RECYPMA

Research Report of WP3: Properties of Aged Polymer Modified Binder

Deliverable Nr.3.1

(Draft version to be updated during the project)

March 2013

The Netherlands Organization for Applied Scientific Research (TNO), the Netherlands
Delft University of Technology (DUT), the Netherlands
The University of Zilina (UNIZA), Slovakia
Danish Road Directorate (DRD), Danish Road Institute, Denmark

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Possibilities for high quality RECYling of Polymer Modified Asphalt

Deliverable Nr 3.1
Research Report of WP3: Properties of Aged Polymer Modified Binder

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Executive summary

Throughout Europe polymer modified asphalt (PMA) is used extensively in the past decades for high trafficked roads and premium pavements; especially for surface layers. The addition of polymers contributes to the durability and functionality of these premium pavements. These pavements are now more and more reaching their end of life. Therefore the road sector is facing a rapidly increasing source of reclaimed asphalt (RA) that contains polymer modified bitumen (PMB), which offers a potential premium binder contribution. It is the challenge to the road sector to ensure that the “RA containing PMB” will be recycled at its highest practical potential. The goal in recycling is not to achieve the highest possible recycling percentage, but to avoid downgrading of RA containing a potential valuable asset.

The aim of the RECYPMA project is to investigate the possibilities for recycling polymer modified asphalt from surface layers into new high quality surface layers using hot mix recycling. The project should give answers to the following questions:

- What is the potential of using PMRA in new asphalt?
- What is the benefit?
- What (do we think, regarding the results of the project) should be done to get this implemented (technically) based on laboratory test results

There are five Work Packages in the project plan as follows:

- WP1 – Management and knowledge dissemination
- WP2 – State of the art on recycling of modified binders
- WP3 – Properties of aged polymer modified binder
- WP4 – Properties of asphalt mixtures using reclaimed material with polymer modified binders
- WP5 – Environmental and economic benefits of the use of polymer modified reclaimed asphalt

Delft University of Technology (DUT) is the coordinator for WP 3. In this work package, we investigate the rheological and chemical properties of aged PMB binder and blended binder after mixing with virgin binder.

Reclaimed Asphalt (RA) samples are taken from well documented roads in three countries and will be used again in the three different types of mixtures:

- Dense asphalt concrete (DAC, from Slovak Republic)
- Stone mastic asphalt (SMA, from Denmark) and
- Porous asphalt concrete (PAC) or thin noise reducing surface layer from the Netherlands.

This research is focused on the possibilities of recycling RA containing SBS modified bitumen. This selection is made because SBS modified bitumen is by far the most used PMB.

From the RA samples polymer modified bitumen (PMB-RA) was extracted/recovered and the binder properties were determined by using some important empirical rheological tests, fundamental rheological tests and chemical tests. After characterisation, the recovered PMB was blended respectively with a soft penetration grade binder and a virgin SBS modified binder. The properties of these lab blended binders were evaluated with the same tests as for the recovered PMB-RA.

The primary aims of the research in WP3 are:

- To obtain rheological properties from the PMB-RA binder of reclaimed polymer modified (SBS) asphalt.
- To study the influence of blending with soft virgin Pen. grade binders and polymer modified (SBS) binders.
- To determine the impact on rheological properties of a “new” binder when an aged PMB-RA is mixed with virgin binder for the production of a new mixture.
- To develop a simple method or model (similar to the logPen. rule) to predict the effect of recycling on a blended binder.
- The developed method has the ability to advise on the type and amount of binder that needs to be added for the design of the mixes that will be tested in WP4.

Main conclusions are drawn as follows:

- Although the polymer in a modified bitumen (PMB) can degrade during the service life of an asphalt pavement, the results of this report indicate that part of the characteristics of the polymer is still available in the PMB reclaimed from a milled old asphalt surface-layer. These characteristics can be manifested when blending with virgin Pen. grade bitumen or with virgin PMB binder. It means that the polymer from the reclaimed binder can function in a new mixture when recycled.

- It is possible to restore the rheological properties of the reclaimed PMB binder to its original state by mixing it with a soft virgin PMB binder.

- As a first step in mixture design for the industry, the logPen. model and the SP model together can be used to approximately predict the penetration value at 25 ºC and the S.P. of the blended binder consisting of reclaimed PMB binder plus virgin Pen. grade binder or plus virgin PMB binder.

- A linear correlation between $\log(G^*_{0.4Hz;\ 25^oC;\ [MPa]})$ and $\log(Pen._{\ 25^oC;[dmm]})$ makes it possible to use the G* to predict the Pen. value for the purpose of evaluating the effect of recycling when a small amount of binder is obtained.

- The Grunberg-Nissan model is an option to describe some fundamentally rheological properties of the blended binder, like viscosity at different temperatures and complex modulus at a wide frequency range.

- Based on the viscosity data, temperatures for mixing and compaction are recommended for work package 4 (WP4) in this project. The used method is also very useful for mix design in industry. Due to the polymer modification and aging of the binder, the required mixing temperatures for the blended binder are high, in some cases above 180°C. Such high temperatures should be avoided to prevent degradation of the polymer.

- The S=O index and SBS index from FTIR can describe the chemical properties of a blended binder; the SBS index value only helps in the case of reclaimed PMB plus virgin Pen. grade bitumen. The SBS index can only reflect the relative SBS content but hardly characterize its degradation behaviour; the GPC test can directly describe this behaviour when original binder is available as a reference.

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List of abbreviations

DSR	Dynamic Shear Rheometer
DSR_PP	DSR with parallel plates device
DSR_CP	DSR with cone & plate device
DAC	Dense asphalt concrete
DUT	Delft University of Technology, The Netherlands
DRD	Danish Road Directorate, Danish Road Institute , Denmark
EN	European norm
FTIR	Fourier Transform Infrared spectroscopy
GPC	Gel Permeation Chromatography – molecular size distribution analysis
I_p	European abbreviation for penetration index, a calculated value based on Penetration in accordance with EN 1426 and softening point EN 1427.
LTA	Long term aging
Pen.	Abbreviation for penetration at 25 °C (EN 1426)
PMB	Polymer Modified Bitumen
PAC	Porous asphalt concrete
RA	Reclaimed asphalt
RAD	RA mix from Denmark, SMA
RAN	RA mix from the Netherlands, PA,
RAS	RA mix from Slovakia, AC
RAD binder	Recovered binder from Danish mix
RAN binder	Recovered binder from Dutch mix
RAS binder	Recovered binder from Slovakian mix
RCAT	Rotating cylinder ageing test
SP	Softening point
STA	Short term ageing
TNO	The Netherlands Organisation for Applied Scientific Research
UNIZA	The University of Zilina, Slovakia

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1 Introduction and focus of the research

Throughout Europe polymer modified asphalt (PMA) is used extensively in the past decades for high trafficked roads and premium pavements; especially for surface layers. The addition of polymers contributes to the durability and functionality of these premium pavements. These pavements are now more and more reaching their end of life. Therefore the road sector is facing a rapidly increasing source of reclaimed asphalt (RA) that contains polymer modified bitumen (PMB), which offers a potential premium binder contribution. It is the challenge to the road sector to ensure that the “RA containing PMB” will be recycled at its highest practical potential. The goal in recycling is not to achieve the highest possible recycling percentage, but to avoid downgrading of RA containing a potential valuable asset.

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- To develop a simple method or model (similar to the logPen. rule) to predict the effect of recycling on a blended binder.
- The developed method has the ability to advise on the type and amount of binder that needs to be added for the design of the mixes that will be tested in WP4.

In addition, laboratory ageing on a fresh PMB binder will be performed in order to have a reference for the observed ageing in practice. The result of the laboratory ageing will be presented in an additional report.

As mentioned above and summarized in the flowchart in Figure 1.1, the following activities are performed in WP3:

- RA for three mixtures has been collected;
- The PMB (SBS modified bitumen) is recovered from the RA.
- The properties of the recovered polymer modified binder (PMB-RA) are characterized for 3 different RA mixtures, by means of empirically and fundamentally rheological tests, as well as chemical tests (GPC and FTIR)
- Blending procedures for aged PMB are developed with:
    - Softer bitumen (70/100)
    - New PMB (SBS modified bitumen)
- Two realistic ratios are used to blend the PMB-RA with new virgin binder
- The properties of the blended binders are determined in a similar way as for the PMB RA.

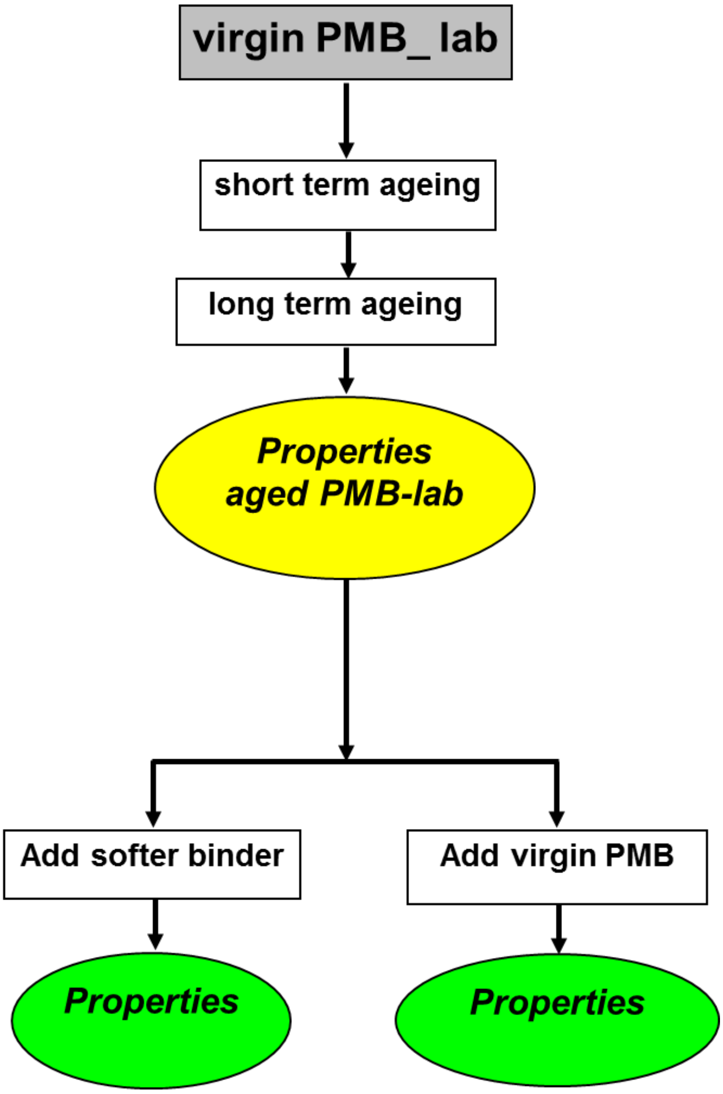


Figure 1.1 Flow chart for the research on PMB_RA

2 Materials, preparation and test methods for the research

2.1 Selected extraction/recovery method and recovery of PMB-RA

The extraction/recovery method used in the research is determined in WP 2 via a literature survey combined with an international questionnaire amongst road laboratories. This resulted in the following conclusion: “The extraction procedure using dichloromethane followed by rotary evaporation according to EN 12697-1 and EN 12697-3 will lead to representative bituminous binder recovery also for SBS modified binders and will be used in this research (E. Nielsen, 2012).”

2.2 PMB-RA binder

Three PMB-RA binders, RAN, RAS and RAD, have been recovered using the method given in the section of 2.1. Detailed information of these binders is given below:

RAN,	reclaimed binder from the top layer of a double porous asphalt system of 7 year old. It located at one section between Den Bosch and Eindhoven on Expressway A2 in the Netherlands. The original binder is Styrelf PMB 40/100-65 HD.
RAS,	reclaimed binder from dense asphalt concrete (AC11) produced by Cesty Nitra in 1996 and paved on a section of motorway in the vicinity of the town Sere. The original binder was Apollobit MCA-S. It was SBS polymer modified bituminous binder with a penetration range 50-100 dmm and a softening point above 70 ºC.
RAD,	reclaimed binder from Stone Mastic Asphalt (SMA 11) produced by Colas Danmark A/S in 1989 and paved on a motorway in Denmark (Jutland, north of the town of Vejle). The original binder was called Caribit Plus 85 which was a SBS polymer modified bituminous binder with a penetration ranging from 70 – 100 x 0,1 mm and a softening point Ring & Ball above 75 °C.

2.3 Fresh virgin bitumen

Preliminary calculations with the logPen. rule indicated that a virgin bitumen with penetration around 90 is needed for the blending in WP3. For the Dutch and the Slovakian mix, the following virgin binders are used:

Q8,	straight run bitumen, paving grade 70/100, provided by Kuwait Petroleum (Nederland) B.V.;
KR,	modified bitumen by mixing10% of D0243 SBS in B160/220 bitumen, produced by Kraton Polymers Nederland BV.

For the Danish mix, the following fresh binders are used:

70/100,	straight run bitumen in accordance with EN 12591. It was produced by blending two different bitumens which were used in a Danish Round Robin on bituminous binders in the winter of 2005/2006. The 70/100 was blended from the two round robin samples 7212-584 (40/60) and 7212-583 (330/430) in the proportion 71.2 % and 28.8 % respectively.
90/150-75,	SBS polymer modified bitumen in accordance with EN 14023. It was provided by Colas Danmark A/S as a reference sample from their production of polymer modified bitumens.

DRD’s experience was used to pour the fresh PMB binder and RA binder into the blending container, i.e. “heat the sample shortly to 180 °C, homogenize the sample and then cool the sample to the pouring temperature in order to “break” the 3-dimensional network of the polymer in the binder”. The procedure is also in accordance with EN 12594 for sample preparation which includes the handling of PMBs. Fresh paving grade binder was heated not more than 100 °C above the expected softening point.

2.4 Blending procedure for PMB-RA with virgin binders at two percentages

Two realistic ratios, 15% and 40% by mass of the PMB-RA were blended with new virgin binder. In total, six binder groups were blended. The codes of these six groups are given in Table 2.1. Note that the Danish blended binder has a slightly different RA percentage.

Table 2.1 Coding system for the six binder groups to be blended

Binder Groups*		RA content	Fresh bitumen content
		[%]	[%]
RAN+Q8	0%RAN+Q8	0	100
	15%RAN+Q8	15	85
	40%RAN+Q8	40	60
	100%RAN+Q8	100	0
RAN+KR	0%RAN+KR	0	100
	15%RAN+KR	15	85
	40%RAN+KR	40	60
	100%RAN+KR	100	0
RAS+Q8	0%RAS+Q8	0	100
	15%RAS+Q8	15	85
	40%RAS+Q8	40	60
	100%RAS+Q8	100	0
RAS+KR	0%RAS+KR	0	100
	15%RAS+KR	15	85
	40%RAS+KR	40	60
	100%RAS+KR	100	0
RAD+70/100	0%RAD+70/100	0	100
	15%RAD+70/100	13.48	86.52
	40%RAD+70/100	36.49	63.51
	100%RAD+70/100	100	0
RAD+90/150-75	0%RAD+90/150-75	0	100
	15%RAD+90/150-75	13.66	86.52
	40%RAD+90/150-75	36.89	63.51
	100%RAD+90/150-75	100	0

*: In total 24 codes of binders are given, but only 19 types of binders are used. 5 couples of binders have different codes but belong to the same type of binder. They are 0%RAN+Q8 and 0%RAS+Q8 (pure Q8), 0%RAN+KR and 0%RAS+KR (pure KR), 100%RAN+Q8 and 100%RAN+KR (pure RAN), 100%RAS+Q8 and 100%RAS+KR (pure RAS), 100%RAD+70/100 and 100%RAD+90/150-75 (pure RAD).

DRD and DUT use both a Silverson L5M high shear mixer (Figure 2.1). It has to be noted that blending the fresh binder and the RA binder is totally different from mixing polymer particles into the bitumen. The blending parameters by DUT are given in table 2.2.

Table 2.2 Blending parameters by using high shear mixer

Temperature [°C]	145 ± 5
Quantity [g]	500
Rotation speed [rpm]	4000 ~ 7000
Blending process	Start with virgin binder and gradually add the RA binder
Time [min]	5~10

Some important issues are:

- The optimum position of the mixing unit should be around 2 cm above the bottom of the blending container and at the same time a little off the center to avoid the vortex.
- To check the blending effect, a fluorescence microscope is used to observe the distribution of SBS after the first 5 minutes.
- For safety, a firm grip or a very good fixture of the blending container is necessary due to the high energy input to a small container.
- To avoid bubbles, the mixing unit is carefully moved down and slowly immersed into the binder before working. Otherwise, some air will be trapped in the room of the unit and dispersed into fine bubbles by high shearing.
- During the blending, the unit is kept in the blended binder to avoid absorbing the air.

Figure 2.1 Silverson L5M high shear mixer at DUT

In order to be able to control the temperature correctly and to have a safe fixture for the blending container during mixing DRD designed a special vessel that was built at a local metal workshop (SCHRØDER metal a/s, Guldalderen, Hedehusene). Figure 2.2 shows the thermal insulated stainless steel vessel with internal dimensions of 580 mm x 380 mm x 340 mm (length x width x depth). The vessel was built to accommodate blending containers from approximately 10 litres to 250 ml. Figure 2.3 shows details of the initial design of the fixture which later on may be changed a little to help centring smaller blending containers with respect to the position of the axis of the high shear mixer.

Figure 2.2 Vessel, thermostat and high shear mixer outside fuming cupboard (DRD)

Figure 2.3 Close-up of the adjustable fixture for the blending container and the thermostat

DRD did a pre-trial in the laboratory with similar bituminous binders as were expected to be handled during the RECYPMA blending procedures. It was observed that the high shear mixer could not properly blend at 145 °C. Therefore, the temperature was increased to 175 °C ± 5 °C. At this temperature an acceptable blending could be realized. The high mixing temperature is necessary because of the high SBS content of the virgin polymer modified bitumen and the ageing level of the recovered binder.

DRD developed the blending procedure by using a high shear mixer with 500 grams in a 1 litre container. Firstly, the oil bath is heated to 170 - 180°C. The container with the hot but unblended sample is placed and fixed in the oil bath with a support beneath the container. The high shear mixer is lowered until the mixer head is approximately 10 - 20 mm from the bottom of the container and the mixer is placed vertical but eccentric to the axis of the blending container. The rotation is started and the speed adjusted to the maximum level at which no air is sucked into the sample and dispersed. This speed is approximately 6.000 rpm. After 10 minutes the polymer dispersion is checked under the microscope. All samples were homogenous after 10 minutes of high shear mixing.

