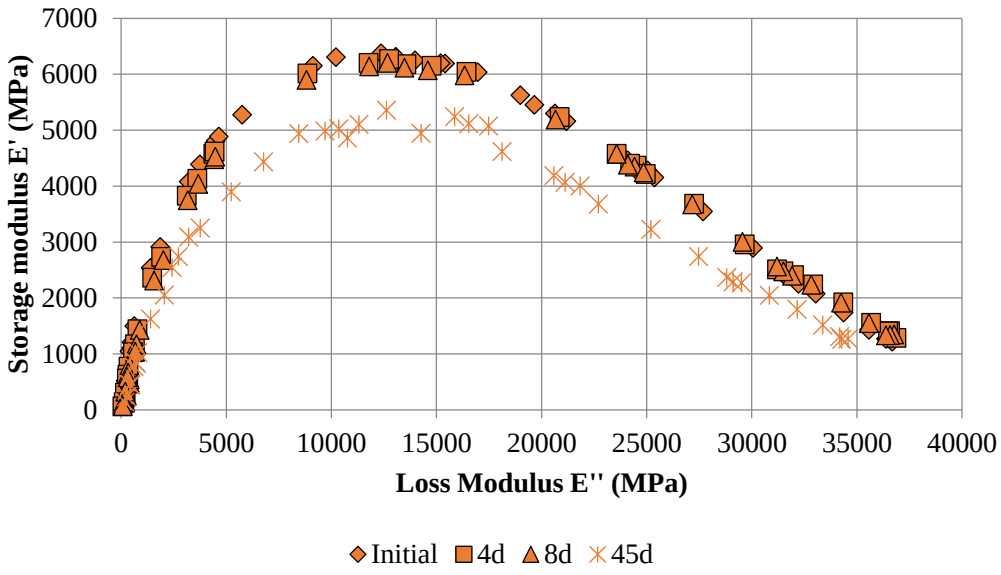


Figure 116. Cole-Cole diagram of aged 50% RA Mix BB

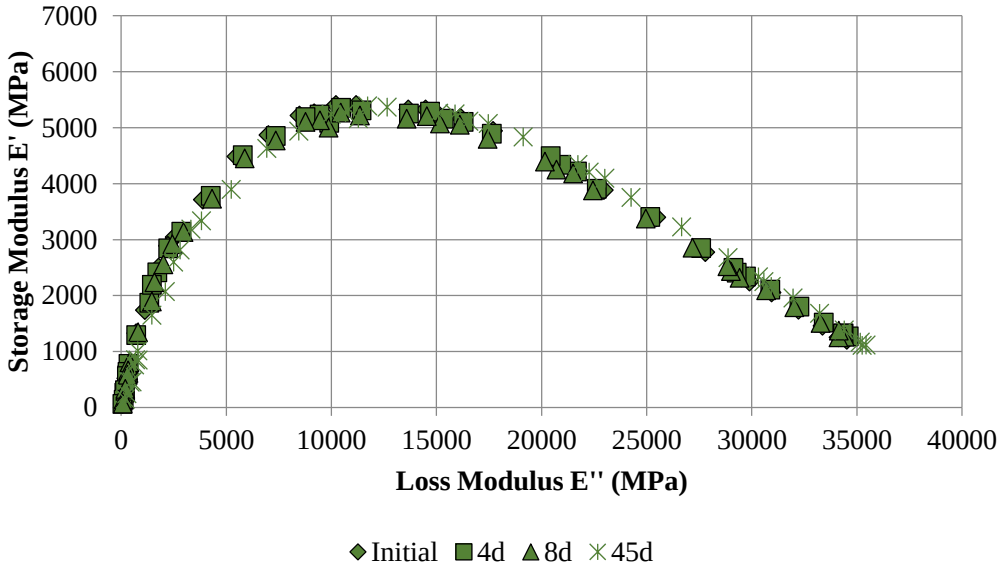


Figure 117. Cole-Cole diagram of aged 50% RA Mix BP

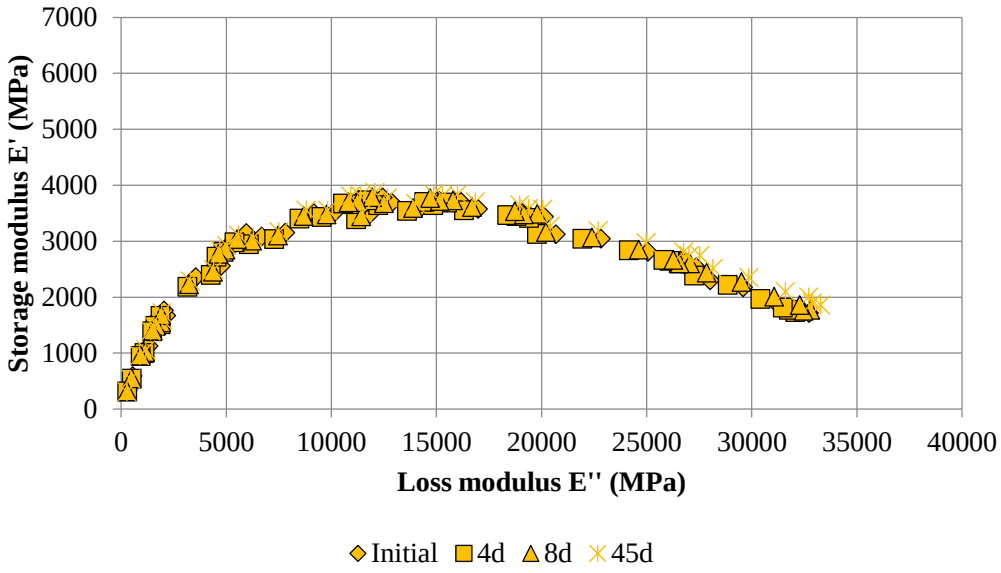


Figure 118. Cole-Cole diagram of aged 50% RA Mix PMB

6.7.3.2.2. Sigmoidal function fitting for the study of ageing

Figures 119, 120 and 121 display the master curves of the norm of the complex modulus of the 50% RA content asphalt mixtures with BB, BP and PMB respectively after the different ageing times. These curves did not show a significant change in the complex modulus of the asphalt mixtures after ageing (only a slight increase at low frequencies for the mixtures with biobinders). Table 32 shows the β, γ and the ageing parameter $(-\beta/\gamma)$ of the asphalt mixtures after the sigmoidal function fitting of the master curves. Figure 122 displays the $(-\beta/\gamma)$ versus γ plot. According to Mensching et al. (2017), a point in this plot should move to the right and down with ageing as the mixture becomes stiffer and lose relaxation capacity. However, this movement is not noticeable in Figure 122 with only in the case of the asphalt mixtures with biobinders moving to the right after 45 days of ageing. For the rest of the cases, the points remain so close to each other that the movement is not detectable. This fact could be expected since the sigmoidal function is fitted using the modulus master curves, and it was shown that the shape of the curves did not meaningfully change.

Nevertheless, the relative position between the points of the mixtures in the plot does reveal the different consistency of the binders used. In this sense, PMB was harder (lower penetration) than the biobinders and therefore the mixture is located at the right and lower part of the plot. This means that the mixture is stiffer and has less relaxation capacity.

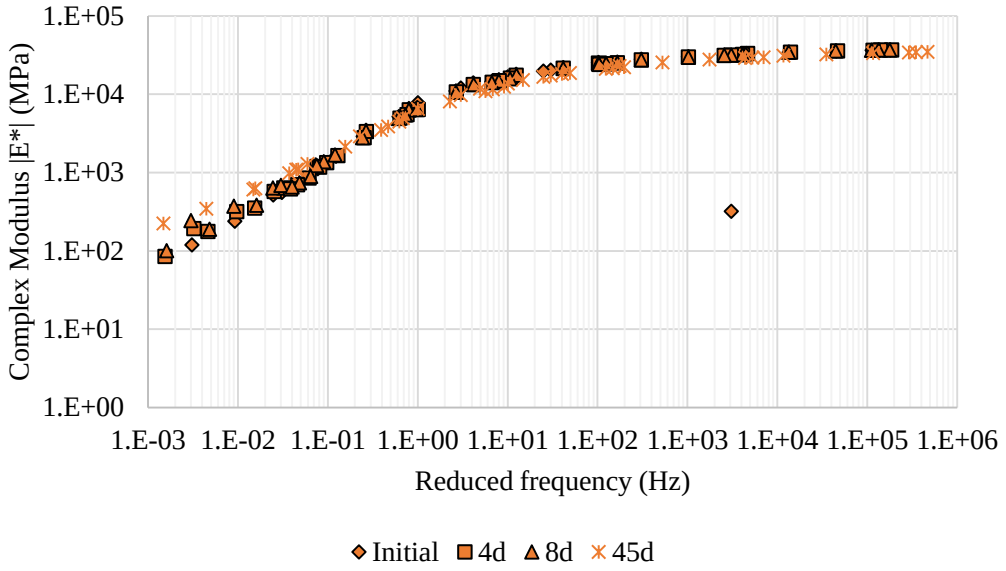


Figure 119. Master curve of the norm of the complex modulus of aged 50% RA Mix BB at Tref=15°C

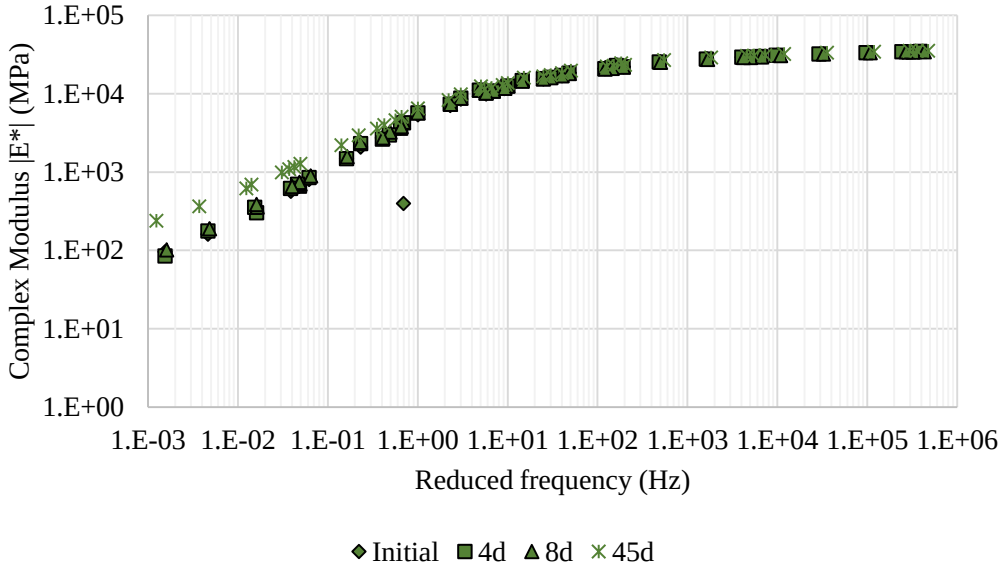


Figure 120. Master curve of the norm of the complex modulus of aged 50% RA Mix BP at Tref=15°C

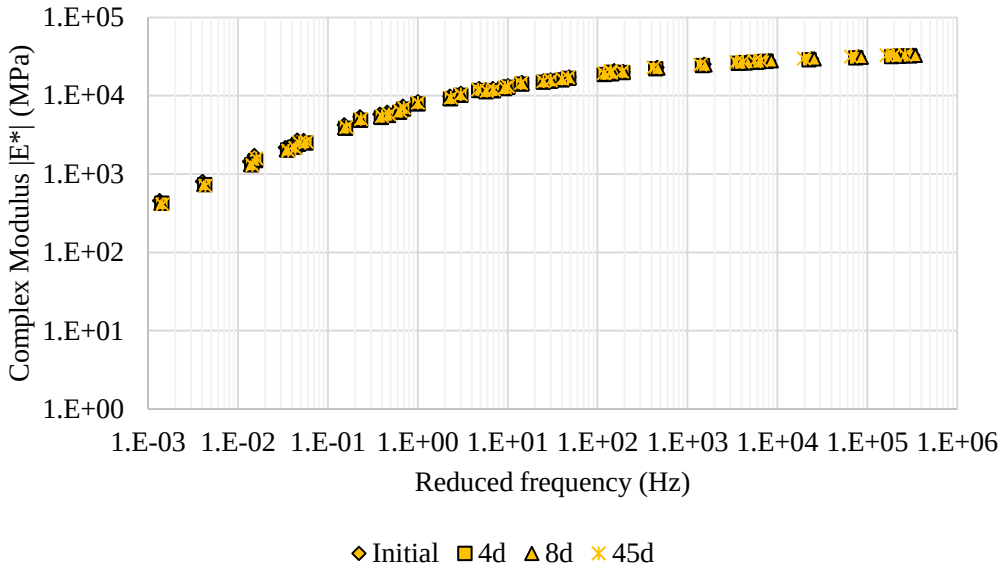


Figure 121. Master curve of the norm of the complex modulus of aged 50% RA Mix PMB at Tref=15°C

Table 32. Sigmoidal model fitting and ageing parameters

	PMB				BP				BB			
	Initial	**4d**	**8d**	**45d**	**Initial**	**4d**	**8d**	**45d**	**Initial**	**4d**	**8d**	**45d**
β	-1.82	-1.67	-1.70	-1.72	-1.01	-1.07	-1.06	-0.93	-1.31	-1.14	-1.09	-0.95
γ	-0.49	-0.51	-0.51	-0.51	-0.86	-0.83	-0.83	-0.80	-0.95	-0.96	-0.96	-0.82
Ageing Parameter	-3.69	-3.27	-3.34	-3.38	-1.17	-1.29	-1.28	-1.16	-1.39	-1.18	-1.13	-1.16

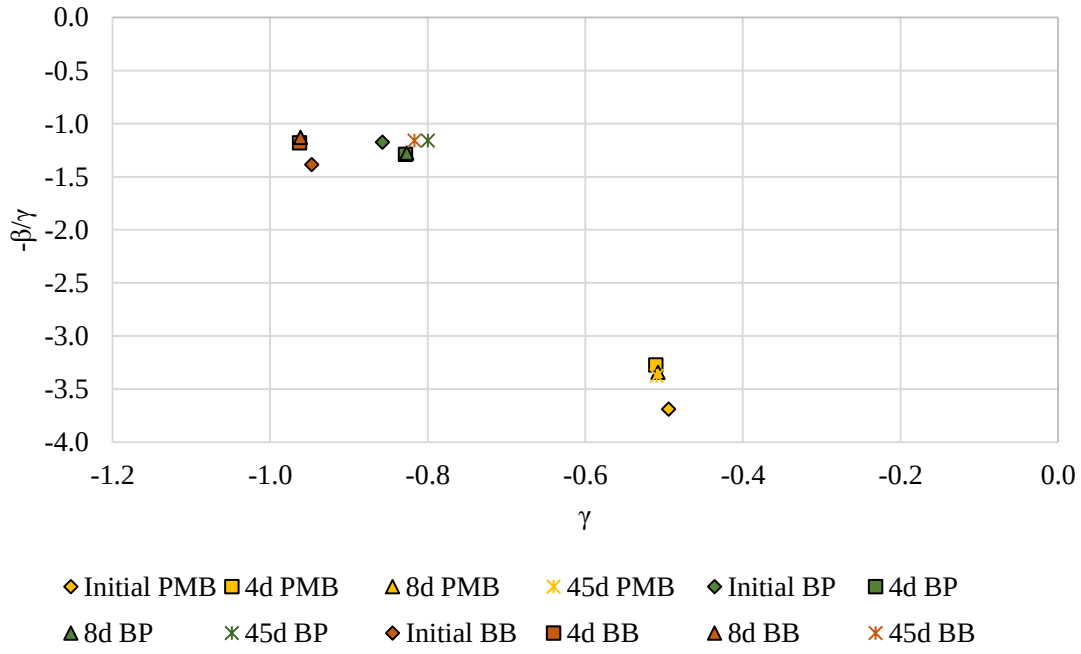


Figure 122. Ageing parameter of mixtures

The results in Figure 122 suggest that the change in the modulus of the mixtures is not representative of ageing in the cases studied. Nonetheless, in Figures 113, 114 and 115 the rheology of the mixtures with biobinders was shown to have changed after the ageing conditioning and consequently this change must be due to changes in the phase angle. To observe this, Figures 123, 124 and 125 show the master curves of the phase angle of the three asphalt mixtures at 15ºC respectively. These master curves reveal the decrease in the phase angle of the mixtures with BB and BP due to the ageing process meaning that the mixtures with biobinders lose relaxation capacity faster than the conventional mixture, which may be a disadvantage for these types of asphalt mixtures.