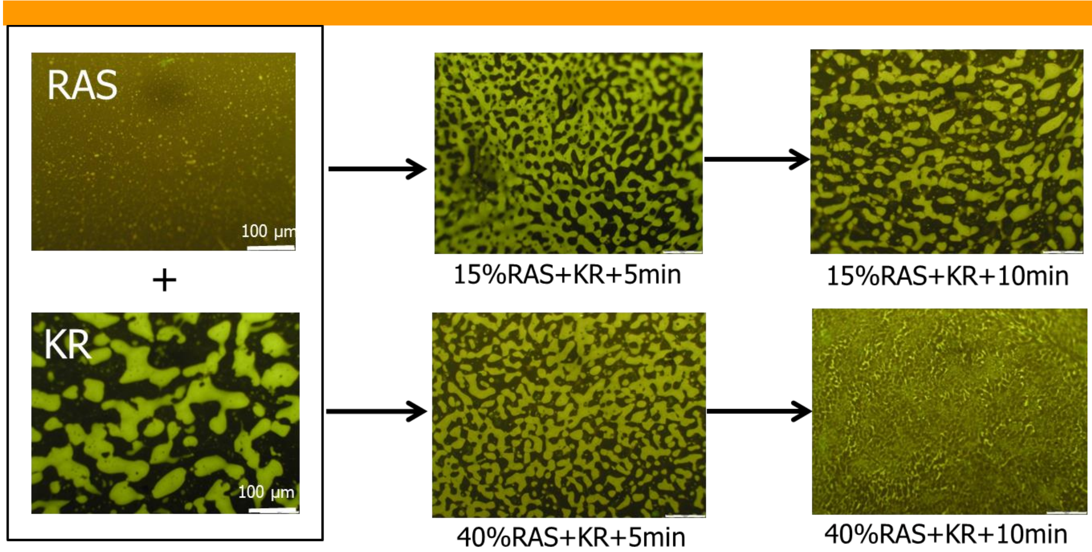


Figure 2.4 Fluorescent images of 15%RAS+KR and 40%RAS+KR before and after mixing for 5 and 10 mins

Figure 2.4 shows fluorescent images of 15%RAS+KR and 40%RAS+KR after mixing for 5 and 10 minutes. The image for RAS proves that there is still polymer in the reclaimed binder. The images for blended binders indicate that the applied mixing process can homogenize the blended-binder system, while at the same time the high-shear mixing function can change the original morphology of SBS in the virgin binder.

3 Testing program

3.1 *General*

In this chapter, information on the performed tests is given. In general, DRD performed all the binder tests related to the RA obtained from the Danish road, except the gel permeation chromatography (GPC) test. DUT performed all the binder tests related to RA binders from Slovakia and the Netherlands, except the GPC tests. TNO performed all GPC tests.

3.2 *Detailed testing program*

The testing program on the recovered PMB-RA from the 3 RA types and the virgin binders included:

- Penetration, Softening Point
- DSR master curves
- Viscosity measurements
- FTIR
- GPC

Detailed information of the methods mentioned above are given in the following sections.

3.2.1 Standard rheological tests: penetration, softening point (SP)

The penetration and softening point (R&B) were measured according to EU specifications (EN 1426 for penetration and EN1427 for softening point). Softening points above 80 °C are determined in a glycerol bath.

3.2.2 Fundamental rheological tests: DSR

The dynamic shear rheometer (DSR) tests were done according to EU specification, EN 14770. A DSR AR 2000ex was used at DUT and a Stress Tech Rheometer from the former Swedish company REOLOGICA at in DRD. Before starting the frequency sweeps, strain sweeps were performed to determine the linear visco-elastic region of the binder. DUT and DRD used two plate sizes depending on the temperature according to Tables 3.1 and 3.2. The DSR value at 25 ºC and 0.4 Hz was recorded to compare with the penetration value.

Table 3.1 Configuration and input parameters of DSR in DUT

Device	Diameter, R [mm]	Temperature [ºC]	Gap, [mm]	Frequency [Hz]
DSR	25	25, 30, 40, 50, 60, 70,	1	0.01 ~ 10
	8	-5, 5, 15, 25, 30	2	0.01 ~ 10

Table 3.2 Configuration and input parameters of DSR at DRD

Device	Diameter, R [mm]	Temperature [ºC]	Gap, [mm]	Frequency [Hz]

DSR	25	30, 40, 50, 60, 70, 80, 90, 100	1	0.01 ~ 10
	8	-5, 5, 15, 25, 30, 35, 40, 45, 50, 55	2	0.01 ~ 10

Both DUT and DRD used the WLF equation (WLF = William, Landel and Ferry) to calculate the shift factors for master curves. The equation is given below:

$$\log a_T = \frac{C_1(T_{measured} - T_{ref})}{C_2 + T_{measured} - T_{ref}} \tag{1}$$

where,

a_T = shift factor at $T_{measured}$,

T_{ref} =reference temperature [ºC],

C_1 =constant [-], and

C_2 =temperature constant [ºC].

Based on the curves of Log G* versus log frequency (measured) the horizontal shift in the frequency is determined in the follow way by DRD:

- The shift factor at the reference temperature of 60 °C is 0 by definition.
- The data points at 60 and 70 °C are fitted together by linear regression in order to determine the horizontal shift (equal to Log a_T) that will bring them to the best fit for a straight line.
- The data points at 80 °C are fitted together with the predetermined line at 60 and 70 °C values to determine the additional shift factor needed to accomplish this.
- This continues until the shift factor at 100 °C is determined.
- The data points at 60 and 50 °C are fitted together by linear regression in order to determine the horizontal shift (equal to Log a_T) that will bring them to the best fit for a straight line.
- The data points for 40 °C are fitted together with the predetermined line of 60 and 50 °C values to determine the additional shift factor needed to accomplish this.
- The next step is then to include the data points at 30 °C in the same way.
- Finally these 8 accumulated shift factors based on a reference temperature of 60 °C are used to determine the constants C_1 and C_2 from the WLF equation by linear regression of the following equation:
  $\log a_T$ (from WLF equation) = $\log a_T$ (determined by measurement)

The shift factors for the "low service temperature" range are determined similarly with a reference temperature equal to 15 °C. Based on the C1 and C2 factors for the WLF equation either at 60 °C and 15 °C as reference temperature, an overall shift factor was determined to shift the two individual parts of the master curve with different reference temperature to the common reference temperature of 25 °C.

DUT used a modified Huet-Sayegh (MHS) model as shown in Figure 3.1 (M.F. Woldekidan, 2011) to construct a master curve. This model is obtained by adding a linear dashpot in series with the original HS model. The data points at all temperatures are fitted together by linear regression in order to determine the horizontal shift factors that will bring them to the best fit to this model at a reference temperature of 25 °C. These shift factors determine the constants C1 and C2 from the WLF equation also by linear regression. Two master curve examples (one for Pen. grade bitumen Q8 and another one for PMB KR) by using this model are given in Figures 3.2 and 3.3. This model can simulate the master curve for the phase angle quite well, also for PMB.

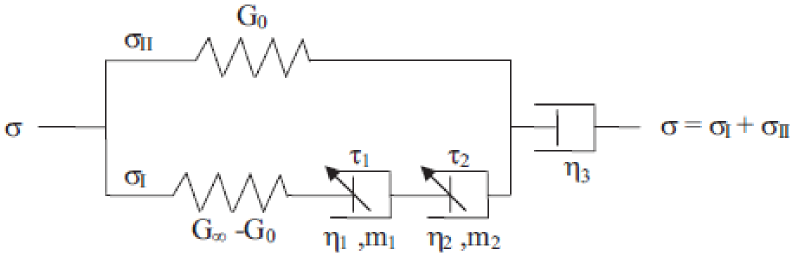


Figure 3.1 Modified Huet-Sayegh (MHS) model (M.F. Woldekidan, 2011)

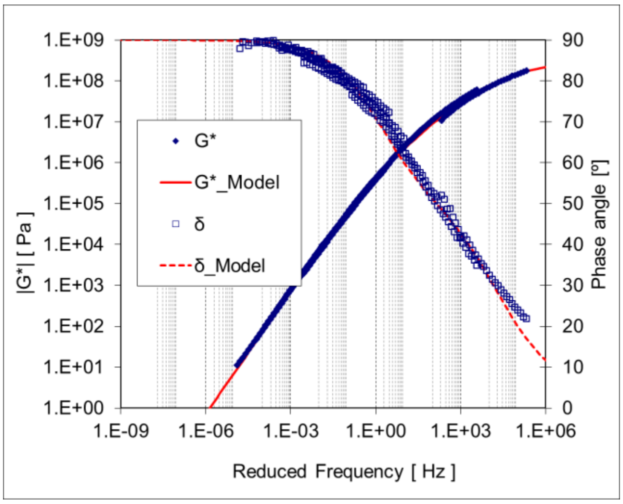


Figure 3.2 Master curves of Pen. grade bitumen Q8 and its MHS model

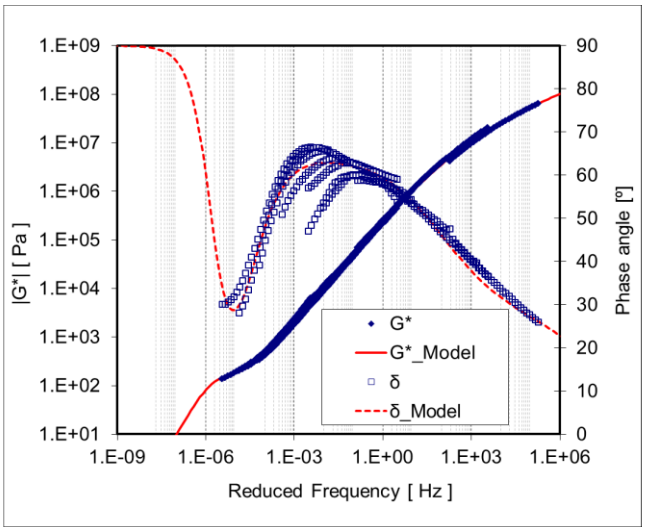


Figure 3.3 Master curves of PMB KR and its MHS model

3.2.3 Viscosity at high temperature

Two methods are used:

- cone and plate viscosity measurements including strain rate sweeps by DUT

- Brookfield rotational co-axial viscosity measurements by DRD

With respect to these two methods, the viscosity needs to be determined at 135 °C, 150°C and 180°C. According to the EU specification [EN 13702], DUT adopted a shear rate of 500 s^{-1} to characterize the viscosity at these three temperatures by using a cone/plate set-up on the DSR. The cone angle is 1°, and the plate diameter is 25 mm. At 150 °C a shear rate sweep (from 0.1 s^{-1} to 500 s^{-1}) was performed with the cone and plate configuration. The Brookfield viscosity values can be compared with the cone and plate viscosities.

3.2.4 Chemical characterization: GPC and FTIR

Gel Permeation Chromatography (GPC) is used to analyse the molecular weight distribution of (polymer modified) bitumen samples. GPC is a chromatographic method in which molecules are separated based on their size. The system used to analyse the samples consists of an auto-sampler, a photodiode array detector (PDA), a column-box, pump and other units. The detector is connected to the system to provide information regarding the concentration and molecular weight of the sample. A standard testing procedure (TNO, Moleculaire Gewichtsverdeling van bitumen (GPC), versie 3, 27-02-2012, in Dutch) is used for analysing the samples. The GPC test conditions are summarized in Table 3.3.

Table 3.3 GPC test conditions

Component	Bitumen
Mobile phase	Tetrahydrofuran (THF)
Solvent (sample preparation)	THF (30 minutes, 100 rpm @ room temperature)
Sample concentration	30 ± 3 mg / 25 ml
Injection volume	50 µl
Flow rate	1,5 ml/min
Test temperature	35 °C
Detector	PDA
Columns	Shodex KF 802; KF 802,5; KF 803 and KF 805
Calibration standards	Polystyrene

To determine the molecular weight of the bitumen samples, calibration standards of polystyrene were used. These standards have a known molecular weight. The retention time (the time at which the peak of a component is detected) of the polystyrene peaks were used to make a calibration curve. The calibration curve relates retention times to known molecular weights. Based on the calibration curve the molecular weight of the bitumen samples has been determined.

The molecular weight values Mn (number average), Mw (weight average), Mz (z-average) and Mz+1 (z+1 average) were determined for the bitumen samples. Mn gives information about the smaller molecules in the samples, whereas Mw, Mz and Mz+1 give information about the larger molecules (see Figure 3.4).

Due to the ageing process of bitumen in general larger molecules will be formed, caused by polymerization and oxidation of different bitumen components. However the polymer component in PMB (specific with SBS) can also degrade during ageing. In general an increase of Mw, Mz and Mz+1 is expected for the bitumen component due to ageing. The indicators can be used to show differences between the bituminous binders and/or as an indicator for the final mixing result in this study.

The GPC curve of bitumen can be treated as a one peak integration. With this integration method no separation has been made for the bitumen and polymer component. Integration has been performed on the “merged” polymer bitumen peak as one peak integration. To determine the molecular weight of the bitumen component and the polymer component full separation of the two components is desirable. However an example given from another project in Figure 3.5 shows for the mixed samples and the reclaimed asphalt samples an overlap between the bitumen component and the polymer component. Then the GPC curve can be treated as a 2 peak integration (polymer plus bitumen). Based on the reference sample a separation between the two components can then be made. The separation of the polymer and the bitumen component is based on the retention time at which the bitumen peak of the reference sample starts. An example is given in Figure 3.6, which is from another project conducted by TNO.

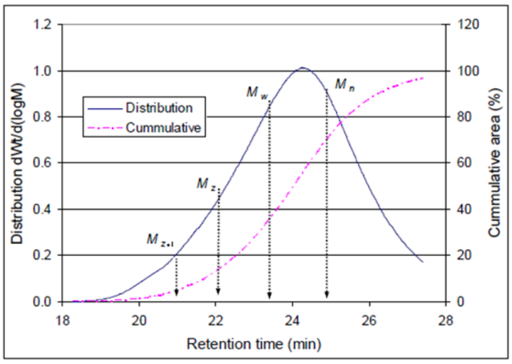


Figure 3.4 Example of the molecular weight distribution of bitumen

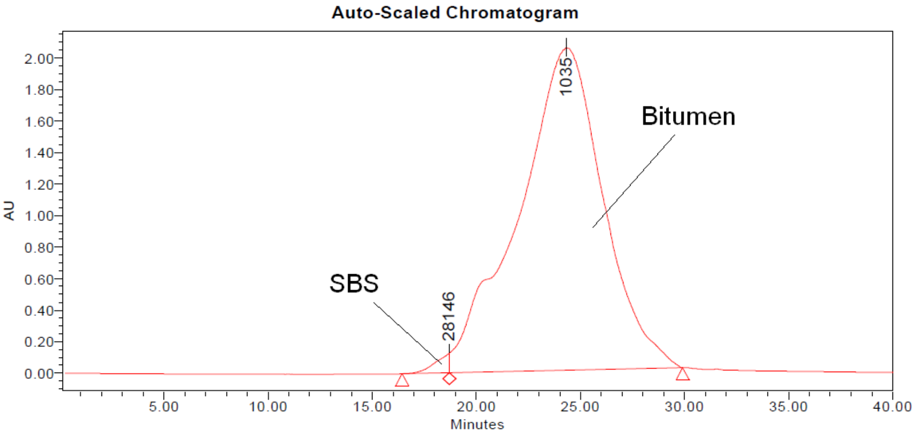


Figure 3.5 Overlap polymer and bitumen component

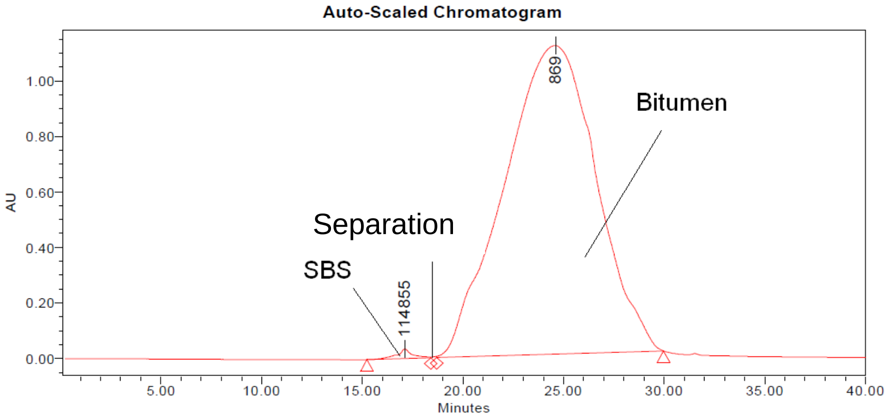


Figure 3.6 Separation based on the reference sample

The Fourier Transform Infrared (FTIR) spectroscopy is a technique used to identify functional groups in organic compounds at molecular level. Infrared (IR) spectra can indicate the existence or absence of chemical functional groups. This is useful especially in characterizing the formation of aging products in bitumen. The PerkinElmer Spectrum 100 FT-IR Spectrometer was used by DUT in the attenuated total reflectance (ATR) mode. The measurement was conducted in the mid-infrared region (600-4000 cm-1) through a thickness of around 5 µm on the bitumen surface. An absorption spectrum diagram was obtained after Fourier transformation using the available computer program.

In the FTIR spectrum of bitumen, the ethylene groups (CH_2) at 1460 cm^{-1} and methyl groups (CH_3) at 1375 cm^{-1} are believed to be very stable and during ageing. Two oxidation groups, the ketones C=O around 1700 cm^{-1} and sulfoxides S=O around 1030 cm^{-1}, are the most important indicators to evaluate ageing in time. For the modified bituminous binders, the existence of SBS in the binder can be evaluated according to its well-known two absorbing peaks at 966 cm^{-1} and 698 cm^{-1}.

For this research, three indices ICO, ISO, and ISBS were used for a qualitative study on the effect of recycling and they are defined as:

$$\text{ICO}=\frac{\text{Area around 1700 cm}^{-1}}{\text{Area around 1460 cm}^{-1}+\text{Area around 1375 cm}^{-1}} \tag{2}$$

$$\text{ISO}=\frac{\text{Area around 1030 cm}^{-1}}{\text{Area around 1460 cm}^{-1}+\text{Area around 1375 cm}^{-1}} \tag{3}$$

$$\text{ISBS}=\frac{\text{Area around 966 cm}^{-1}+\text{Area around 698 cm}^{-1}}{\text{Area around 1460 cm}^{-1}+\text{Area around 1375 cm}^{-1}} \tag{4}$$

For the calculation of the band areas, the positions of the vertical limits are shown in Table 3.4. The baseline position is defined by intersections of the curve with the respective vertical limits.

Table 3.4 Band area in FTIR spectrum for functional groups

Functional group	SBS		C=O	S=O	CH_2	CH_3
Band ID	Area 698 cm^{-1}	Area 966 cm^{-1}	Area 1700 cm^{-1}	Area 1030 cm^{-1}	Area 1460 cm^{-1}	Area 1375 cm^{-1}
Base line and vertical limit wave numbers [cm^{-1}]	692-712	956-980	1660-1753	1047-994	1400-1525	1350-1390

4 Results and discussion

This chapter presents the test results of RA binders, fresh binders and their blends for the rheological properties by penetration, softening point, viscosity, dynamic response (DSR) and for the chemical characterization with GPC and FTIR. Some discussion based on the results is also given in this chapter.

4.1 Penetration and softening point

4.1.1 Test results

Figures 4.1-4.3 show the penetration (Pen.) results for six binder groups. From RA binders, RAN has the lowest penetration (11 dmm), RAD the highest (35 dmm) and the RAS penetration (22 dmm) is in between. After mixing with virgin Q8 and KR, the penetration of RAN and RAS increases gradually with the increase of virgin binder content (Figures 4.1 and 4.2). The penetration of 40%RAN+Q8 (31 dmm) is still very low and does not satisfy the design value for the mixture. Virgin binders 70/100 and 90/150 used by DRD are softer than Q8 and KR used by DUT. For example 15%RAD+70/100 has the same Pen. value (78 dmm) as the virgin binder from Q8.

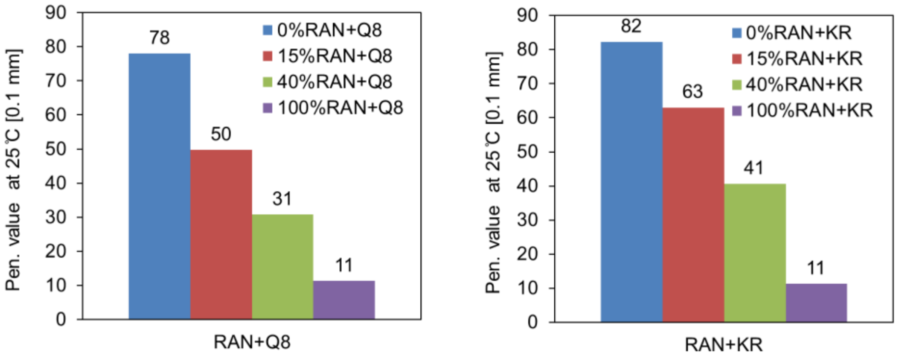


Figure 4.1 Penetration values at 25 °C for binder groups of RAN+Q8 (left) and RAN+KR (right)

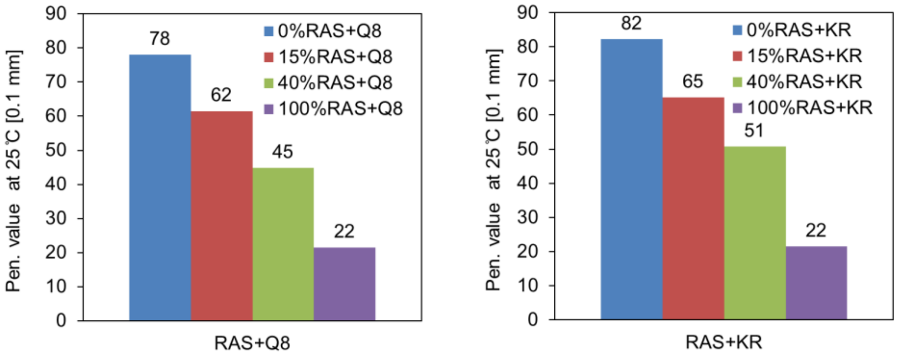


Figure 4.2 Penetration values at 25 °C for binder groups of RAS+Q8 (left) and RAS+KR (right) (*same)*

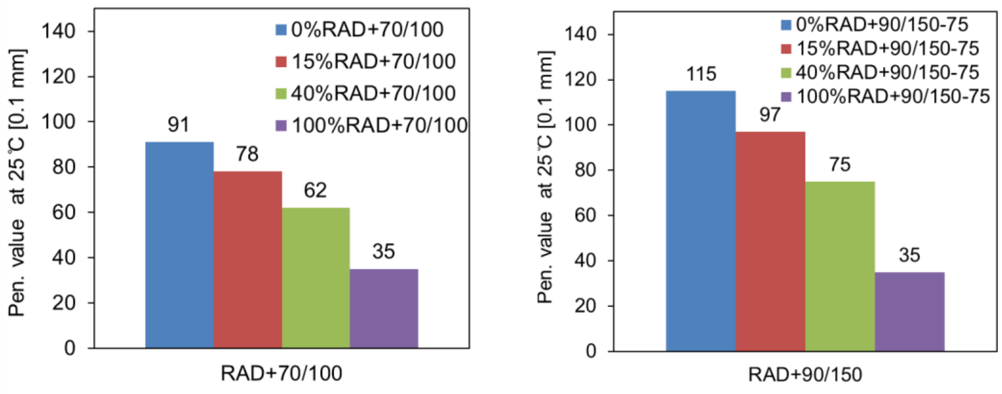


Figure 4.3 Penetration values at 25 °C for binder groups of RAD+70/100 (left) and RAD+90/150-75 (right)

To compare how the virgin binder influences the penetration of RA binder, a penetration increase rate for RA is defined as:

$$\text{RA Pen. increase rate}=\frac{\text{Pen.}_{\text{blended}}-\text{Pen.}_{\text{RA}}}{\text{Pen.}_{\text{RA}}} \qquad (5)$$

Following this definition, the influence of the virgin binder on the RA penetration is quantified and the results are shown in Figures 4.4 and 4.5.

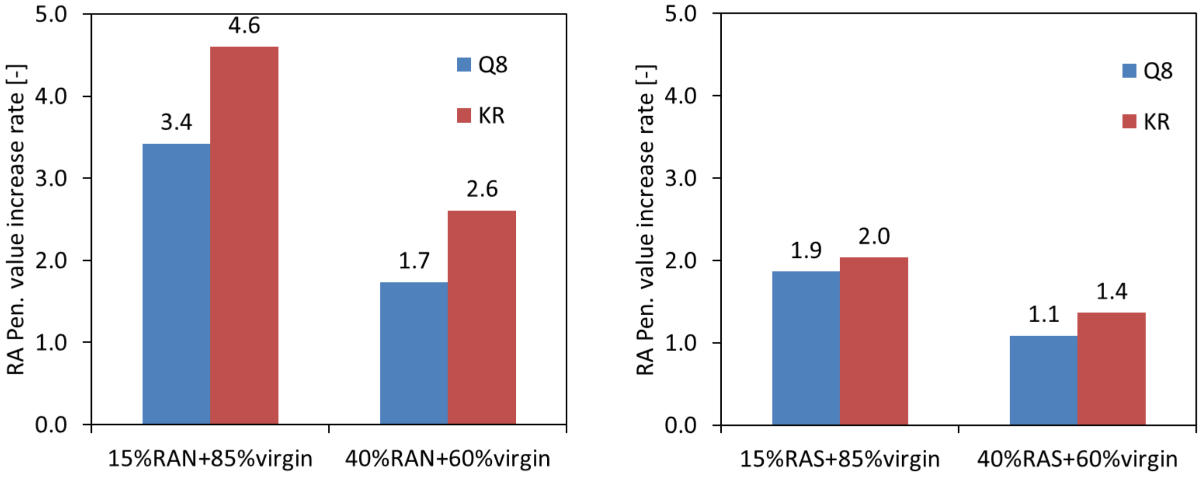


Figure 4.4 Influence of virgin binder Q8 and KR on the Pen. value of RAN (left) and RAS (right)

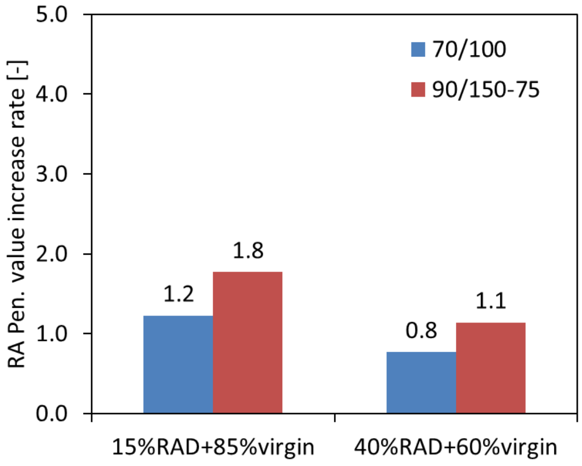


Figure 4.5 Influence of virgin binder 70/100 and 90/150-75 on the Pen. value of RAD at 15% RA content and 40% RA content

For the same content of virgin binder mixed in, RAN and RAS show different changes in Penetration values. For example, the Pen. value of RAN is more influenced by virgin Q8 and KR than the Pen. value of RAS by its virgin additions, at both RA contents of 15% and 40% (Figure 4.4). When comparing the influence of the two virgin binders, KR has a larger influence on the Pen. value of RAN, with increase rates of 4.6 and 2.6 at 15% and 40% RA content, respectively although it has a comparable penetration with Q8 (82 versus 78) . The reason could be better compatibility between KR and RAN than the Q8 binder. On the other hand, these two virgin binders have almost a similar influence on the RAS. At the same RA content, the penetrations of RAD+90/150-75 are higher than of RAD+70/100 (Figure 4.5). In this case, the higher Pen. value of virgin 90/150-75 can be a main reason.

Figures 4.6 to 4.8 show the softening point (S.P.) values for the six binder groups. In order to obtain correlations as precise as possible the softening point values were not rounded off in accordance with EN 1427 (nearest 0.2 °C in water below 80 °C and nearest 0.5 °C in glycerine above 80 °C). Mixing with virgin Pen. grade binder will result in a decrease of the S.P. of RA. However, the S.P. of RA will increase when mixed with virgin PMB due to the high S.P. of the virgin PMB. An exception to these expectations is the S.P. from the RAN+KR binder group, because RAN and KR have a similar S.P. value separately.

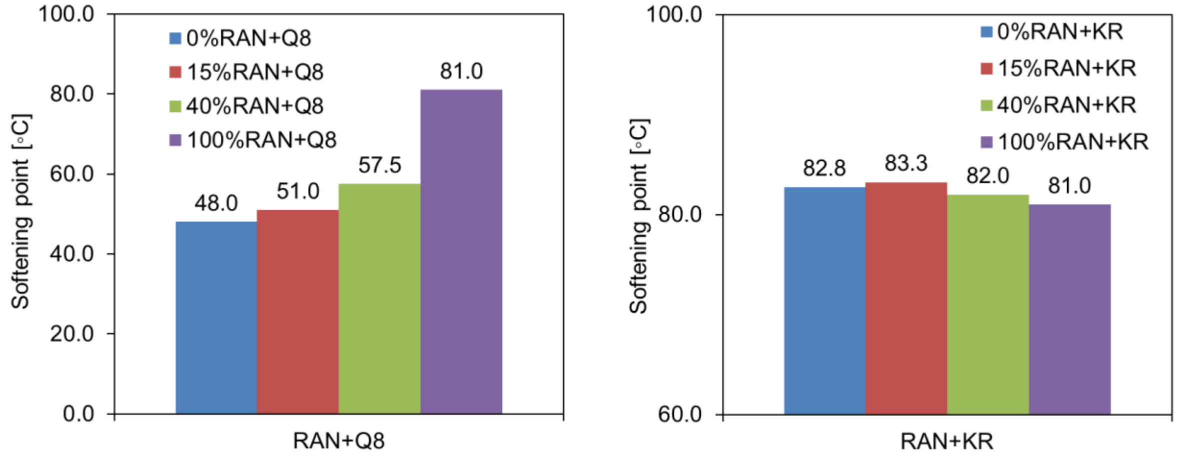


Figure 4.6 Softening point for binder groups of RAN+Q8 (left) and RAN+KR (right)

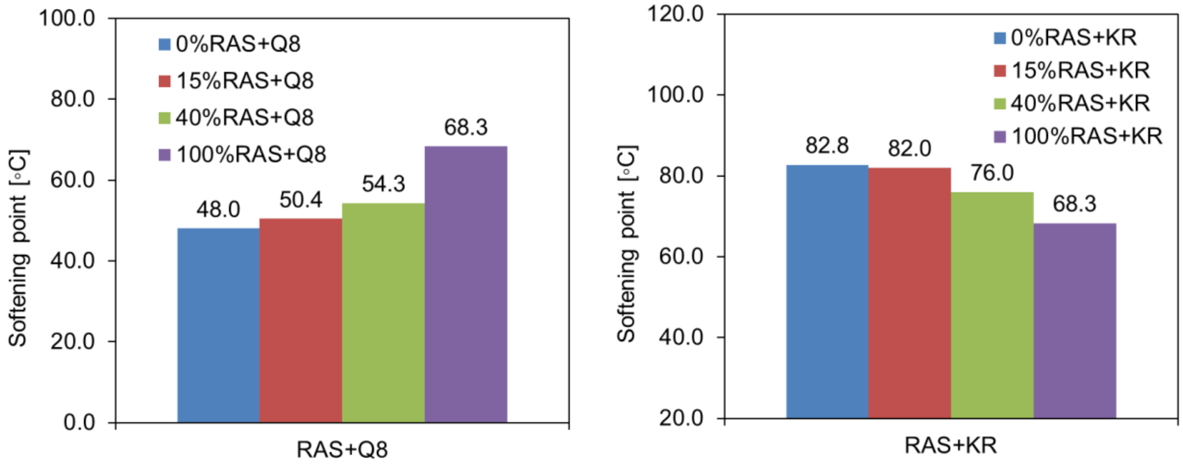


Figure 4.7 Softening point for binder groups of RAS+Q8 (left) and RAS+KR (right)

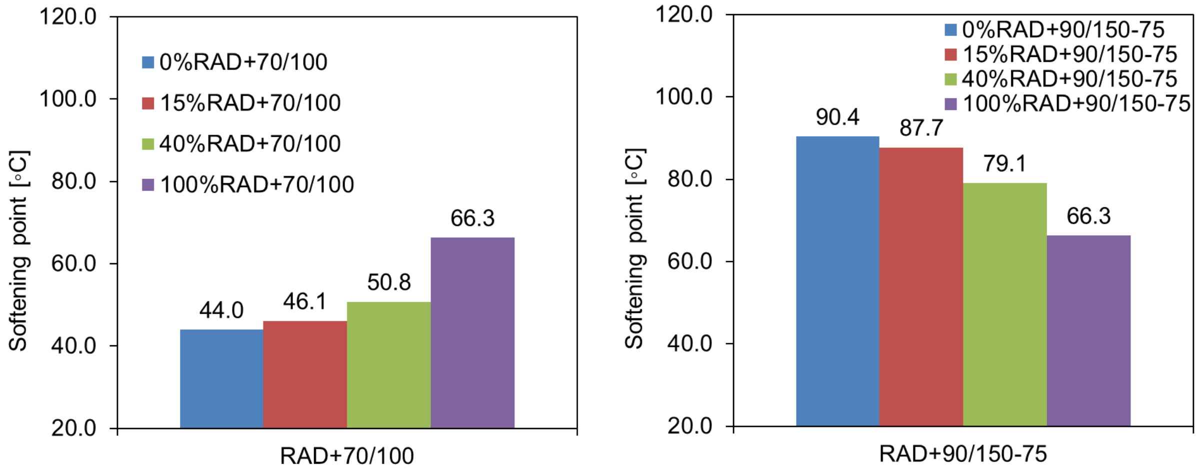


Figure 4.8 Softening point for binder groups of RAD+70/100 (left) and RAD+90/150-75 (right)

From the penetration and S.P. results, the penetration index (I_p) can be determined with the formula:

$$I_p = \frac{1952 - 500\log Pen. - 20 S.P.}{50\log Pen. - S.P. - 120} \qquad (6)$$

The I_p gives an indication of the temperature susceptibility and is normally only used for Pen. grade bitumens. The I_p value can vary between -3 (very temperature susceptible) and +7 (almost no temperature susceptibility). For the interpretation of the results it should be realized that this parameter is normally not used for PMB. As shown in Figure 4.9, the I_p value of the RA binder decreases when mixed with soft Pen. grade binder; however it is the other way around by mixing with PMB. It indicates that the addition of virgin Pen. grade binder can increase the temperature susceptibility of RA.

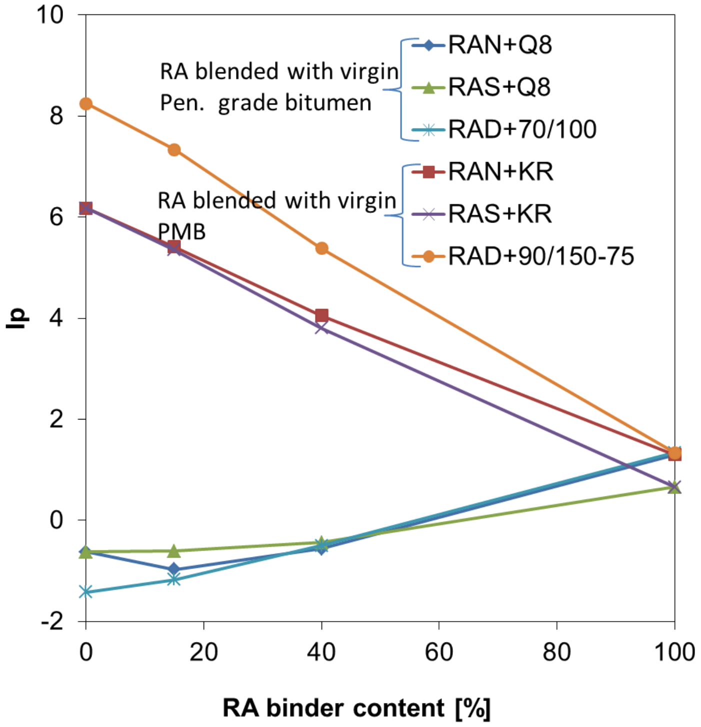


Figure 4.9 Penetration index (Ip) of six binder groups as function of RA content and the virgin binder type

4.1.2 Modeling

In EN 13108-7 the logPen. model and the linear S.P. model are given to predict the Pen. value and S.P. value of binder mixed with RA. These formulas are in principle given for standard penetration grade bitumen. The formulas are:

$$\log Pen_{mix} = a \log Pen_{1} + b\,l \tag{7}$$

$$T_{S.P.mix} = a \times T_{S.P.1} + b \times T_{S} \tag{8}$$

where,

Pen_{mix}	is the calculated penetration of the binder in the mixture containing reclaimed asphalt;
Pen_1	is the penetration of the binder recovered from the reclaimed asphalt;
Pen_2	is the penetration of the added binder;
$T_{S.P.mix}$	is the calculated softening point of the binder in the mixture containing reclaimed asphalt;
$T_{S.P.}$	is the softening point of the binder recovered from the reclaimed asphalt;
$T_{S.P.}$	is the softening point of the added binder;
a and b	are the portions by mass of binder from the reclaimed asphalt (a) and from the added binder (b) in the mixture; $a + b = 1$.