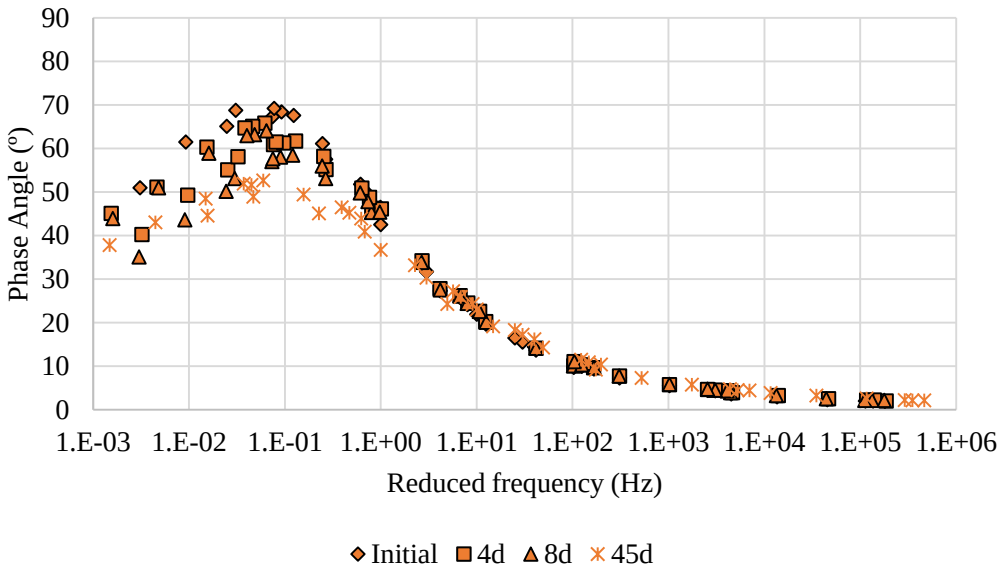


Figure 123. Master curve of the phase angle of aged 50% RA Mix BB at Tref=15°C

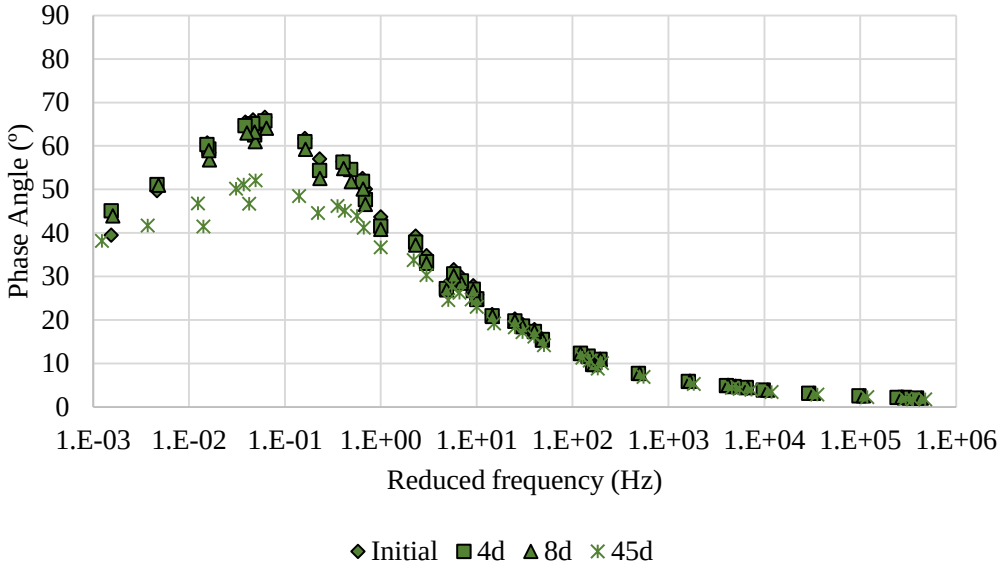


Figure 124. Master curve of the phase angle of aged 50% RA Mix BP at Tref=15°C

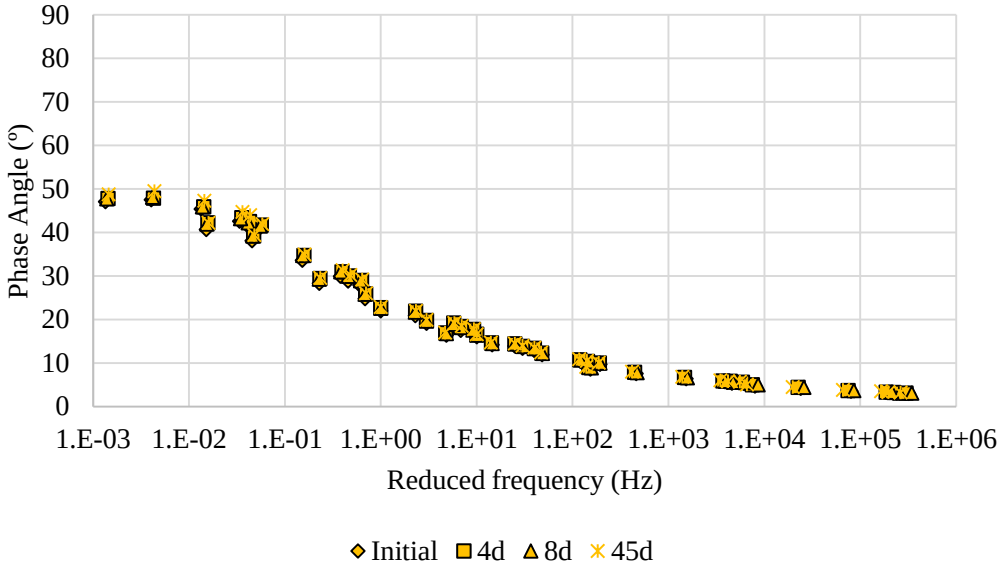


Figure 125. Master curve of the phase angle of aged 50% RA Mix PMB at Tref=15°C

6.7.3.2.3. Accelerated ageing

Figures 126, 127 and 128 display the evolution of the phase angle with ageing time for the different conditionings procedures (storage at room temperature, storage at 60ºC and storage in water at 60ºC) measured at 15ºC and 10Hz. Table 33 shows the change of the phase angle of each mixture under the different conditionings procedures in percentage relative to the unaged one.

The first noticeable result is that there is a decrease in the phase angle of all the asphalt mixtures independent of the storage conditions. In the case of the asphalt mixtures with biobinders, both show a decrease when they were stored at room temperature, being especially true for BB (54.5%). The decrease of the phase angle becomes more remarkable after the two ageing conditioning protocols (being double from room temperature to 60ºC in the case of BP). However, there is no significant difference between the storage at 60ºC and in water at 60ºC. This fact could mean that only the temperature is producing changes in the mixtures; hence, ageing is taking place and no moisture damage. The change of the phase angle of the asphalt mixtures with biobinders after hot storage and water conditioning is nearly double that of the mixture with the conventional PMB, which finally leads to state that these materials have a faster ageing process than conventional binders.

To compare the two ageing methods in terms of specimen size, the change in percentage of the phase angle of the mixtures tested in two-point bending mode at 15ºC, 10Hz after 45 days in water at 60ºC is shown in Table 33. There is a significant difference between the methods, being the change in the phase angle much higher in the three-point bending tests. This means that the ageing was effectively accelerated in the thin samples.