Normally, these two models are applied when RA binder and virgin binder are Pen. grade bitumen. However, it is suggested that these models cannot be applied to predict the properties of the blended binder when a PMB is involved in the RA and/or the added binder. In this study, the possible use of these models when PMB is involved will be investigated.

Figures 4.10 and 4.11 show the comparison of test results and simulation by using the logPen. model and the S.P. model at different RA contents. Note that the exact RAD content is used in the calculations by using the models. As shown, the test results are more close to the simulated value obtained by using the logPen. than by using the S.P. model. A special problem that originates from the softening point determination itself in EN 1427 can be seen in the bottom-right subfigure of figure 4.11. There seems to be a rather large deviation between the linear model and the determined value. But the softening points for 0 % and ~15 % RAD are determined in glycerine while the 40 % RAD (with a value of 79.1 °C) is determined in water. If the determination of the 40% RAD was performed in glycerine this could very well lift the determined value closer to the line of the model. The higher correlation coefficients in Figure 4.10 also show this. However, it is difficult to conclude that the logPen. model is more suitable to predict rheological properties of blended binders than the S.P.model because it is based on a logarithmic scale and the S.P. model on a linear scale. In this study, the logPen. model becomes more acceptable when the S.P. values between RA and virgin binder are very close, such as in RAN+KR binder group.

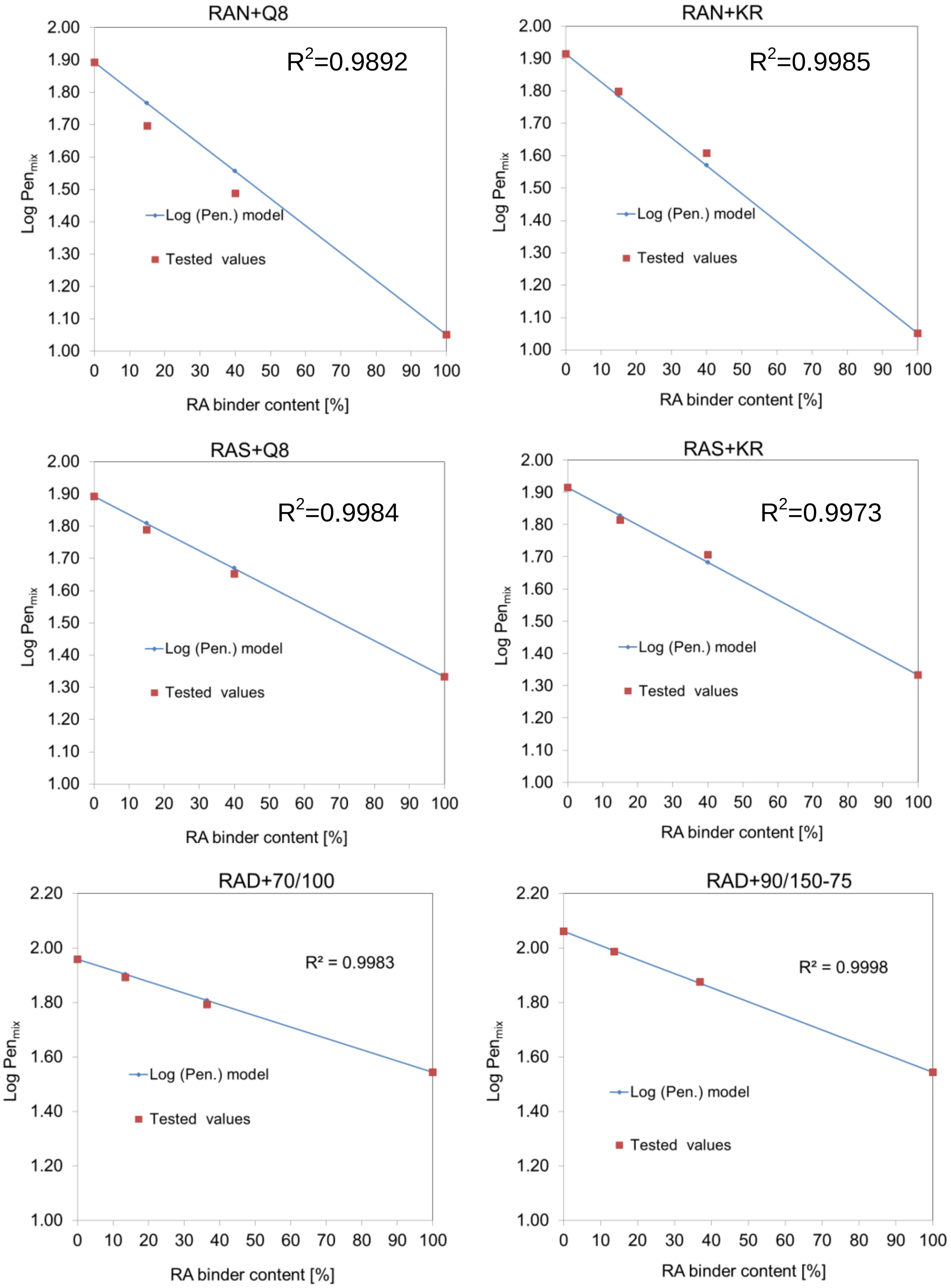


Figure 4.10 Relation between Pen. value at 25 ºC and RA binder content for six binder groups

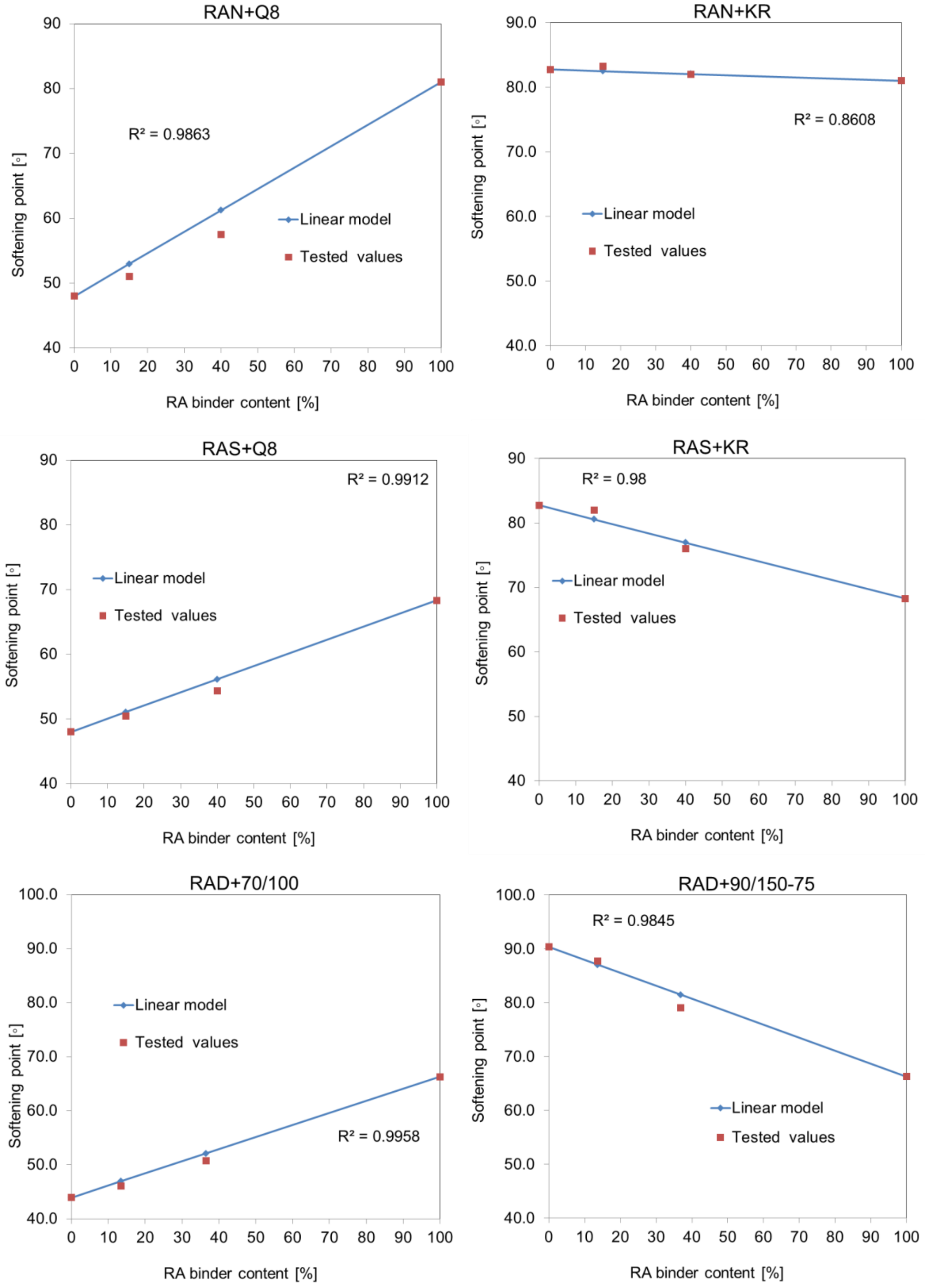


Figure 4.11 Relation between S.P. value and RA binder content for six binder groups

4.2 *Viscosity*

4.2.1 Viscosity results

Figures 4.12 and 4.13 show the viscosity results at a shear rate of 500/s for four binder groups (RAN+Q8, RAN+KR, RAS+Q8 and RAS+KR) at 135ºC, 150 ºC and 180 ºC measured with the cone/plate rheometer. The viscosity for all binders decreases with the increase of temperature. Especially RA binders show a sharp decline in viscosity with the change of temperature. They also have a higher viscosity at each temperature. From the virgin binders, PMB KR has a higher viscosity than the Q8 Pen. grade bitumen. After mixing, the viscosity of the blended binder is between those of the RA and the virgin binder and gradually becomes very close to the viscosity of the virgin binder as the temperature increases to 180 ºC.

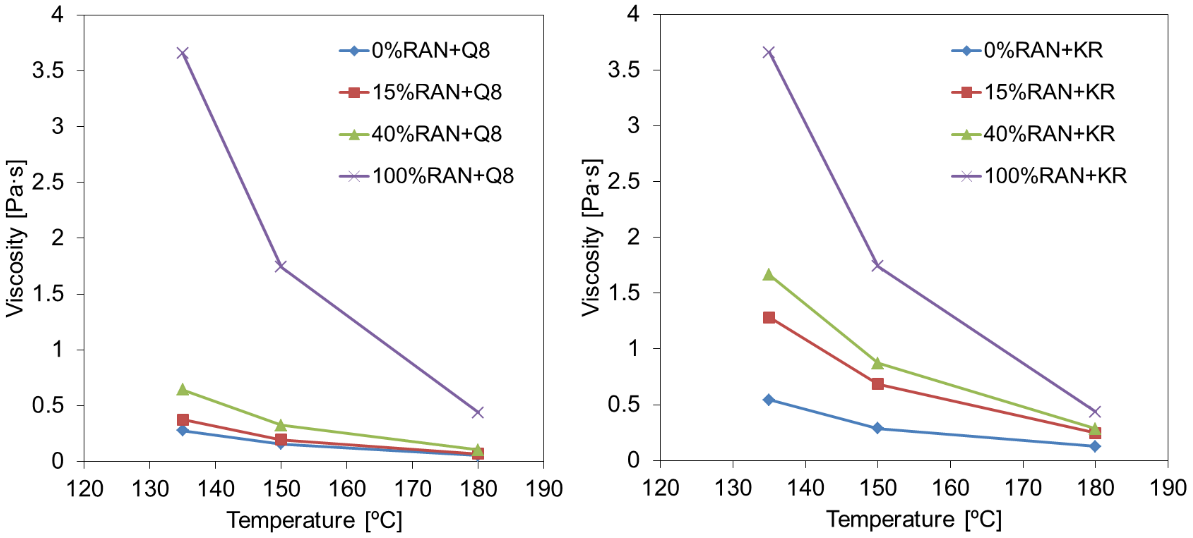


Figure 4.12 Viscosities at a shear rate 500/s and at three temperatures for binder groups of RAN+Q8 (left) and RAN+KR (right), measured with the cone/plate rheometer

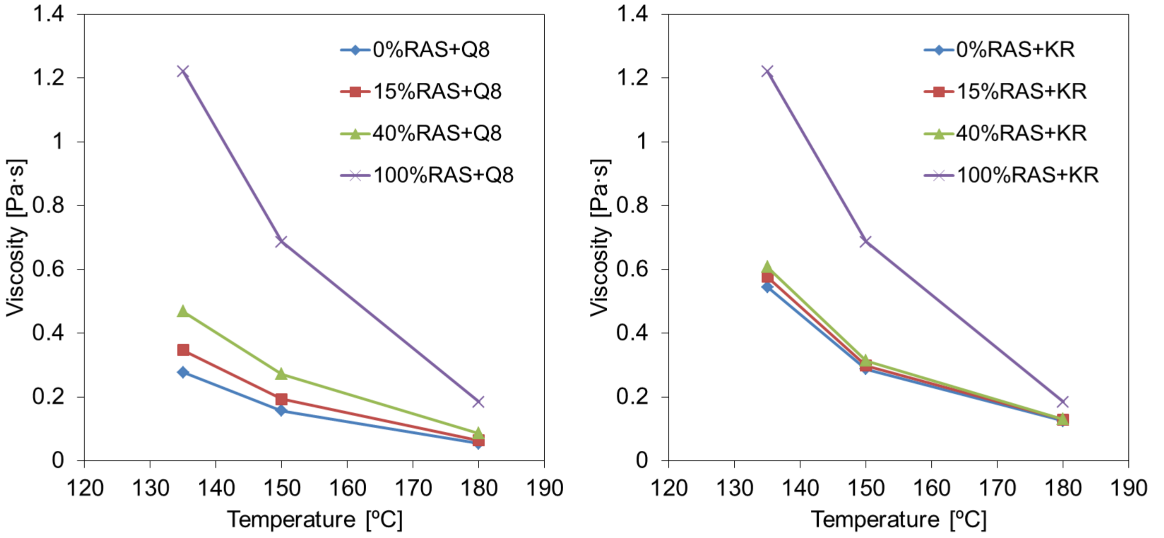


Figure 4.13 Viscosities at a shear rate 500/s and at three temperatures for binder groups of RAS+Q8 (left) and RAS+KR (right), measured with the cone/plate rheometer

Figure 4.14 shows the viscosity of two binder groups from DRD measured with the Brookfield rheometer. The trend of the viscosity for these two groups is very similar to the trend seen from the cone/plate rheometer results in Figures 4.12 and 4.13. The tests results from the two methods are comparable. It indicates that these two methods are both suitable to characterize the viscosity of RA, virgin and blended binders.

Based on the viscosity results, the laboratory mixing and compaction temperatures are recommended for WP4 and given in Table 4.1, within a viscosity range of 0.15 to 0.19 Pa.s and 0.25 to 0.31 Pa.s, respectively, for mixing and compaction. As shown, mixing temperatures of some binders are higher than 180 °C due to that the viscosity at 180 °C is a little bit out of the recommended range. In this case, mixing temperature of 180 °C is still recommended to avoid ageing of the virgin binder.

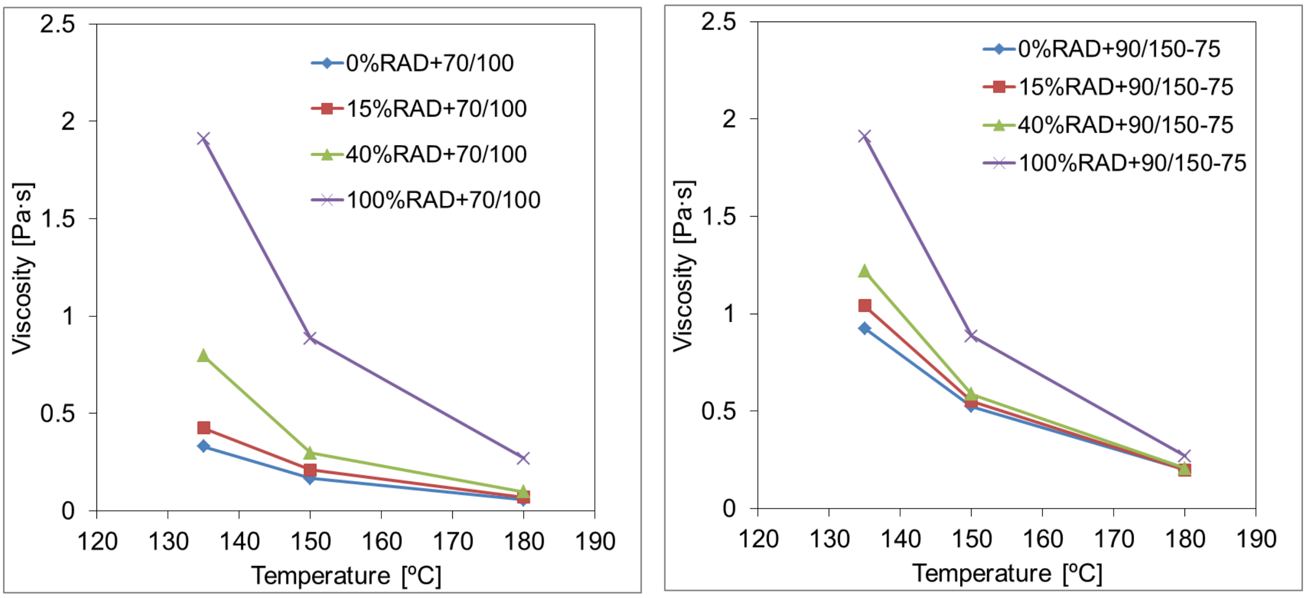


Figure 4.14 Viscosities at three temperatures for binder groups of RAD+70/100 (left) and RAD+90/150-75 (right), measured by using Brookfield rheometer

Table 4.1 Mixing and compaction temperatures recommended for WP4

	Mixing Temperature [°C]		Compaction Temperature [°C]	
Binders	Max. (0.15 Pa.s)	Min. (0.19 Pa.s)	Max. (0.25 Pa.s)	Min. (0.31 Pa.s)
Q8	155	145	140	130
15%RAN+Q8	160	150	145	140
40%RAN+Q8	175	170	160	150
KR	175	170	160	150
15%RAN+KR	>180	>180	180	175
40%RAN+KR	>180	>180	185	178
15%RAS+Q8	160	150	145	140
40%RAS+Q8	170	165	155	145
15%RAS+KR	175	170	160	150
40%RAS+KR	175	170	160	150
70/100	155	145	145	135
15%RAD+70/100	165	155	147	143
40%RAD+70/100	175	165	158	150
90/150-75	>180	>180	175	170
15%RAD+90/150-75	>180	>180	175	170
40%RAD+90/150-75	>180	>180	177	172

4.2.2 Mixing law for viscosity using the Grunberg-Nissan model

Arrhenius proposed the following expression for the viscosity of a solution:

$$\log \eta_{mix} = a \log \eta_1 + b \log \eta_2 \tag{9}$$

where, η_{mix} is the viscosity of the solution; η_1 and η_2 are the viscosity of the two components. This equation is similar to the logPen equation.