Table 33. Percentage of change of the phase angle after 45 days

	3PB			**2PB**
Mixture	**Storage at room temperature**	**Storage at 60ºC**	**Storage in water at 60ºC**	**Storage in water at 60ºC**
50% RA Mix PMB	-26.8	-34.0	*-37.0*	*3.8*
50% RA Mix BP	-32.2	-64.7	*-62.9*	*-10.9*
50% RA Mix BB	-54.5	-66.3	*-65.4*	*5.0*

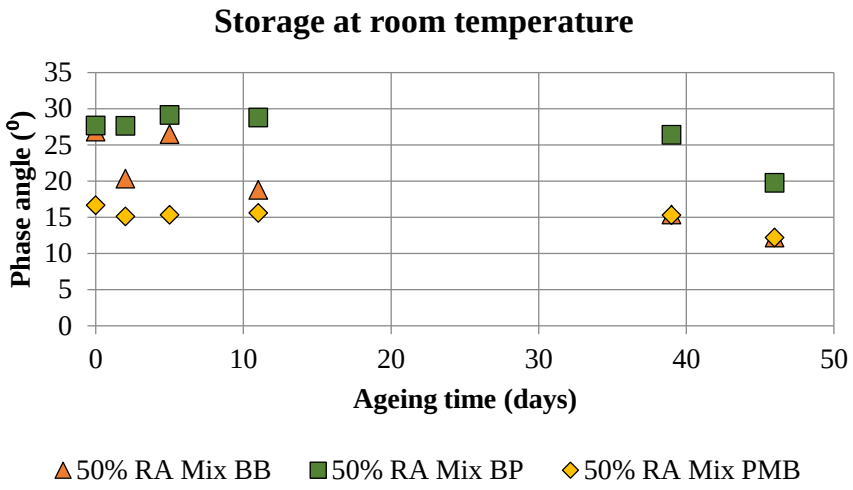


Figure 126. Evolution of the phase angle without ageing

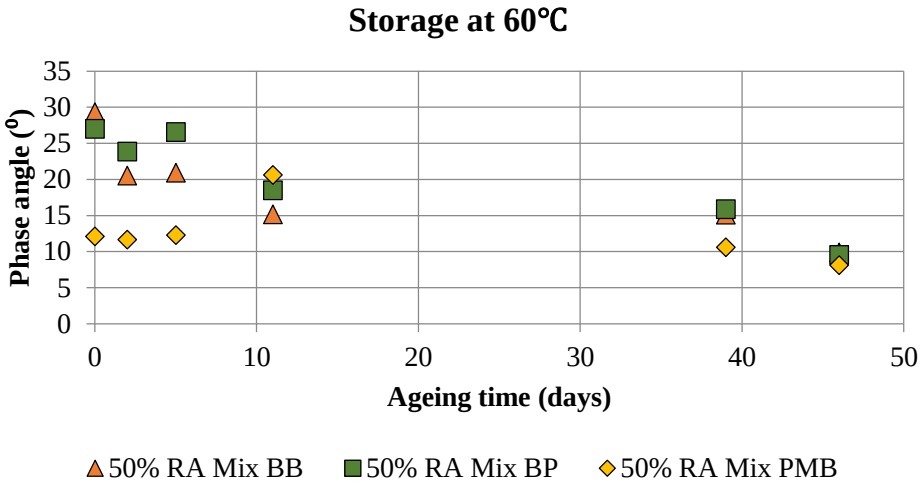


Figure 127. Evolution of the phase angle after dry storage at 60ºC

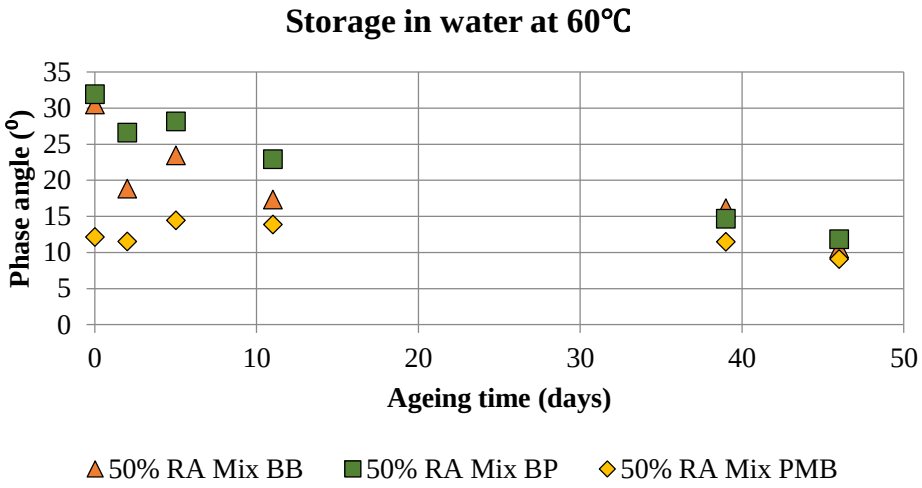


Figure 128. Evolution of phase angle after conditioning in water at 60ºC

CHAPTER 7. RECLAIMED ASPHALT CONTENT INFLUENCE ON THE MECHANICAL PROPERTIES OF BIO-ASPHALT MITURES

7. RECLAIMED ASPHALT CONTENT INFLUENCE ON THE MECHANICAL PROPERTIES OF BIO-ASPHALT MIXTURES

This chapter deals with the study of the influence of the RA content on the bio-mixtures. For this purpose, the three asphalt mixtures with 50% RA content and the three asphalt mixtures with 70% RA content manufactured and compacted in Ifsttar are analysed and compared in terms of rheological properties, stiffness modulus, resistance to rutting, fatigue and moisture damage.

7.2. Methods

The rheological and mechanical characterisation of the six asphalt mixtures were performed. Regarding their rheology, the six asphalt mixtures were tested in two-point bending mode according to EN 12697-26 (2012) Annex A from -10°C to 40°C and from 40Hz to 1Hz to obtain their dynamic modulus and phase angle. In terms of mechanical properties, the asphalt mixture were tested to obtain their stiffness modulus (ITSM), resistance to rutting (RLAT), fatigue (ITFT) and moisture damage (ITSR) was carried out.

7.3. Results and discussion

7.3.1. Rheological properties

The LVE properties of the 50% and 70% RA asphalt mixtures are shown in Figures 129, 130 and 131 in terms of Black diagrams and master curves of the norm of the dynamic modulus and phase angle at 15°C. On one hand, the increase of the RA content does not appear to produce a significant change in the rheology of the asphalt mixtures with PMB. However, the effect of the increase of the RA content is clear for the mixtures with biobinders. In Figure 129,

the increase of RA content produces a displacement of the Black curves of the mixtures with BP and PMB to lower phase angles, showing therefore a more elastic response. The fact that the influence of the RA content can be observed for the biobinders and not for the PMB is due to the rheology of the RA binder compared to the added binders. In Section 5.3.1, it was shown that the Black curve of the RA binder is similar to that of the PMB. Consequently, the blend of them exhibits an equivalent curve regardless of the amount of RA binder or PMB present, and the same effect occurs for the asphalt mixtures. On the other hand, the rheology of the biobinders was shown to be greatly different to that of the RA binder. Therefore, the behaviour of their blend would strongly depend on the amount of each one present in the blend and asphalt mixture as observed in Figure 129. If the RA content increases, the rheology of asphalt mixtures moves towards the rheology of the RA.

In terms of dynamic modulus, Figure 130 shows equivalent values regardless of the RA content for the asphalt mixtures with PMB and BB, while an increase of modulus is observed for the asphalt mixture with BP. In Figure 131, the decrease of the phase angle of the asphalt mixtures with biobinders confirms the increase of the elastic response with the increase in RA content.