Grunberg and Nissan (1949) found that both positive and negative deviations from thee Arrhenius model could occur, and thus they improved the model to:

$$\log \eta_{mix} = a \log \eta_1 + b \log \eta_2 + a \cdot b \cdot d, \tag{10}$$

where, d is a characteristic constant of the system.

Through linear regression with the Grunberg-Nissan model, we obtained parameter d for six binder groups at three temperatures (see Table 4.2). R^2 in Table 4.2 indicates that the data fit this model very well. An example for RAD+70/100 is given in Figure 4.15.

Table 4.2 Parameter d in the Grunberg-Nissan model to describe the viscosity

Binder group	135 ºC		150 ºc		180 ºC	
	d	R^2	d	R^2	d	R^2
RAN+Q8	-0.346	1.0000	-0.424	0.9999	-0.341	0.9999
RAN+KR	0.643	0.9468	0.705	0.9366	0.587	0.9150
RAS+Q8	-0.122	0.9993	-0.070	1.0000	-0.031	1.0000
RAS+KR	-0.387	0.9962	-0.470	0.9974	-0.210	0.9915
RAD+70/100	0.431	0.9960	-0.075	0.9996	-0.071	0.9996
RAD+90/150-75	0.016	0.9995	-0.146	0.9987	-0.147	0.9997

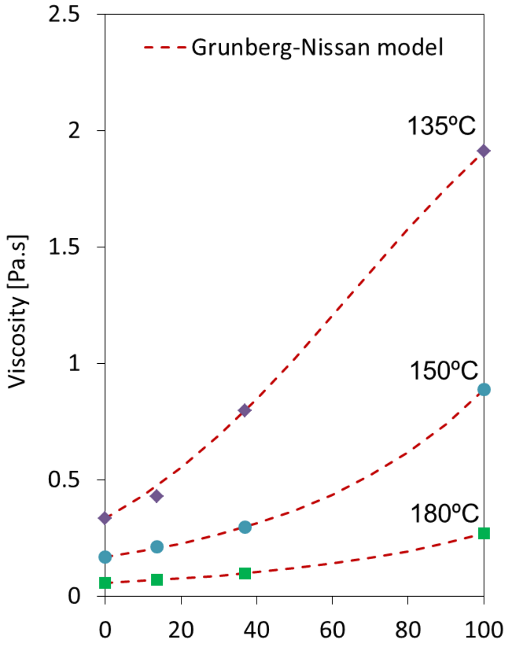


Figure 4.15 Relation between RA content and viscosity, an example for RAD+70/100 binder

A positive d value implies that a blended binder is more viscous than predicted by the Arrhenius model, and the other way around. In Table 4.2, the d values are negative for most cases,. It indicates that the viscosity of the blended binder is lower than the values obtained through the Arrhenius model. It means that the virgin binder dominates this property. An exception is the RAN+KR binder group in which d values at three temperatures are positive. The reason can be that the RAN binder which is the most viscous influences the blended binder more. Also the testing temperature can influence the d value. For binder groups of RAN+70/100 and RAN+90/150-75, d values change from negative at 135 °C to positive at 150 °C and 180 °C. In these cases the fresh binder can dominate the viscosity of the blended binder system, especially at a higher temperature.

4.2.3 Shear rate sweep at 150 ºC

To fundamentally understand the rheological properties of binders, a shear rate sweep was performed at 150 ºC with the cone/plate rheometer and the results are shown in Figures 4.16 and 4.17. As shown in the left side of Figure 4.16, three binders 0%RAN+Q8 (pure Q8), 15%RAN+Q8 and 40%RAN+Q8 behave practically like a Newtonian liquid because the viscosity is independent of the shear rate; however, the viscosity of 100%RAN+Q8 (pure RAN) decreases continuously by increasing the shear rate from 0.1 and 500 s-1, which means its viscosity is shear rate dependent. 0%RAN+KR (pure KR) also shows a shear thinning behaviour at low shear rates and gradually reaches a Newtonian liquid at a shear rate of about 10 s-1 (the right side of Figure 4.16). SBS modified bitumen often shows shear thinning behaviour due to the orientation effect of SBS molecules. For 15%RAN+KR and 40% RAN+KR, this behaviour can still be observed, but much less pronounced than for the pure KR binder. The reason could be that the preparation process with high shear mixing decreases the phase size of SBS and makes it easier to orient when applied with a shear rate. As an RA-PMB binder, pure RAS (100%RAS+Q8) did not display this behaviour (the left side of Figure 4.17). It could be due to the complete degradation of SBS in RAS. Besides 100%RAS+Q8, other binders in this group also behave like a Newtonian liquid. For 15%RAS+KR binder as shown in the right of Figure 4.17, shear thinning behaviour can still be observed at the low shear rate range due to the high KR content (85%). A higher viscosity at low shear rates indicates better drainage resistance of the bitumen. Therefore, the addition of virgin SBS modified bitumen can improve drainage behaviour of new mixture with RA mixture, a feature especially important for porous asphalt and stone mastic asphalt.

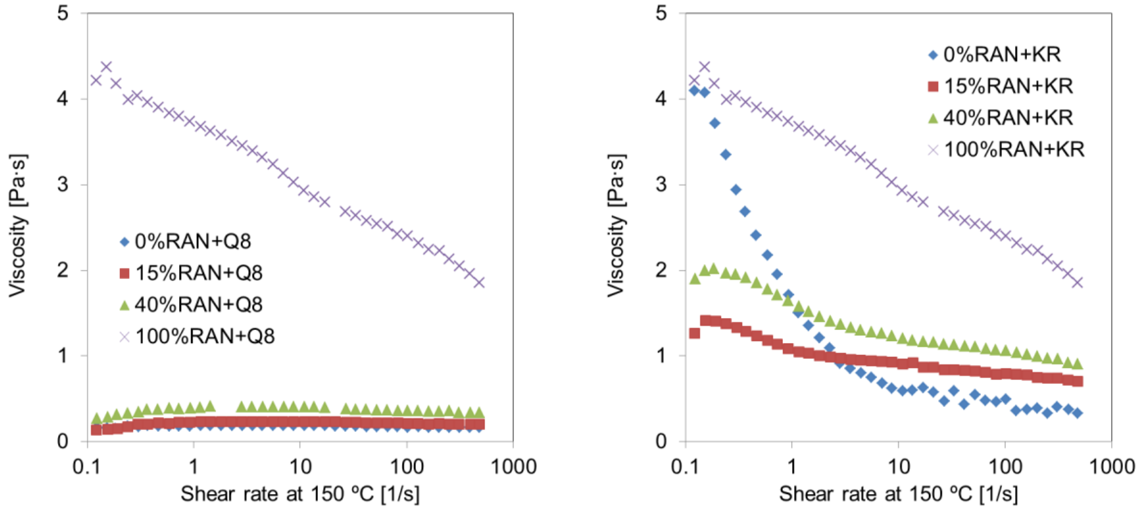


Figure 4.16 Viscosity at 150 ºC as function of the shear rate measured with the cone/plate rheometer, for binder groups of RAN+Q8 (left) and RAN+KR (right)

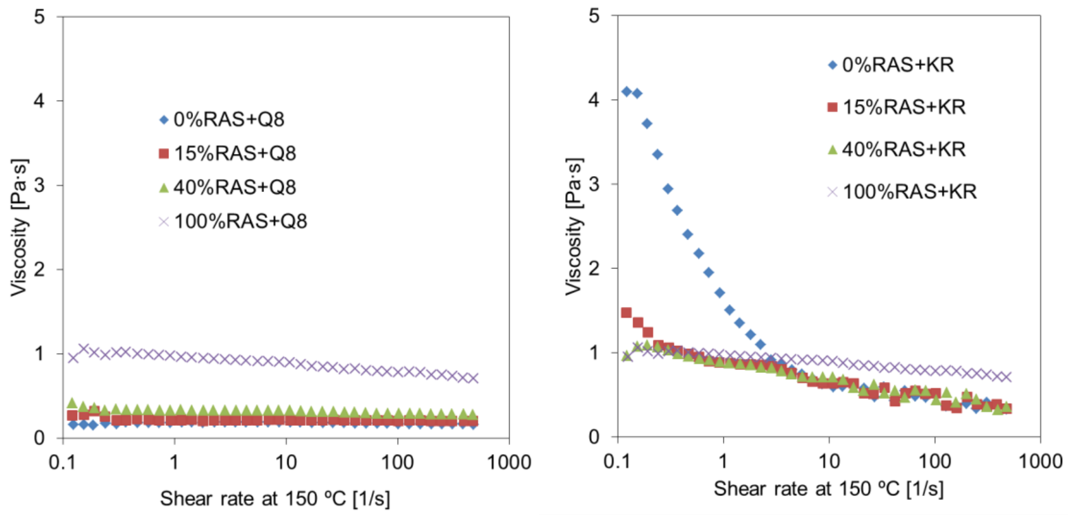


Figure 4.17 Viscosity at 150 ºC as function of the shear rate measured with the cone/plate rheometer, for binder groups of RAS+Q8 (left) and RAS+KR (right)

4.3 DSR

4.3.1 Master curves

Figures 4.18 and 4.19 show master curves of the complex shear modulus (G*) and phase angle (δ) at a reference temperature of 25 °C for RAN+Q8 and RAN+KR binder groups. Pure RAN has a higher G* and a lower δ than other binders at the same reduced frequency. Some influence of the SBS modification on this binder can still be observed from the phase angle plateau at a frequency range between 10^{-1}-10^{-4} Hz. Compared with the RA binder, the virgin Q8 (0%RAN+Q8) binder is less stiff (Figure 4.18). For example, there is a more than 2 orders of magnitude difference in G* at a low frequency (around 10^{-5} Hz) between them. After blending, 15%RAN+Q8 behaves still like a Pen. grade bitumen, with a relatively higher G* and lower δ than Q8. With respect to 40%RAN+Q8, a remarkable influence of the SBS modification in the RAN can still be observed on the master curve of the phase angle (δ).

In the RAN+KR group, virgin KR (with 10% SBS content) behaves as a typical polymer modified binder (Figure 4.19). It has a higher δ above the frequency of 10^{-1}Hz, but a sharp decline in δ at reduced frequencies lower than 10^{-2} Hz. These characteristics indicate a good resistance of the binder to high-temperature permanent deformation. After blending, 15%RAN+KR exhibits a very similar G* master curve to the pure KR, but a small change in δ can be observed. For 40%RAN+KR, the master curves, especially for the phase angle, are more similar to pure RAN. This indicates that the RAN binder starts to dominate the rheological properties of the blended binder at a higher RA content as far as can be measured with master curves.

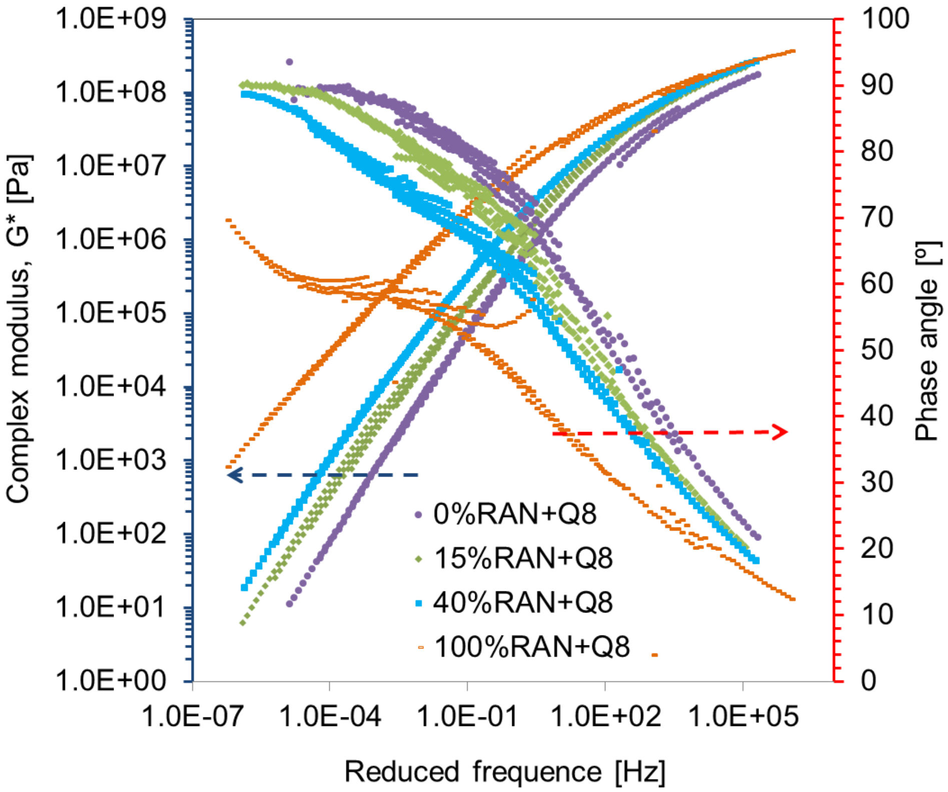


Figure 4.18 Master curves of the complex shear modulus and phase angle for binders in the RAN+Q8 group at a reference temperature of 25 °C

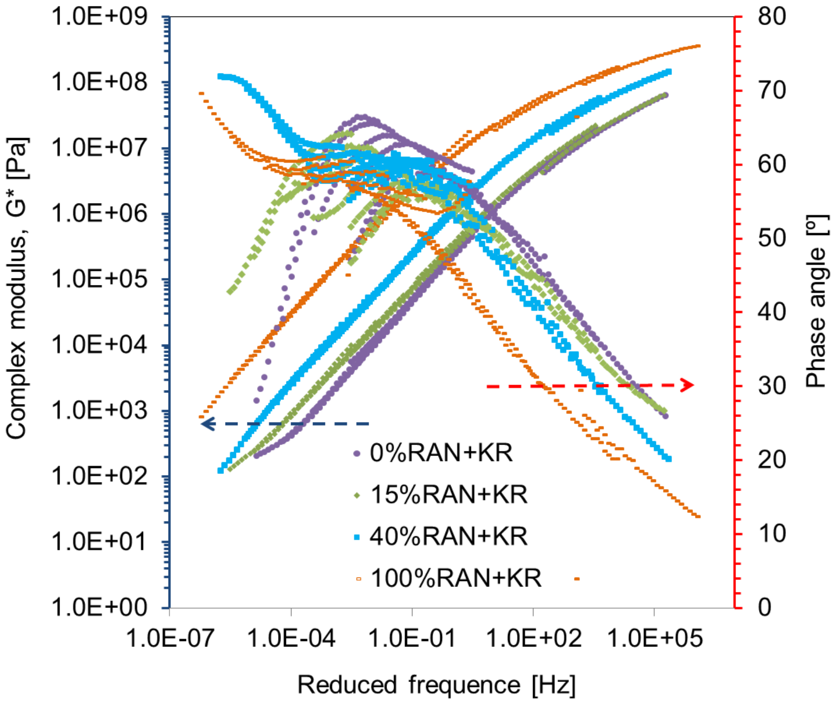


Figure 4.19 Master curves of the complex modulus and phase angle for binders in the RAN+KR group at a reference temperature of 25 °C

According to the master curves shown in Figure 4.20, pure RAS (100%RAS+Q8) does still marginally show the influence of the SBS modification in the master curve of the phase angle. The same trend was also found for the viscosity at 150 °C when applied with a shear rate sweep as shown in Figure 4.17. It seems that the virgin Q8 dominates the properties of the blended binder even at a high RA content of 40%. After blending with KR binder, there is a clear transition for the phase angle from 0%RAS+KR to 40%RAS+KR, and a very close G* between these three binders (Figure 4.21). Based on the master curve results, it can be concluded that the rheological properties of the RAS can be easily influenced by the soft virgin binder.

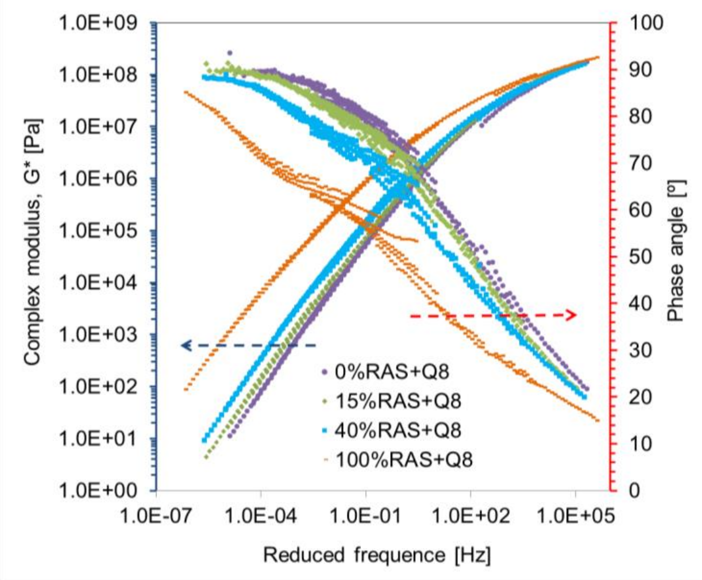


Figure 4.20 Master curves of the complex shear modulus and phase angle for binders in the RAS+Q8 group at a reference temperature of 25 °C

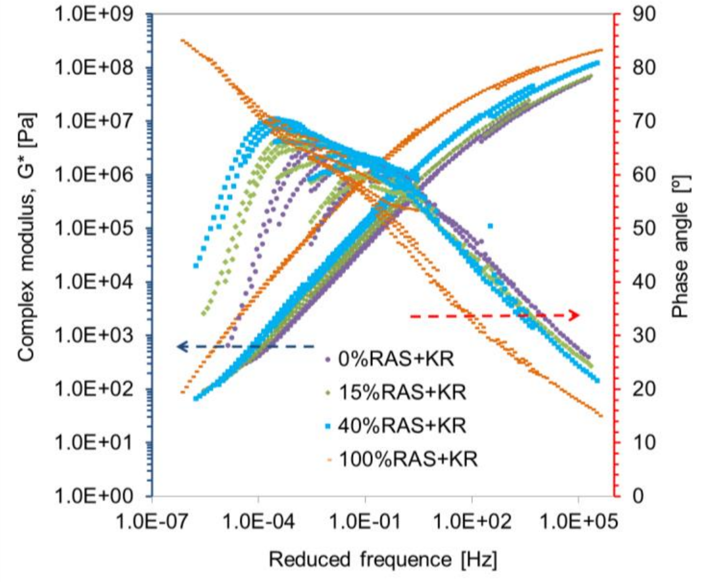


Figure 4.21 Master curves of complex modulus and phase angle for binders in the RAS+KR group at a reference temperature of 25 °C

DRD provided the DSR data of the original RAD binder (shown in Figures 4.22 and 4.23) which is very useful to explain the influence of the virgin soft binder on the rheological properties of the RA binder. As shown in Figure 4.22, the RAD binder has a higher G* than the original binder due to the ageing after about 16 years in service. However, the RAD binder still shows a similar plateau (with δ around equal to 65º) as the original one in the middle frequency range between 10^{-2} and 1 Hz. After blending, 15%RAD+85%70/100 shows a similar G* as the original one, but a higher δ. When blended with PMB 90/150-75, there is almost an overlap for the master curves of both G* and δ between 40%RAD+90/150-75 and the original RAD binder (see Figure 4.23). This indicates that it is possible to restore the rheological properties of RA binder to the original ones by adding a soft PMB binder in this case.

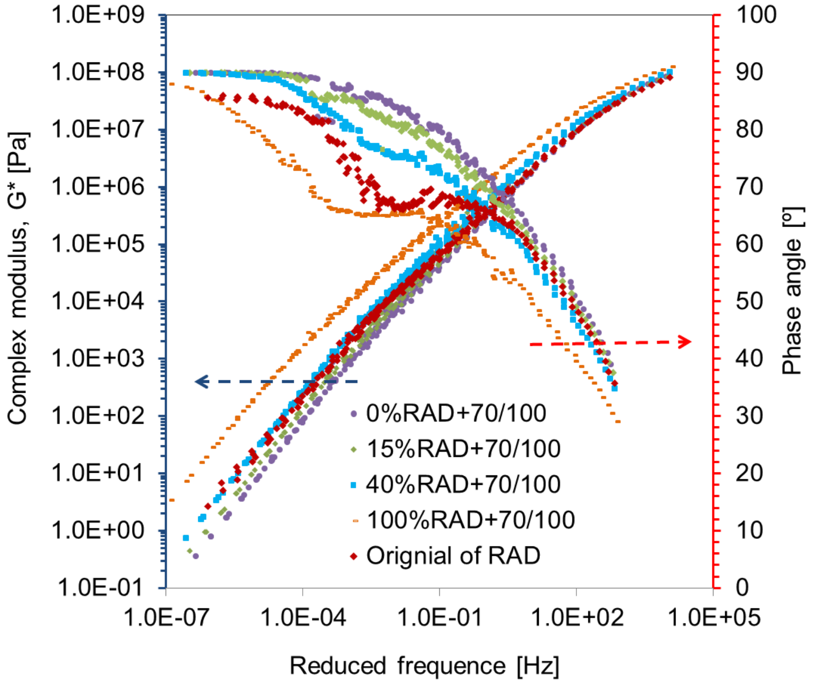


Figure 4.22 Master curves of complex modulus and phase angle for binders in the RAD+70/100 group at a reference temperature of 25 °C

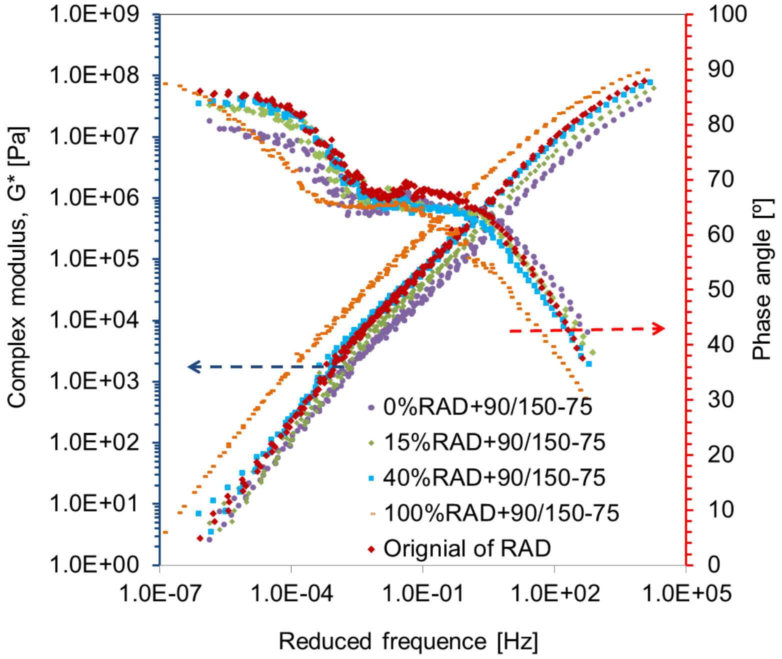


Figure 4.23 Master curves of complex modulus and phase angle for binders in the RAD+90/150-75 group

4.3.2 Relation between G* and Pen. value

Saal and Labout (1958) found that for both unmodified and modified bitumens, the penetration test correlates well with the stiffness of bitumen as measured with the DSR, at the same temperature (25 ºC) and at a frequency of 0.4 Hz. In rheological terms, a good correlation has been identified between $\log(G^*_{0.4\mathrm{Hz};\ 25^{o}\mathrm{C};\ [\mathrm{MPa}]})$ and $\log(\mathrm{Pen.}_{\ 25^{o}\mathrm{C};[\mathrm{dmm}]})$. The correlation can be written as a linear equation:

$$\log(G^*_{0.4\mathrm{Hz};\ 25^{o}\mathrm{C};\ [\mathrm{MPa}]})=2.923-1.9\log(\mathrm{Pen.}_{\ 25^{o}\mathrm{C};[\mathrm{dmm}]}) \tag{11}$$

In this study, the correlation between the results obtained from a DSR and penetration test was determined and expressed as a linear equation (Figure 4.24):

$$\log(G^*_{0.4\mathrm{Hz};\ 25^{o}\mathrm{C};\ [\mathrm{MPa}]})=2.9376-2.0369\log(\mathrm{Pen.}_{\ 25^{o}\mathrm{C};[\mathrm{dmm}]}) \tag{12}$$

This equation compares very well with the previously relation found by Saal and Labout. It indicates that it is possible to use $\log(G^*_{0.4\mathrm{Hz};\ 25^{o}\mathrm{C};\ [\mathrm{MPa}]})$ to predict the penetration of an RA binder if not sufficient material can be recovered for the penetration test.

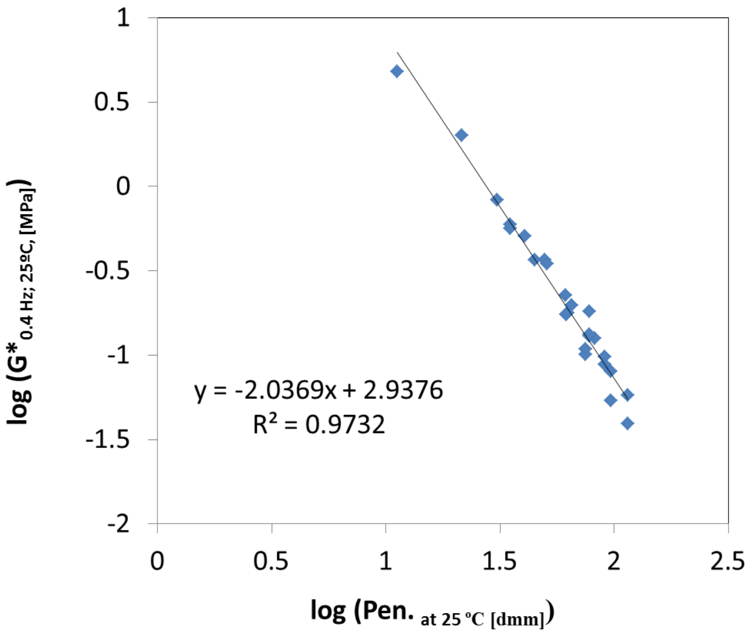


Figure 4.24 Correlation between the complex modulus at 25 ºC and 0.4 Hz and Pen. Value for six binder groups (in total 19 binders)

4.3.3 Complex modulus fitted by the Grunberg-Nissan model

As discussed in the previous section, there is a linear relation between $\log(G^*_{0.4Hz;\ 25^oC;\ [MPa]})$ and $\log(Pen._{25^oC;[dmm]})$ for different binders, including SBS RA binder, virgin Pen. grade binder, virgin PMB binder, and blended binder. This linear relation indicates that $\log(G^*_{0.4Hz;\ 25^oC;\ [MPa]})$ can also be used to predict the blending effect of SBS RA and virgin binders, as the same as using logPen. value at 25 ºC which was discussed in the section of 4.1.2. Note that G* here only refers to a frequency of 0.4Hz. With respect to G* at a wide frequency range, we tried to use the Grunberg-Nissan model to describe the blending rule.

First the MHS model was used to describe the G* master curve of the RA binder and the virgin binder. This model has been described in Figure 3.1 and is mathematically expressed as:

$$(G^*(\omega))^{-1} = (G_0^* + \frac{G_\infty^* - G_0^*}{1+\delta(i\omega\tau)^{-m_1} + (i\omega\tau)^{-m_2}})^{-1} - \frac{i}{\eta_3\omega} \quad , \qquad (13)$$

where, $G^*(\omega)$ is the complex modulus at a frequency ω; G_∞^* and G_0^* are the complex modulus when the frequency is infinite and infinitesimal, here assumed as 4×108 Pa and 0, respectively; m_1, m_2 , τ , δ , η_3 are model parameters; i is the imaginary number in a complex number notation.

After linear regression with the MHS model, parameters for the RA binder and virgin binder are obtained and given in Table 4.3.

Table 4.3 Parameters in the MHS model

Binders	m_1	m_2	δ	τ	η_3
RAN	0.214	0.611	5.999	6.31E-05	4.49E+08
RAS	0.282	0.672	6.386	2.31E-04	2.44E+07
RAD	0.010	0.649	4.457	2.04E-05	5.16E+06
Q8	0.560	0.191	0.603	9.82E-07	1.14E+05
KR	0.322	0.715	9.681	5.37E-06	1.57E+07
70/100	0.557	0.557	3.628	2.14E-05	1.02E+05
90/150-75	0.088	0.757	2.009	7.89E-05	2.81E+05

After this exercise, the master curve of the blended binder is described using the Grunberg-Nissan model at a wide frequency range, based on the master curves of the RA binder and the virgin binder represented by the MHS model. Through the linear regression, parameter d in this model is obtained and given in Table 4.4. One example in Figure 4.25 shows that this model fits master curves of 40%RAN+KR and 15%RAN+KR very well. It indicates that the Grunber-Nissan model can be used to describe the rheological properties of blended binder.

Table 4.4 Parameter d in the Grunberg-Nissan model to describe the modulus of blended binder

Binder group	d	R^2
RAN+Q8	-0.846	0.9997
RAN+KR	0.044	0.9977
RAS+Q8	-0.422	0.9998
RAS+KR	-0.340	0.9992
RAD+70/100	0.058	0.9995
RAD+90/150-75	0.060	0.9997

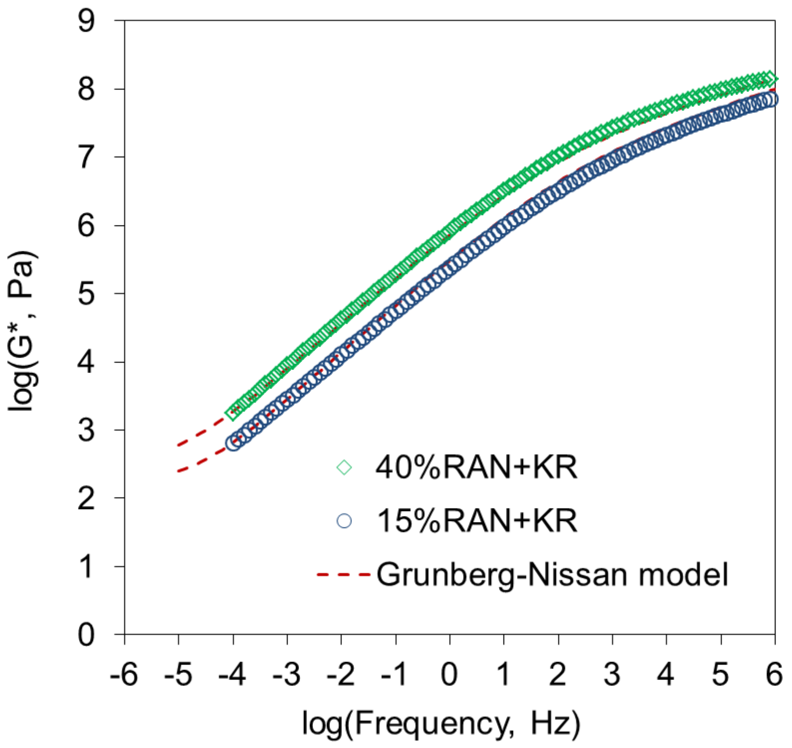


Figure 4.25 Master curves of 40%RAN+KR and 15%RAN+KR fitted by the Grunberg-Nissan model

4.4 GPC

The chromatograms of all binder groups are shown in Figures 4.26 to 4.28. The chromatograms are quantified in the different molecule size groups (Mn, Mw, Mz en Mz+1) in Figures 4.29 to 4.31. For binders mixed with Pen. grade bitumen, there is a clear shift of GPC curve in retention time with the increase of RA content (see left parts of Figures 4.26 to 4.28). It means that the large molecular size (LMS) has increased with a higher RA content. It can be validated by the molecular weights (Mz and Mz+1) in Figures 4.29 (left) to 4.31 (left). The larger LMS can explain the higher stiffness of binders at a high RA content in the section of 4.3.1.

When the RA binder is blended with PMB, the GPC curves become more complicated. There is no clear transition on the curve with the change of RA content (see right parts of Figures 4.26 to 4.28). When fresh PMB is added, the SBS distribution can be easily observed at the LMS region with the retention time ranging from 15 mins to 19 mins. For blended binders in each group, large molecular weights (Mz and Mz+1) hardly change. Especially in RAS+KR and RAD+90/150-75 groups, large molecular weights among each binder become very comparable (see right parts of Figures 4.30 and 4.31). This could be explained by the fact that the LMS in fresh PMB and in the RA binder is very similar.

As introduced in Chapter 3, the GPC curves treated as one peak integration can be separated into two peaks. In this way, the molecular weights of the bitumen component and the polymer component are determined and the results are shown in Figures 4.32 to 4.37. One can observe a clear transition of molecular weight in the bitumen component with the change of RA content, even for the PMB plus RA binder groups. This transition is also associated with rheological properties of the binder. With respect to the polymer component, its molecular weight distribution still cannot give some indication on the blending effect due to the complexity of the LMS which is relevant to fresh SBS from new binder and remaining SBS from RA binder, as well as the aged bitumen component in the RA binder.

The chromatograms of RAD and its original binder show different GPC curves (Figure 4.28 left) but very comparable molecular weights in terms of Mn, Mw, Mz and Mz+1 (Figure 4.31 left). If the GPC curve is separated into two peaks, it is observed that in the bitumen component of RAD, its large molecular weight (Mz and Mz+1) is obviously higher than that of its original (see Figure 4.37 left), but the other way around for the polymer component probably due to its degradation (see Figure 4.37 right). These phenomena are directly related to the ageing effect in the field.

In order to evaluate the polymer content in the aged and the blended binders, the area of these two peaks in the GPC curves had been calculated and the ratio between them is shown in Figure 4.38. Except the RAN+KR group, the ratio of Area Polymer/ Area Bitumen is increasing with the increase of RA content. When the RA binder is mixed with Pen. grade bitumen, it is logical that this ratio starts from zero and gradually increases. With respect to mixing with PMB, the trend of the ratio is determined by the initial values of PMB and RA binder. Due to a lower initial value of RAN, a decrease for this ratio value can be observed with the increase of RA content. Compared to the original binder, the RAD ratio increased almost by one order of magnitude due to the ageing effect. However it must be stated that the limits that determine which part is considered as polymer and which part is considered as binder is arbitrary. Therefore this analysis shows trends in behaviour, however it cannot be used to asses polymer content with a defined reliability.

The GPC tests performed in this study cannot give direct insight in the material changes. This is caused by the nature of the GPC test, which shows a weight distribution of the molecules and the possible complex effects of the SBS modified binder during ageing (growing of larger molecules, but also breaking of SBS molecules in smaller ones) .