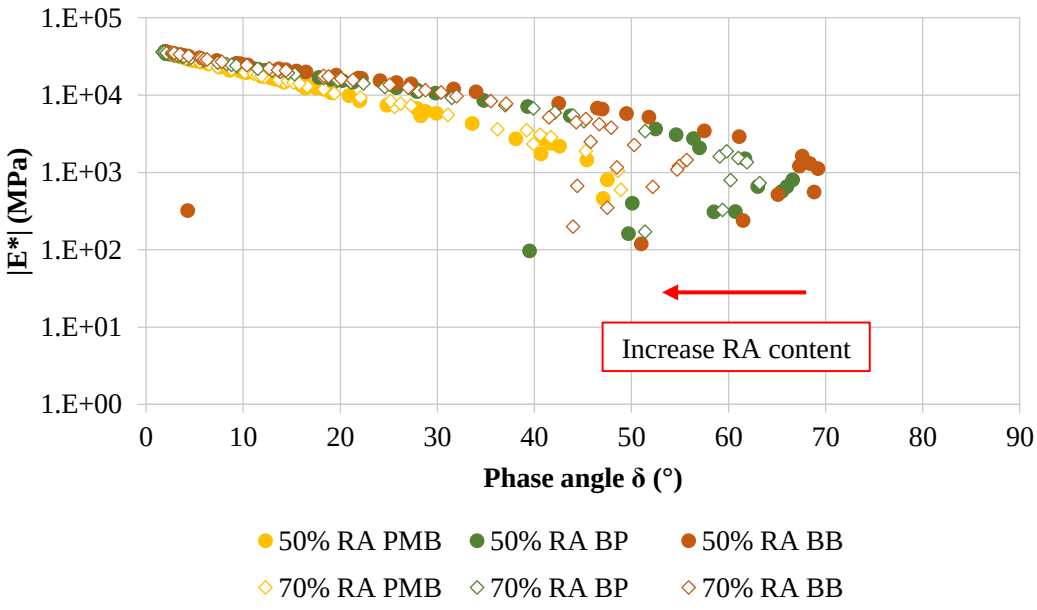


Figure 129. Black diagram of the 50% and 70% RA content mixtures

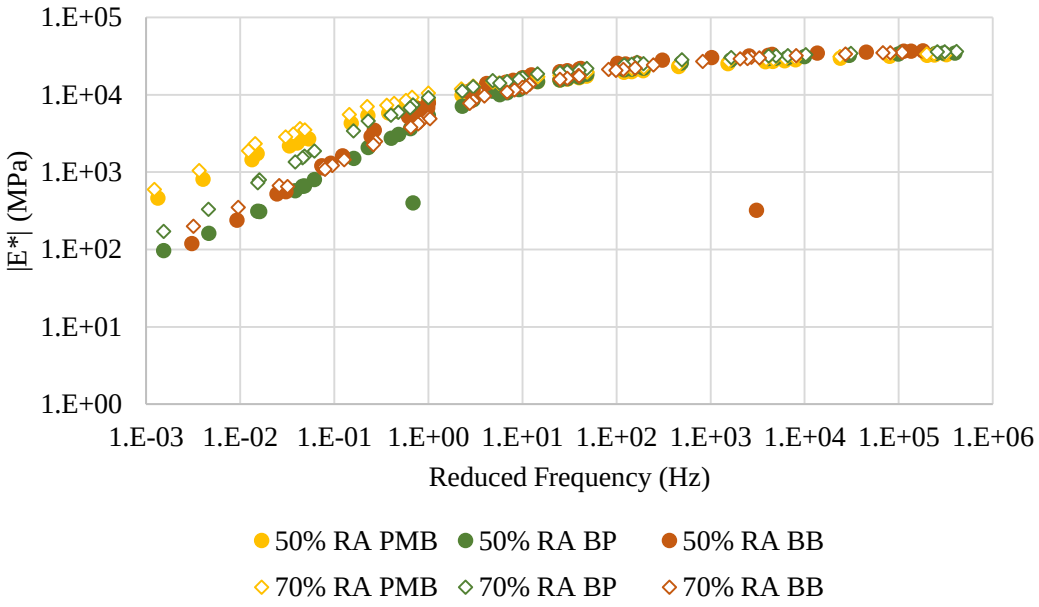


Figure 130. Master curves of the norm of the dynamic modulus of 50% and 70% RA content mixtures at a Tref=15°C

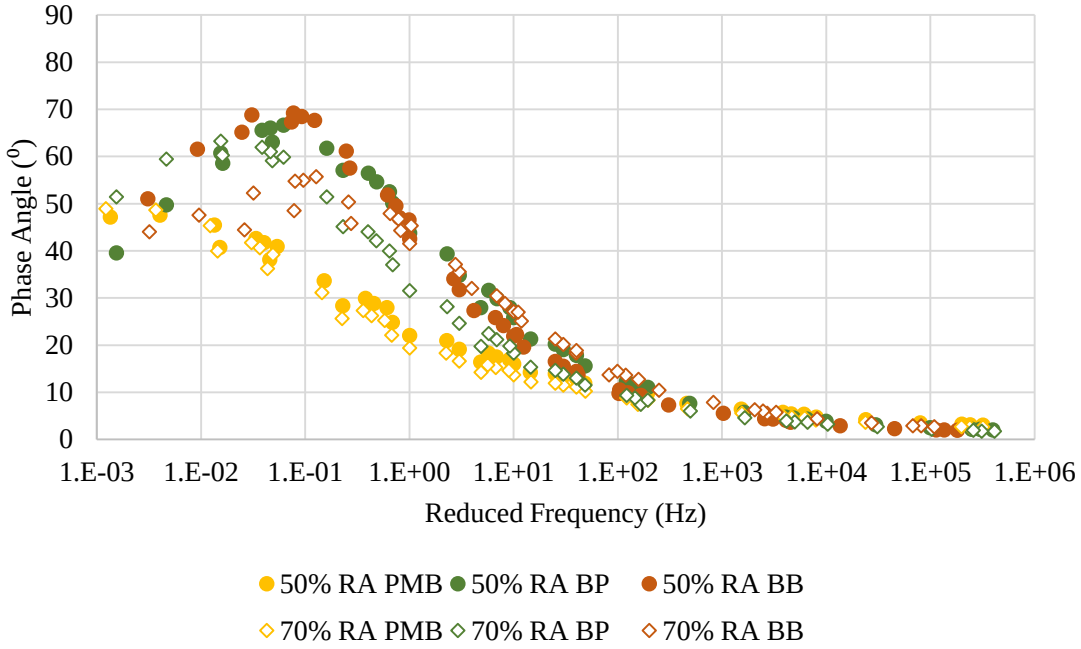


Figure 131. Master curves of the phase angle of 50% and 70% RA content mixtures at a Tref=15°C

7.3.2. Mechanical properties

The influence of the increase of RA content on the stiffness modulus of the asphalt mixtures is shown in Figure 132. The increase of the stiffness modulus of the asphalt mixtures with the

increase in RA content is more evident in terms of this property than in the dynamic modulus of the mixtures in Figure 130. The asphalt mixtures with PMB and BB increase their stiffness modulus by 35% while the asphalt mixture with BP increases by 65%. This increase of the stiffness modulus with the increase of RA content is due to the high stiffness of RA due to hardening process that the RA binder suffered during its service life (Li et al. 2004). The higher stiffness modulus due to a higher RA content usually results in an enhanced rutting resistance of asphalt mixtures (Hajj et al. 2009; Aschuri et al. 2009). Regarding this, the effect of the 20% RA increase on the stiffness modulus of the three mixtures is shown in Figure 133 in terms of axial deformation after RLAT (the results are the average of two specimens and error bars represent the standard deviation). The increase of RA content barely affects the asphalt mixtures with PMB and BP while greatly reducing the axial permanent deformation of the mixture with BB. The improvement in rutting resistance can also be related to the increase of the elastic response of the mixtures, which may reduce the permanent deformation that they suffer. In this respect, it was shown in the previous section that the elastic response of the mixture with BB was the most affected by the increase in RA content, and consequently its rutting resistance is the one showing a greater improvement.