Differences in weight distribution between old and new binders provide insight in changes due to aging, however in this case only the original binder from Denmark was available. A second challenge comes with the Polymer Modified Binders, due to aging the polymer degrades into molecule sizes that are comparable to molecule sizes of bitumen and due to aging of the molecule sizes of the bitumen increase up to the sizes of polymer. This means that in an aged polymer modified binder it is impossible to discern polymer and bitumen based on the molecular weight. For future research it is advised to only perform GPC tests if the original binder is also available so that a reference is available

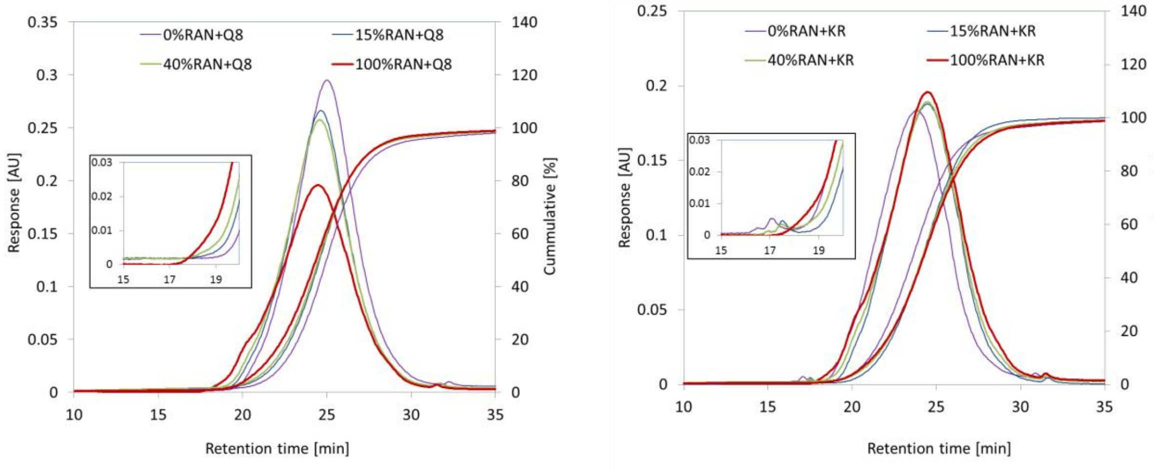


Figure 4.26 Molecular weight distribution of RAN+Q8 group (left) and RAN+KR group (right)

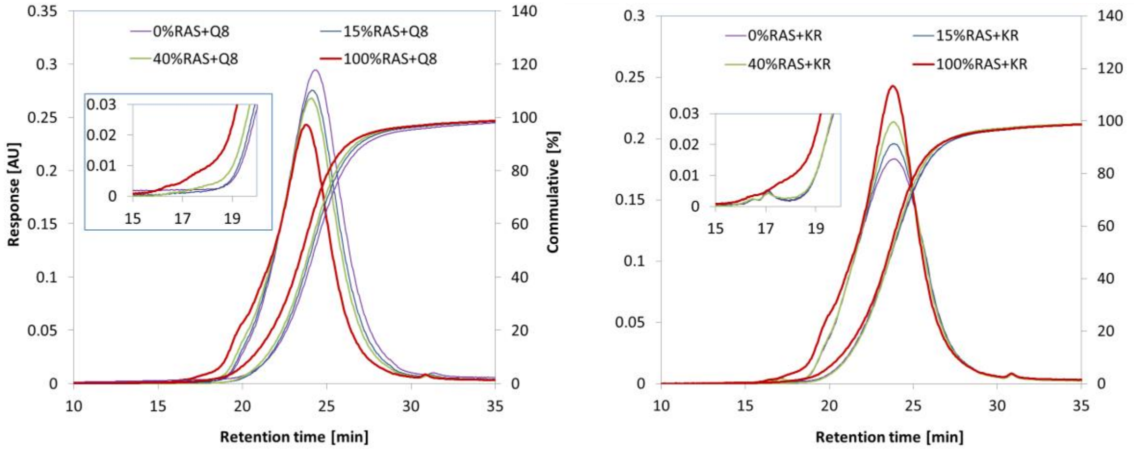


Figure 4.27 Molecular weight distribution of RAS+Q8 group (left) and RAS+KR group (right)

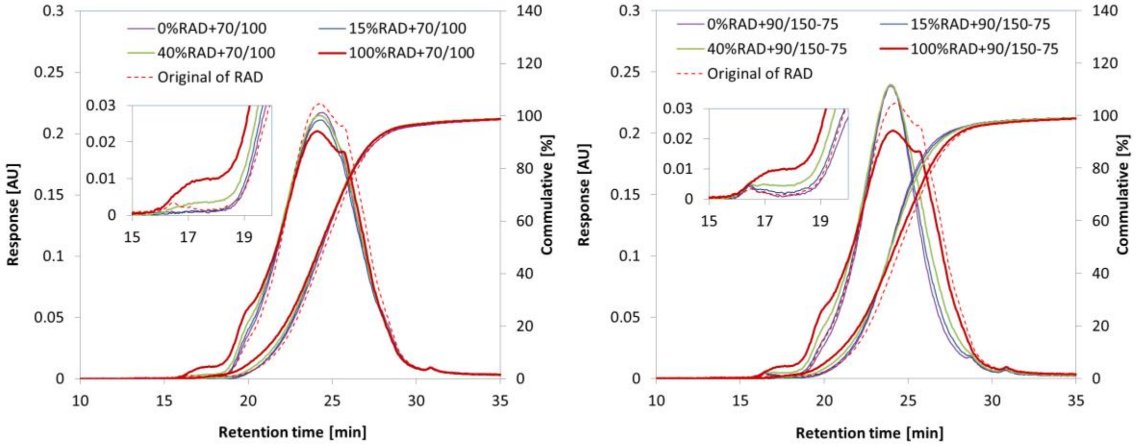
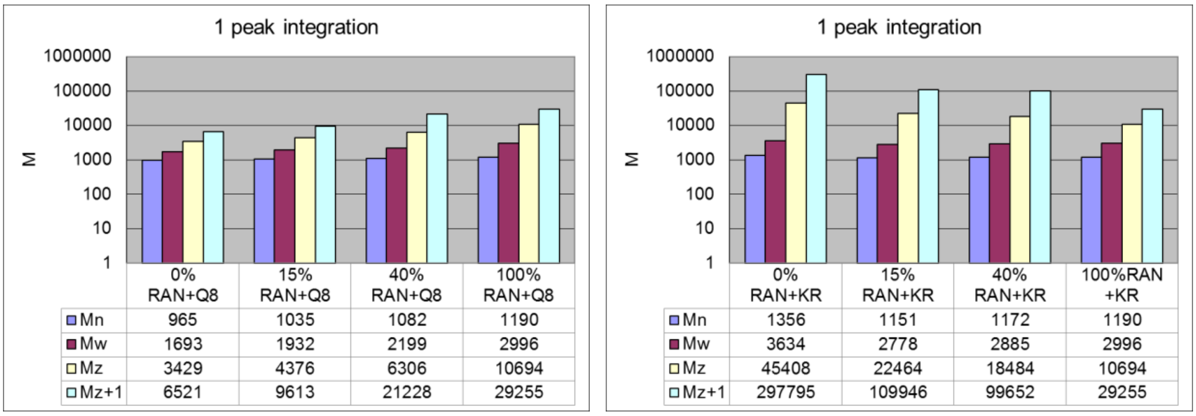


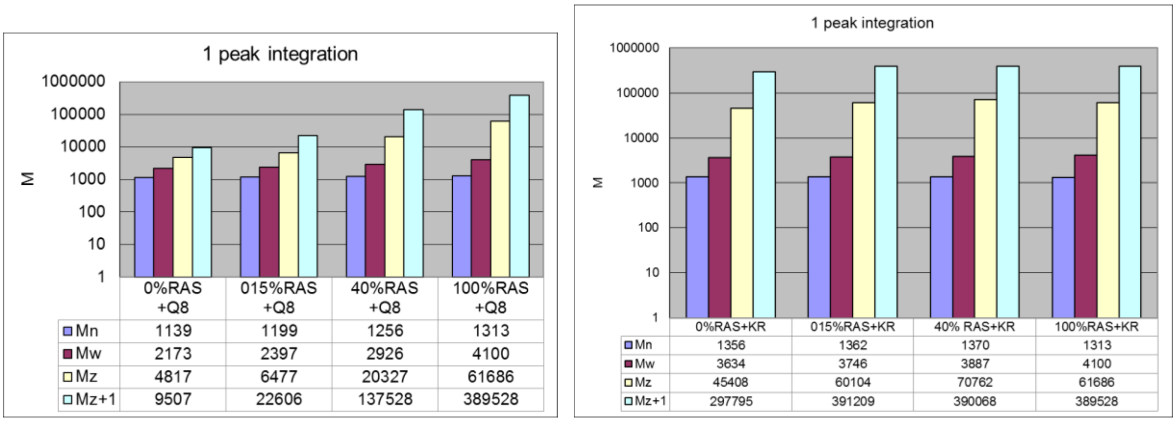
Figure 4.28 Molecular weight distribution of RAD+70/100 group (left) and RAD+90/150-75 group (right)



	0% RAN+Q8	15% RAN+Q8	40% RAN+Q8	100% RAN+Q8
□ Mn	965	1035	1082	1190
■ Mw	1693	1932	2199	2996
□ Mz	3429	4376	6306	10694
□ Mz+1	6521	9613	21228	29255

	0% RAN+KR	15% RAN+KR	40% RAN+KR	100%RAN +KR
□ Mn	1356	1151	1172	1190
■ Mw	3634	2778	2885	2996
□ Mz	45408	22464	18484	10694
□ Mz+1	297795	109946	99652	29255

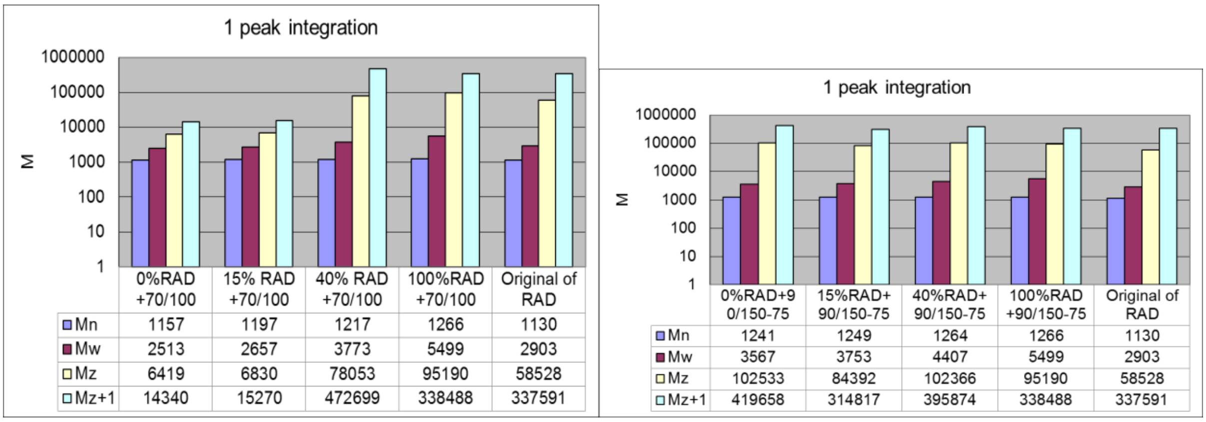
Figure 4.29 Molecular weights for RAN+Q8 group (left) and RAN+KR group (right)



	0%RAS +Q8	015%RAS +Q8	40%RAS +Q8	100%RAS +Q8
□ Mn	1139	1199	1256	1313
■ Mw	2173	2397	2926	4100
□ Mz	4817	6477	20327	61686
□ Mz+1	9507	22606	137528	389528

	0%RAS+KR	015%RAS+KR	40% RAS+KR	100%RAS+KR
□ Mn	1356	1362	1370	1313
■ Mw	3634	3746	3887	4100
□ Mz	45408	60104	70762	61686
□ Mz+1	297795	391209	390068	389528

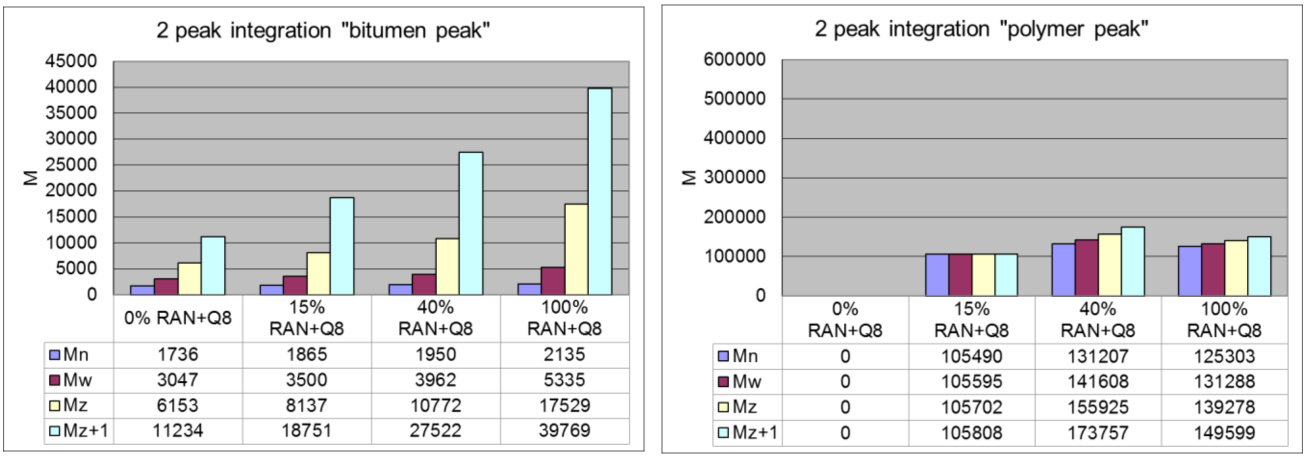
Figure 4.30 Molecular weights for RAS+Q8 group (left) and RAS+KR group (right)



	0%RAD +70/100	15% RAD +70/100	40% RAD +70/100	100%RAD +70/100	Original of RAD
□ Mn	1157	1197	1217	1266	1130
■ Mw	2513	2657	3773	5499	2903
□ Mz	6419	6830	78053	95190	58528
□ Mz+1	14340	15270	472699	338488	337591

	0%RAD+9 0/150-75	15%RAD+ 90/150-75	40%RAD+ 90/150-75	100%RAD +90/150-75	Original of RAD
□ Mn	1241	1249	1264	1266	1130
■ Mw	3567	3753	4407	5499	2903
□ Mz	102533	84392	102366	95190	58528
□ Mz+1	419658	314817	395874	338488	337591

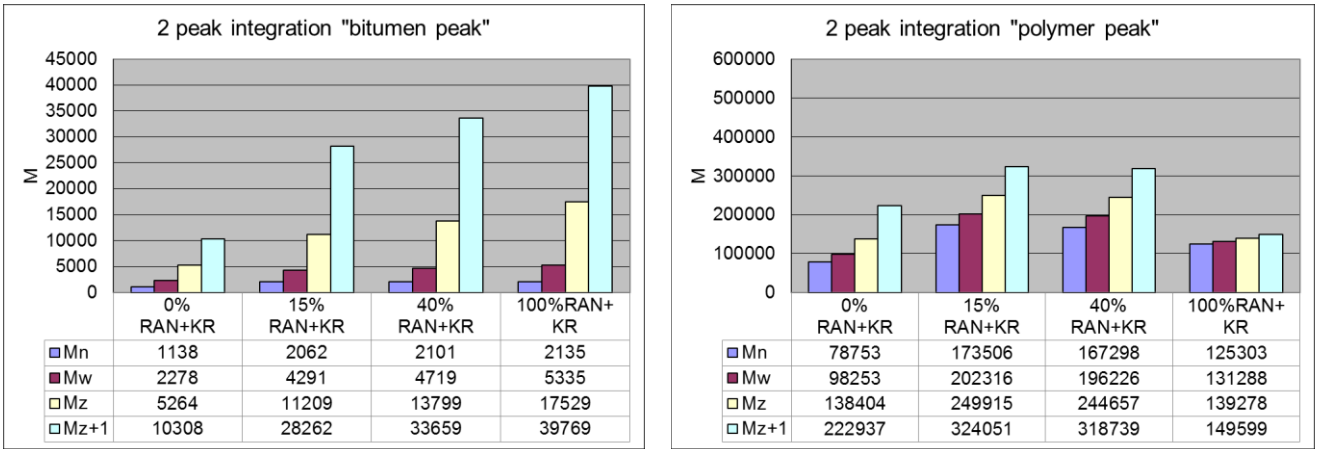
Figure 4.31 Molecular weights for RAD+70/100 group (left) and RAD+90/150-75 group (right)



	0% RAN+Q8	15% RAN+Q8	40% RAN+Q8	100% RAN+Q8
□Mn	1736	1865	1950	2135
■Mw	3047	3500	3962	5335
□Mz	6153	8137	10772	17529
□Mz+1	11234	18751	27522	39769

	0% RAN+Q8	15% RAN+Q8	40% RAN+Q8	100% RAN+Q8
□Mn	0	105490	131207	125303
■Mw	0	105595	141608	131288
□Mz	0	105702	155925	139278
□Mz+1	0	105808	173757	149599

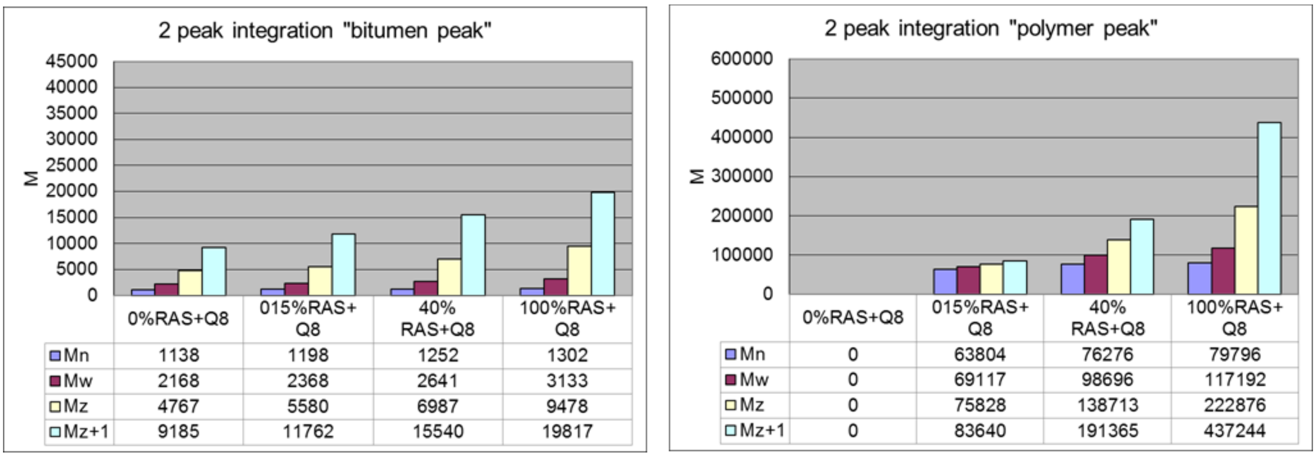
Figure 4.32 Molecular weights of RAN+Q8 for bitumen part (left) and polymer part (right)



	0% RAN+KR	15% RAN+KR	40% RAN+KR	100%RAN+KR
□Mn	1138	2062	2101	2135
■Mw	2278	4291	4719	5335
□Mz	5264	11209	13799	17529
□Mz+1	10308	28262	33659	39769

	0% RAN+KR	15% RAN+KR	40% RAN+KR	100%RAN+KR
□Mn	78753	173506	167298	125303
■Mw	98253	202316	196226	131288
□Mz	138404	249915	244657	139278
□Mz+1	222937	324051	318739	149599

Figure 4.33 Molecular weights of RAN+KR for bitumen part (left) and polymer part (right)



	0%RAS+Q8	015%RAS+Q8	40% RAS+Q8	100%RAS+Q8
□Mn	1138	1198	1252	1302
■Mw	2168	2368	2641	3133
□Mz	4767	5580	6987	9478
□Mz+1	9185	11762	15540	19817

	0%RAS+Q8	015%RAS+Q8	40% RAS+Q8	100%RAS+Q8
□Mn	0	63804	76276	79796
■Mw	0	69117	98696	117192
□Mz	0	75828	138713	222876
□Mz+1	0	83640	191365	437244

Figure 4.34 Molecular weights of RAS+Q8 for bitumen part (left) and polymer part (right)