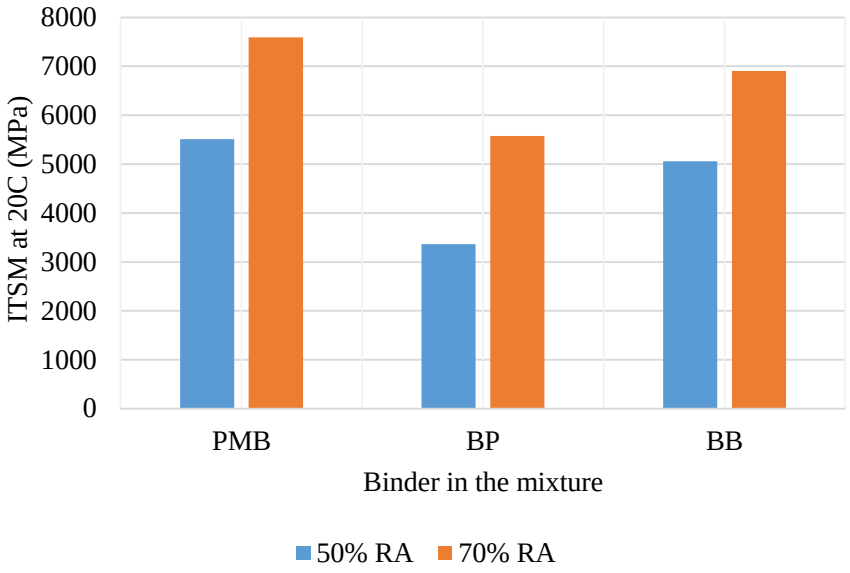


Figure 132. Stiffness modulus of the 50% and 70% RA content mixtures

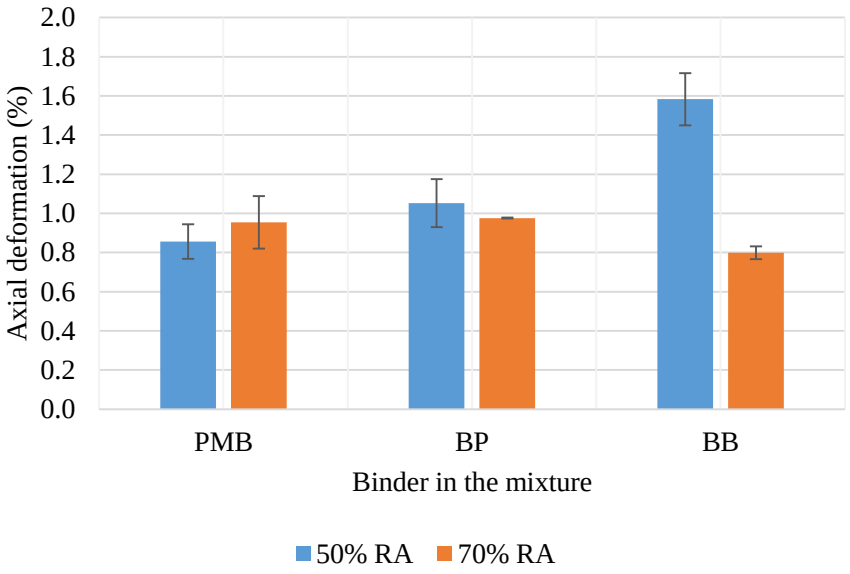


Figure 133. Rutting resistance of 50% and 70% RA content mixtures

On the other hand, the general influence of RA on the fatigue performance of asphalt mixtures is currently uncertain. As was reported in Section 2.5.1, different studies have shown either equivalent, improved or worse fatigue resistance of asphalt mixtures due to the presence of RA. In this regard, the fatigue life of the six asphalt mixtures is shown in Figure 134. In this case, it can be observed that the increase of the RA content decreased the fatigue resistance of the asphalt mixtures, especially for those containing BP. As observed in the previous chapter, the

fatigue lines of the six asphalt mixtures are nearly parallel, reinforcing the dominancy of the aggregate gradation on the slope of the lines and the influence of the binder on their relative position. The reduction of the fatigue life of the asphalt mixtures is related to the increase in stiffness shown and the consequent loss of flexibility due to the increase of the RA content. Even if the increase in RA content produced an increase in elasticity which could be beneficial for fatigue, the increase in stiffness seems to be more significant, adversely affecting the fatigue resistance.

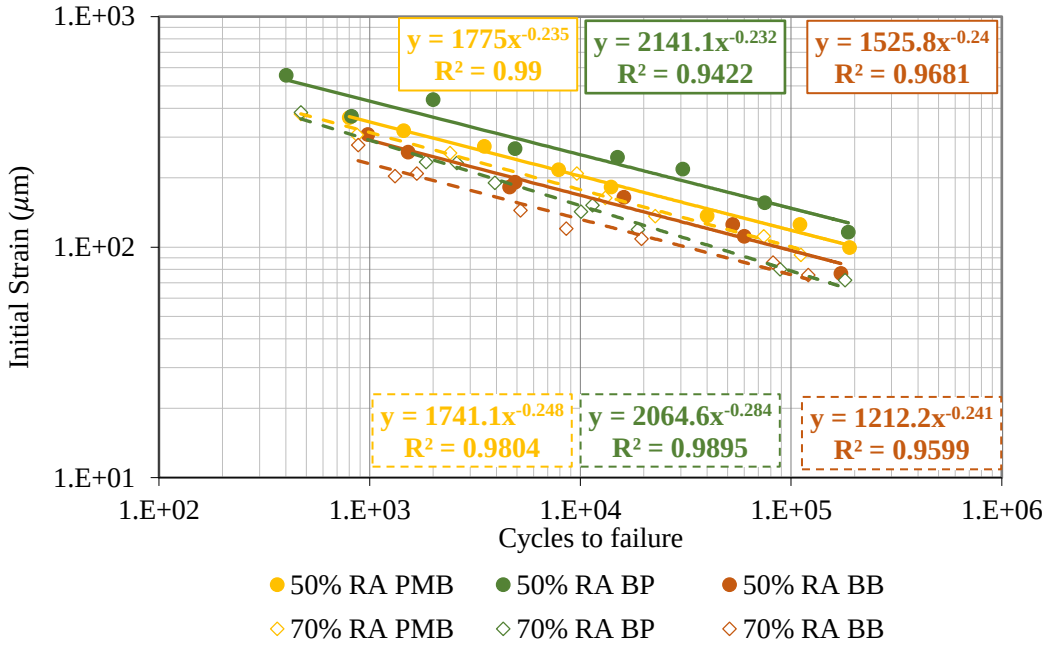


Figure 134. Fatigue life of 50% and 70% RA content mixtures

Regarding moisture damage, given that RA aggregates are already covered with binder, water sensitivity is expected to decrease in asphalt mixtures with high percentages of RA (Mogawer et al. 2012; Karlsson & Isacsson 2006; Tran et al. 2012). In Figure 135, the influence of the RA content on the water sensitivity of the asphalt mixtures is reported in terms of ITSR. Contrary to what could be expected, only the asphalt mixture with BP showed less resistance to moisture damage with the increase of RA content but still maintained a value close to 80%, which could be acceptable for a base layer (Ministerio de Fomento 2004). It has to be

mentioned that the six asphalt mixtures showed cohesive failure after wet conditioning. This means that the b between the aggregates and the binder was not damaged after wet conditioning and the presence of more already coated aggregates by RA binder because of the increased RA content could have been favourable in terms of water damage resistance.

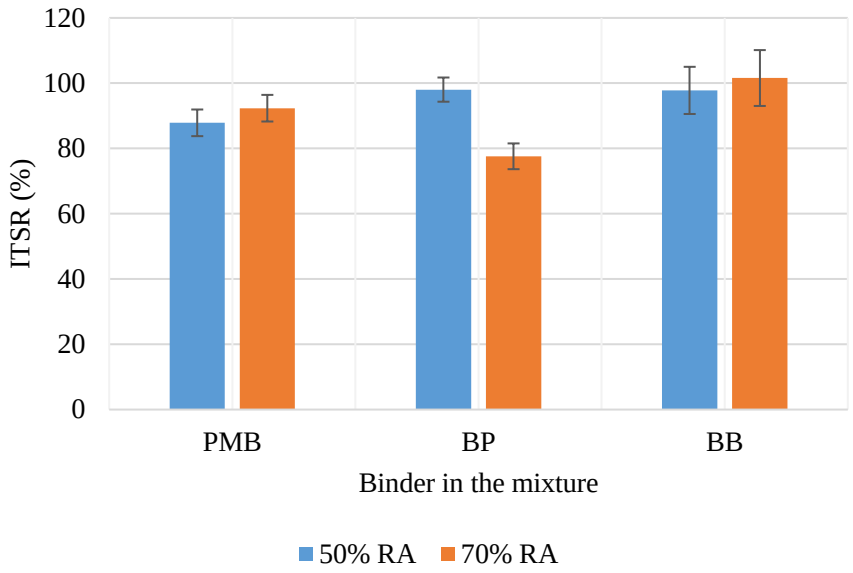


Figure 135. Moisture damage of 50% and 70% RA content mixtures

In summary, the increase of RA content produced an increase in the elastic response of the asphalt mixtures and increase in stiffness modulus. This fact resulted in an improved resistance to rutting but slightly decreased fatigue life of the asphalt mixtures. Only the mixture with BP presented a reduced resistance to moisture damage with the increase in RA content. In this regard, the 20% increase of RA in the mixtures with biobinders could be suitable in warm places in which the main distress in pavements is rutting.

CHAPTER 8. CONCLUSIONS AND FUTURE WORKS

8. CONCLUSIONS AND FUTURE WORKS

The main objective of the work described in this thesis was to study the performance of RA mixtures with biobinders at binder and asphalt mixture scale in order to gain further understanding of their suitability to be used in actual pavements. For this purpose, biobinders manufactured from pine resin, linseed oil and byproducts of the paper industry have been investigated as binders for the total replacement of the virgin bitumen needed in high RA content asphalt mixtures.

The work firstly focused on the characterization of binders and the design of the blend of RA binder and biobinders through the study of their conventional and rheological properties to be used as an input in the design of asphalt mixtures. Once the design parameters were fixed, the blends of RA binder and biobinders were characterised in terms of rheological, ageing and adhesion properties, and their performance was tested to study rutting, fatigue and thermal cracking resistance. Then, 50% RA mixtures and 70% RA mixtures were characterised for the same properties and the relationships between binder blends and asphalt mixtures were studied.

Given the results obtained, the following conclusions can be drawn:

- The RA binder is a hard and brittle binder showing a highly elastic component due to its ageing. The biobinders BBs exhibit greatly different properties depending on their resin/oil composition which allows their behaviour to be adapted. This is an advantageous feature since resin/oil proportions can be worked out based on the user needs. BP is a soft and highly modified binder. Both biobinders showed adequate properties to be used as virgin binders in high RA content asphalt mixtures.

- The blend design provided fundamental inputs for the RA mixture design which allowed a specific target for the blend of RA binder and biobinders to be achieved. In

addition, the design was able to show the effect on binder performance in the asphalt mixture, even if full blending did not occur.

- Biobinders produced comparable or greater rejuvenating effect on the RA binder compared to traditionally used bitumens. The desired rejuvenating effect implied the increase of the viscous component of the RA binder to improve relaxation properties and the decrease in stiffness to enhance flexibility.

- The ageing of biobinders follows the same tendency as conventional bitumens. Only RA+BB seemed to experience greater stiffening during the manufacturing of the asphalt mixtures. In addition, the comparison of the recovered RA+BB after the manufacturing of the asphalt mixture and the short-term laboratory aged RA+BB showed that standard protocols are not able to simulate the ageing of this material. All the aged blends of RA binder and biobinders, even after long-term ageing, appeared to have adequate properties to resist fatigue cracking.

- Regarding adhesive and cohesive properties of the biobinders and RA blends, BP showed comparable cohesive properties to a conventional PMB, while BB showed a slightly lower cohesion with respect to a conventional bitumen. The blends of biobinders with the RA binder showed improved cohesive properties compared to the RA binder and better adhesive properties compared to the blend of RA binder and a conventional binder.

- Biobinders have an important effect on the LVE behaviour of asphalt mixtures providing an increased viscous component in comparison to the reference asphalt mixture. However, no direct links between their LVE properties of binder blends and asphalt mixtures were found in terms of the parameters of the mechanical model used. Since the LVE properties of asphalt mixtures are provided by their binders, the fact that

they are not directly related suggests that the tested blends and the blends in the asphalt mixtures are not the same. This could be possibly due to the hypothesis of full blending between RA and biobinders that was made to manufacture binder blends and which may not be taking place in the asphalt mixtures. In this regard, if full blending does not take place, the binder blend under study is not the actual blend in the asphalt mixture. This was reflected using the normalized Cole-Cole diagrams.

- The rutting, fatigue and moisture damage resistance of the bio-asphalt mixtures was found to be equivalent to that of conventional asphalt mixtures and highly related to that of the blends of the RA binder and biobinders manufactured under the full blending assumption. In this regard, the study of the blend of the RA binder and biobinders still provides valuable information about the RA mixture performance even if full blending does not occur.
- Although the binder blends showed low thermal cracking resistance, the bio-asphalt mixtures exhibited comparable performance to conventional mixtures, dispelling the concerns about their use in this aspect. Given that thermal cracking phenomenon is controlled by the binder in asphalt mixtures, the fact that they are not related may be attributed to have tested different binders blends to those present in the asphalt mixtures. This can be due to the binders' blend having been prepared under full blending assumption (which might not be happening in the asphalt mixture); or the different ageing state of the blends in the binder (long-term ageing) and asphalt mixture (short-term ageing) testing respectively, especially for RA+BB which laboratory ageing showed not to reproduce the ageing during the asphalt mixture manufacturing.
- The use of 70% RA content asphalt mixtures increased the stiffness and elastic component of the asphalt mixtures. It improved rutting performance and maintained the moisture damage resistance, while showing a decrease in fatigue life.

- The ageing protocols lead to the conclusion that the bio-asphalt mixtures experience a faster ageing than the conventional one, becoming slightly stiffer and increasing their elastic component after ageing. This is the main drawback found in the performance of the bio-asphalt mixtures. The accelerated ageing methodology resulted in ageing of the asphalt mixtures being 10 times greater than that seen for conventional methodology in terms of phase angle, revealing the potential to observe ageing in a faster way.

Finally, it can be said that the blend design of the RA binder and biobinders performed as the first step has been found to satisfactorily work to gain inputs for the design of high RA content asphalt mixtures leading to obtain bio-asphalt mixtures with adequate performance.

In the light of the results obtained in this thesis for the materials studied, high RA content asphalt mixtures with biobinders can be considered to be promising materials to be used in pavement engineering. However, according to the literature review, different biobinders perform very differently in asphalt mixtures depending on their composition. For instance, waste cooking oil improve low temperature properties while switchgrass oil improves rutting resistance. In this regard, the selection of a biobinder has to be carefully done depending on which properties are required in a specific location, so the adequate composition of a biobinder cannot be generalised. In order to provide some guidance in this respect, the table in Annex I shows a summary of the currently known properties of different biobinders collected after the literature review. If a new biobinder is to be employed, its performance has to be fully characterised over the whole range of service temperatures of a pavement and for the different distresses affecting asphalt mixtures.

The following points are recommended for future research work:

- The use of the blend design between RA and fresh binders to gain inputs for the asphalt mixture design can be applied with conventional binders and rejuvenating additives to further assess its suitability to obtain adequate asphalt mixtures. This methodology should be compared to standard asphalt mixture design procedures (such as Marshall, Superpave, etc.) for the design of high-RA content asphalt mixtures to compare whether the outcomes are the same. In any case, carrying out the binders' blend design is highly recommended for high-RA content asphalt mixtures at least as a complement to standard asphalt mixture design procedures.
- Further study of the ageing of high-RA content asphalt mixtures with biobinders. There are different points to address in the continuation of the ageing study:
    - The comparison of the recovered biobinders blend after the manufacturing of the asphalt mixture and the short-term laboratory aged biobinders blend showed that the standard ageing protocol for conventional binders in the laboratory does not simulate the ageing process for some biobinders. Therefore, it is necessary to develop new laboratory ageing protocols able to reproduce the ageing of biobinders during the manufacturing of asphalt mixtures and service life.
    - Biobinders have been shown to age faster than conventional binders. This higher ageing rate should be translated into reduction of years of service life of a pavement to obtain further conclusions.
    - In this respect, the ageing behaviour of biobinders might be improved by the addition of modifiers, such as recycled crumb rubber, which have shown to enhance the ageing resistance of conventional binders. For this purpose, the compatibility and interaction of the specific modifier and biobinder would be a key point of the study.

- The development of a reliable methodology to determine the degree of blending of RA binder and virgin binders occurring in RA mixtures would greatly improve the characterisation and understanding of these materials, not only in the case of biobinders but also with conventional binders. Since the LVE properties of asphalt mixtures are given by the binder on them, a starting point for the study of the degree of blending is the comparison of binders' blends and asphalt mixtures' rheology. This comparison can be done in terms of mechanical element models' parameter for blends manufactured under the assumption of different degrees of blending (i.e. 100%, 60%, 40%, etc.) and asphalt mixtures. Finding a correlation between them might shed light on how the LVE properties of blends evolve with the degree of blending and how they compare to those of the corresponding asphalt mixtures.
- Further analysis of the chemical interaction between biobinders and aggregates is needed to understand their adhesion/cohesion performance, since they showed different results to conventional binders. This can be carried out testing fundamental properties such as surface energy of binders and aggregates by means of sessile drop methods.
- To increase the temperature range of testing of the asphalt mixtures. Specifically, rutting and fatigue performance in this thesis have been studied at the standard temperatures. More temperatures can be analysed to characterise the temperature susceptibility of high-RA content asphalt mixtures with biobinders.
- Full-scale experiments would be the last step for the development of the high RA content asphalt mixtures with biobinders.

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ANNEX I. SUMMARY OF THE INFLUENCE OF BIOBINDERS COMPOSITION ON BINDERS PROPERTIES

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Symbol	Meaning
✓	Good comparison to conventional materials
x	Bad comparison to conventional materials
↓	Decrease compared to conventional materials
↑	Increase compared to conventional materials
-	Not known

	Biobinder	Studies	Replacement %	Rheology	Viscosity	Complex modulus	Rutting resistance	Fatigue resistance	Thermal cracking resistance	Moisture damage resistance	Temperature susceptibility	Ageing resistance	Durability in field
100% bitumen replacement	**Polyethyl acrylate (PEA)**	Airey & Mohammed (2008)	100	✓	-	✓	-	-	-	-	-	-	-
	Polymethyl (PMA) acrylate	Airey & Mohammed (2008)	100	✓	-	✓	-	-	-	-	-	-	-
	Polybutyl acrylate (PBA)	Airey & Mohammed (2008)	100	x	-	x	-	-	-	-	-	-	-

	Biobinder	Studies	Replacement %	Rheology	Viscosity	Complex modulus	Rutting resistance	Fatigue resistance	Thermal cracking resistance	Moisture damage resistance	Temperature susceptibility	Ageing resistance	Durability in field
100% bitumen replacement	**Oakwood oil**	Raouf (2010)	100	-	-	-	✓	-	X	-	-	-	-
	Switchgrass oil	Raouf (2010)	100	✓	-	-	✓	-	X	-	-	-	-
	Corn stover oil	Raouf (2010)	100	-	-	-	✓	-	X	-	-	-	-
	Algaenan with free fatty acid oil	Chailleux et al. (2012)	100	✓	-	✓	-	-	-	-	-	-	-
	Oakwood oil and crumb rubber	Peralta et al. (2012a)	100	-	-	-	✓	✓	✓	-	-	-	-
	Biobinder (no composition specified)	Pouget & Loup (2013)	100	✓	-	-	-	-	✓	-	-	X	-

	Biobinder	Studies	Replacement of conventional binder (%)	Rheology	Viscosity	Complex modulus	Rutting resistance	Fatigue resistance	Thermal cracking resistance	Moisture damage resistance	Temperature susceptibility	Ageing resistance	Durability in field
Bitumen extenders (20-75% replacement)	**Waste Cooking Oil**	Wen, Bhusal, & Wen (2012)	10-60	-	-	-	x	x	✓	✓	-	-	-
	Pine wood chips processed by fast pyrolysis	Mohammad et al. (2013)	20-50	-	-	-	✓	x	✓	✓	-	-	-
	Cedar chips from the residue of wood	Yang & Suciptan (2016)	2-50	✓	-	-	✓	-	-	-	✓	x	-
Bitumen modifier (<20%)	**Oakwood oil**	Williams et al. (2009)	3-9	-	-	-	✓	-	x	-	-	-	-
	Switchgrass oil	Williams et al. (2009)	3-9	-	-	-	✓	-	x	-	-	-	-
	Corn stover oil	Williams et al. (2009)	3-9	-	-	-	✓	-	x	-	-	-	-

	Biobinder	Studies	Replacement %	Rheology	Viscosity	Complex modulus	Rutting resistance	Fatigue resistance	Thermal cracking resistance	Moisture damage resistance	Temperature susceptibility	Ageing resistance	Durability in field
Bitumen modifier (<20%)	**Heavy residue from the thermochemical liquefaction process to convert swine manure to bio-oil**	Fini et al. (2011) Fini et al. (2012) You et al. (2011) Mills-Beale et al. (2014)	2-10	-	↓	↓	-	-	✓	-	-	✓	-
	Soy fatty acids (a specific portion of soybean oil)	Seidel & Haddock (2012)	1-3	-	↓	↓	-	-	-	-	-	-	-
	Waste coffee beans	Zofka & Yut (2012)	2-4	-	-	-	-	-	-	-	✓	Served as a solvent instead of antioxidant	-
	Heavy residue from the thermochemical liquefaction process to convert swine manure to bio-oil + crumb rubber	Fini, Oldham, & Abu-Lebdeh (2013)	5	-	↓	-	-	-	✓	-	✓	-	-
	Ashes made from rice husk and wood sawdust	Xue et al. (2014)	0-20	-	✓	✓	✓	-	-	-	-	✓	-

	Biobinder	Studies	Replacement %	Rheology	Viscosity	Complex modulus	Rutting resistance	Fatigue resistance	Thermal cracking resistance	Moisture damage resistance	Temperature susceptibility	Ageing resistance	Durability in field
Bitumen modifier (<20%)	**Bio-oil from waste wood**	Yang et al. (2014) Yang & You (2015) Yang et al. (2017)	2-10	-	-	✓	✓	✓	-	-	-	✓(Only if low percentages are used, i.e. 2%)	-
	Methyl ester of a fatty acid from sunflower	Somé et al. (2016)	0.5-5	-	↓	✓	-	-	-	-	-	x	Good after 5 years
	Plant resin fluxed with monoalkyl esters from vegetable and animal oils	Somé et al. (2016)	0.5-5	-	↓	✓	-	-	-	-	-	x	Good after 5 years
	Heavy biological oil from pyrolysis of biomass with SBS polymers	Zhang et al. (2017)	5-20	-	↑ (before ageing)	-	x (before ageing) ✓ (after ageing)	-	-	-	x (before ageing) ✓ (after ageing)	Properties completely changed after ageing	-
	Waste Cooking Oil	Sun et al. (2016)	2-8	-	↓	-	x	✓	✓	-	-	-	-
	Waste Cooking Oil (as aged binder rejuvenator)	Gong et al. (2016) Zhu et al. (2017)	1.5-10	✓	↓	-	x	✓	✓	x	-	-	-

	Biobinder	Studies	Replacement %	Rheology	Viscosity	Complex modulus	Rutting resistance	Fatigue resistance	Thermal cracking resistance	Moisture damage resistance	Temperature susceptibility	Ageing resistance	Durability in field
Bitumen modifier (<20%)	**Bio-oil from swine manure (as aged binder rejuvenator)**	Hill et al. (2013) Mogawer et al. (2016)	5	-	-	-	x	✓	✓	x	-	-	-
	Pongamia oil (as aged binder rejuvenator)	Nayak & Sahoo (2015)	5-15	-	-	-	✓	✓	-	-	✓	-	-
	Composite rejuvenator made of castor oil and coke oven gas (as aged binder rejuvenator)	Nayak & Sahoo (2015)	5-15	-	-	-	✓	✓	-	-	✓	-	-
	Derived from natural bean oil	Gong et al. (2017)	1-3	-	-	-	-	-	-	Depends on base bitumen	-	-	-