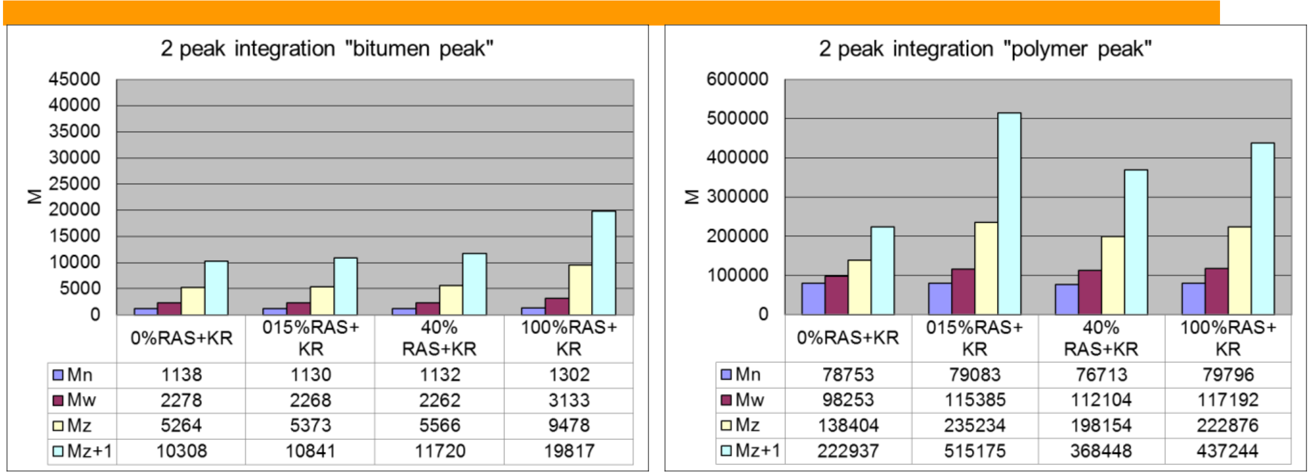


Figure 4.35 Molecular weights of RAS+KR for bitumen part (left) and polymer part (right)

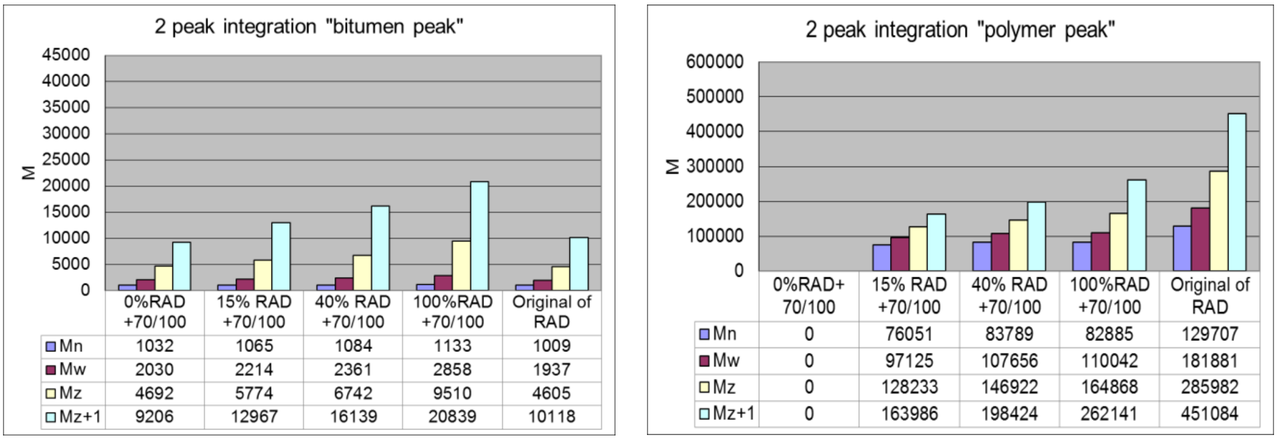


Figure 4.36 Molecular weights of RAD+70/100 for bitumen part (left) and polymer part (right)

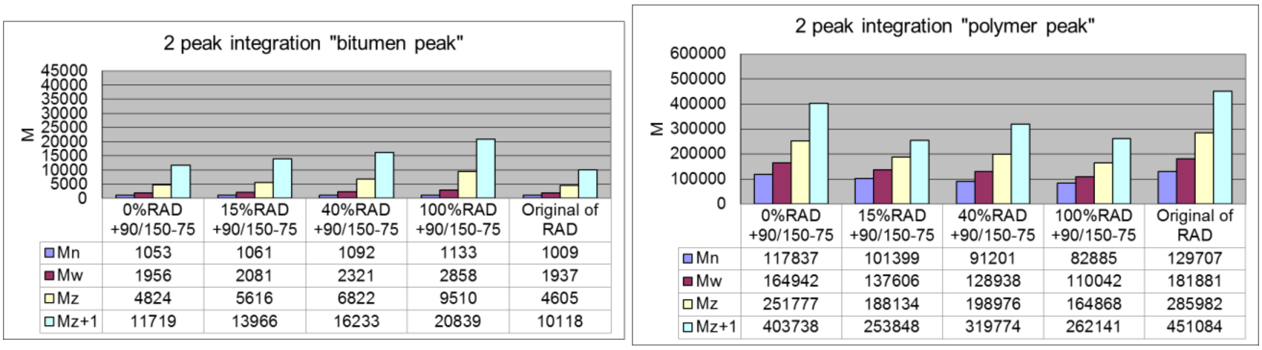


Figure 4.37 Molecular weights of RAD+90/150-75 for bitumen part (left) and polymer part (right)

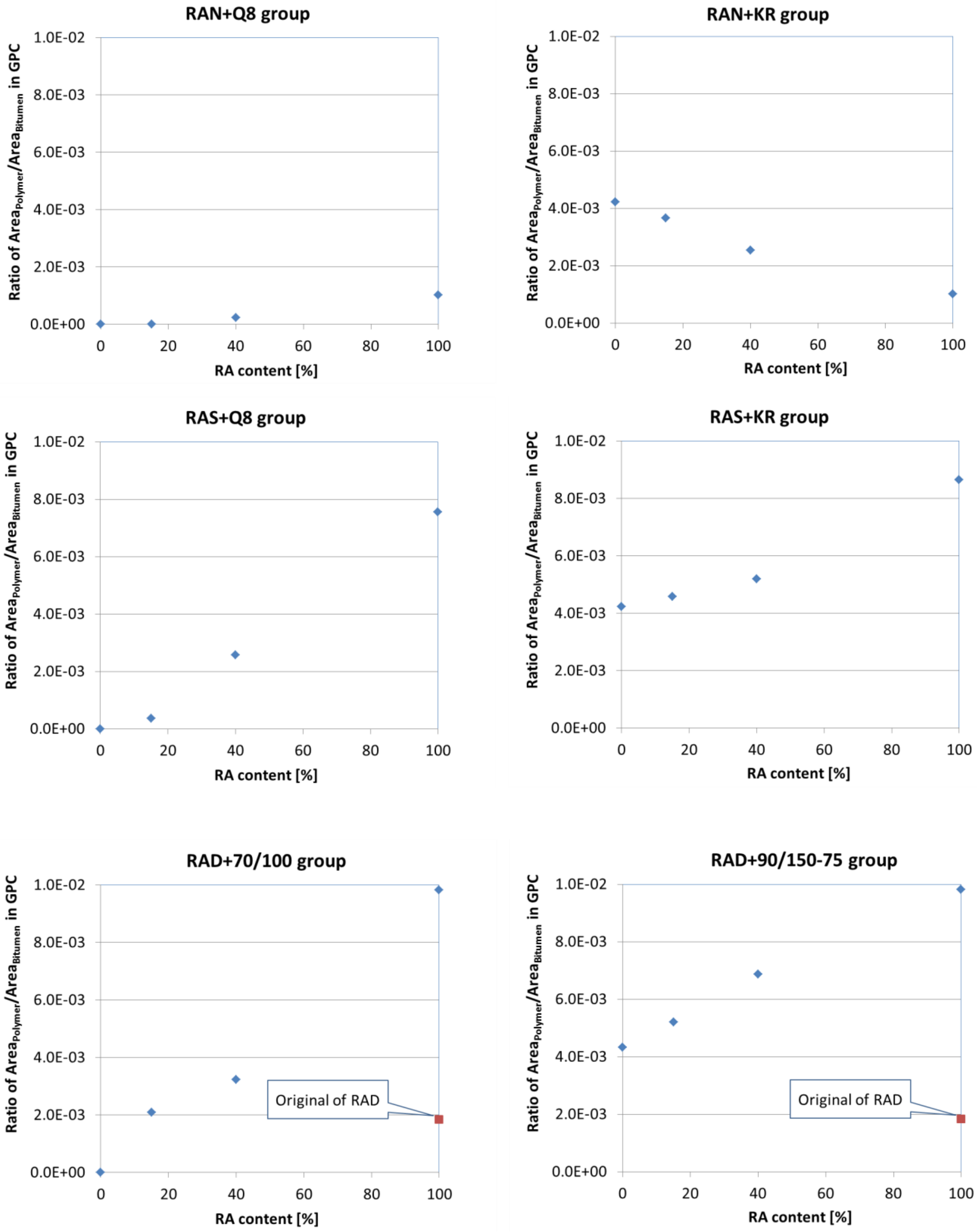


Figure 4.38 Ratio of Area$_{Polymer}$/Area$_{Bitumen}$ in GPC curve

4.5 FTIR

Two examples of FTIR curves are given in Figures 4.39 and 4.40. One can observe that fresh Q8 and KR show the lowest peaks for the C=O and S=O bands. The addition of RA binder results in an increase of these peaks. It is noticed that the width of the peaks for C=O and S=O increase with the addition of more RA together with a small shift to a lower wave number for the peak position. For the Q8 binder, the addition of the RA binder also leads to an increase of the SBS peak. However, for the KR binder, it is difficult to judge the size of this peak with the addition of RA binder due to the existence of SBS already in KR (see Figure 4.40).

All data related to the indices of ICO, ISO and ISBS are given in Table 4.5 which clearly indicates the blending effect in terms of these peaks. With respect to ICO this value equals to zero for fresh Q8, KR and 90/100. Due to the very low concentration of C=O, it is hard to observe its existence in binders of 15%RAN+Q8, 15%RAN+KR, 15%RAS+KR and 15%RAD+90/150-75. Therefore, an ICO value of zero is given. It is noticed that fresh Danish 70/100 binder contains some C=O that may form during the manufacture process. A gradual increase of this index with the increase of RA content is observed in the binder group RAD+70/100.

With regards to ISO, it is observed in most binder groups that this value increases with the increase of RA content. This trend also corresponds to the stiffness change of binders from the DSR result. The relation with the RA content is shown in Figure 4.41Figure 4.41. However, it is hard to observe a clear linear relation for all binder groups.

Similar to ISO, ISBS is zero for fresh Pen. grade bitumen and increases with the increase of RA content. In this case, ISBS is relevant to the stiffness of binders from the DSR result. When the fresh PMB is blended with RA binder, ISBS is determined by the SBS content from both binders, but in this case there will be not be a relation with the stiffness of the binder. For example, fresh KR (0%RAN+KR) has a higher ISBS value than pure RAN (100%RAN+KR), but it has a much lower stiffness than RAN. Another example is that in the RAD+90/150-75 group, all binders have a comparable ISBS value but totally different stiffness. Therefore, there is no relation between the ISBS value and the stiffness of the blended binder when fresh PMB and RA (PMB) binder are blended with each other.

Compared with the original binder of RAD, an increase in ICO and ISO for RAD binder is observed due to the ageing effect. However, it seems that there is no change in ISBS. This indicates that the degradation of the SBS in this RA binder cannot be characterized by FTIR. However, it can be characterized by GPC (see Figure 4.39).

DRD has a special spread sheet called List which contains a list of all the references for the individual sample and measurement in their folder. The list also shows the individual spectra selected for a calculation of the content of SBS. Erik Nielsen from DRD mentioned that it is not a precise estimation, but a value with some uncertainty. The determination is based on the two SBS peaks at 966 cm^{-1} and 698 cm^{-1} and a reference peak at 1376 cm^{-1}. From the corrected heights of these two peaks, ratios are calculated which later are used as entrance values for the calibration curve. Both ratios should give the same value of SBS content but some deviations can occur. The mean value of these two estimations is calculated and can be found in Table 4.6. A comparable SBS content of 4.4% and 4.5% can be found in the RAD binder and its original binder, respectively. These estimated results are very consistent with ISBS values in Table 4.5 and further prove that the degradation of SBS in the RA binder is not characterized with FTIR.

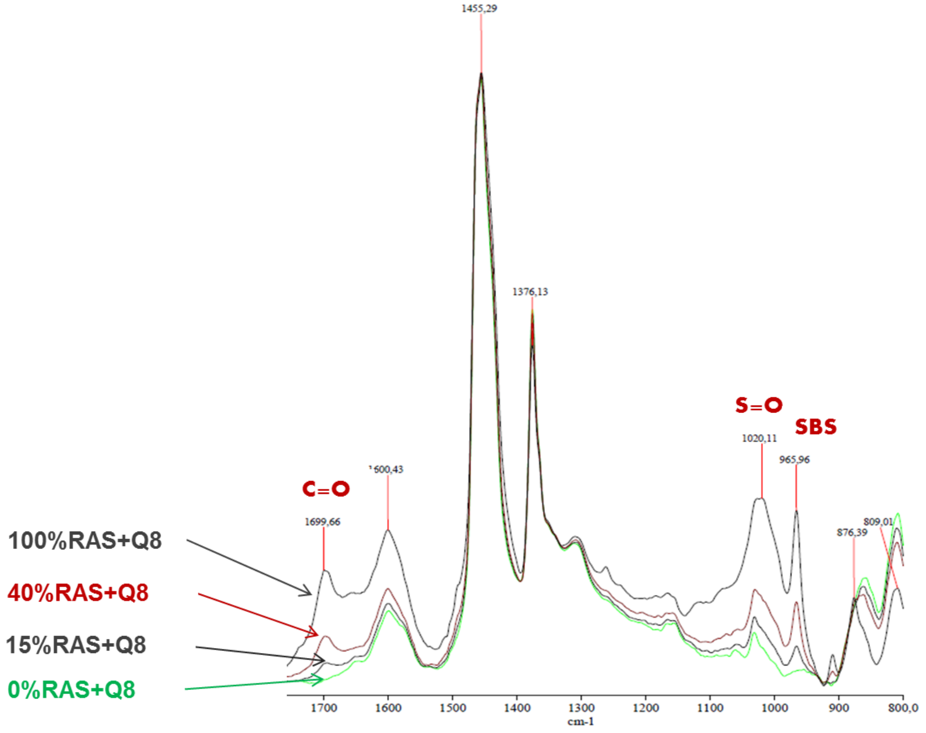


Figure 4.39 FTIR curves of RAS+Q8 group

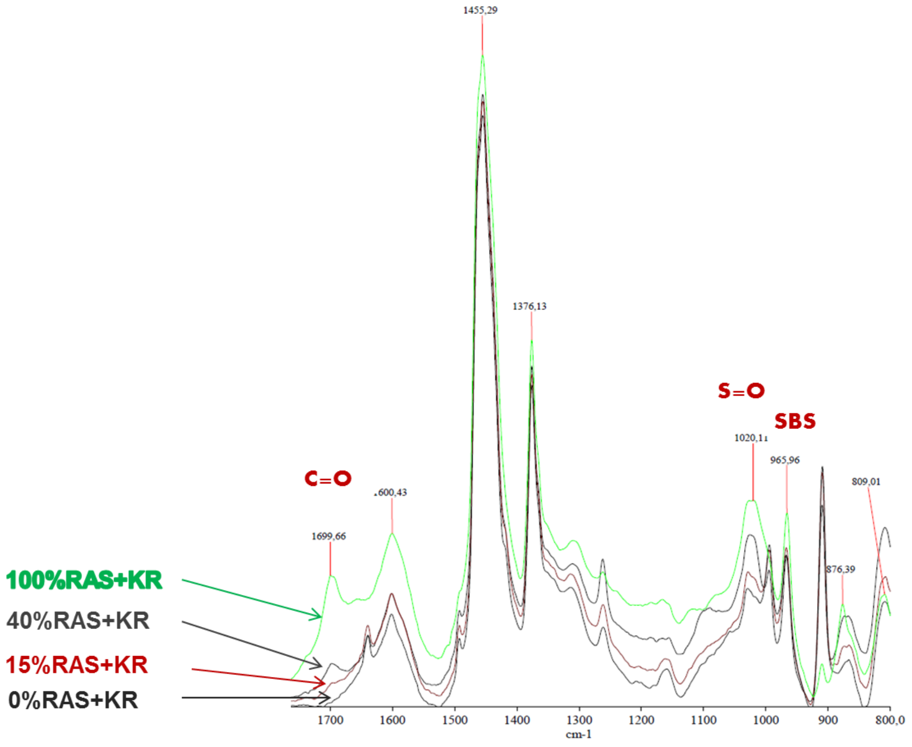


Figure 4.40 FTIR curves of RAS+KR group

Table 4.5 Indices of ICO, ISO and ISBS for all binders

Binder groups	Mean values			Coefficients of Variation [%]		
	ICO	ISO	ISBS	ICO	ISO	ISBS
0%RAN+Q8	0	0.024	0	-	7.1	-
15%RAN+Q8	0	0.035	0.024	-	0.04	3.8
40%RAN+Q8	0.018	0.041	0.039	1.6	0.6	3.1
100%RAN+Q8	0.044	0.065	0.078	23.3	5.0	2.0
0%RAN+KR	0	0.028	0.140	-	18.9	0.3
15%RAN+KR	0	0.038	0.155	-	7.6	1.4
40%RAN+KR	0.019	0.041	0.124	17.2	1.1	1.1
100%RAN+KR	0.044	0.065	0.078	23.3	5.0	2.0
0%RAS+Q8	0	0.024	0	-	7.1	-
15%RAS+Q8	0.002	0.026	0.026	24.7	5.1	3.0
40%RAS+Q8	0.030	0.031	0.050	3.2	4.9	0.7
100%RAS+Q8	0.069	0.046	0.096	22.7	5.1	2.4
0%RAS+KR	0	0.028	0.136	-	12.5	3.4
15%RAS+KR	0	0.039	0.139	-	10.7	3.0
40%RAS+KR	0.013	0.048	0.126	23.8	5.7	1.3
100%RAS+KR	0.069	0.046	0.096	22.7	5.1	2.4
0%RAD+70/100	0.034	0.020	0	55.8	22.8	-
15%RAD+70/100	0.044	0.022	0.022	23.2	21.6	42.2
40%RAD+70/100	0.050	0.024	0.029	24.5	20.7	29.0
100%RAD+70/100	0.089	0.033	0.057	29.3	15.2	20.1
0%RAD+90/150-75	0	0.023	0.058	-	15.0	19.7
15%RAD+90/150-75	0	0.024	0.062	-	25.6	34.1
40%RAD+90/150-75	0.040	0.026	0.056	31.1	17.0	24.3
100%RAD+90/150-75	0.089	0.033	0.057	29.3	15.2	20.1
Original of RAD	0	0.028	0.058	-	17.2	10.7

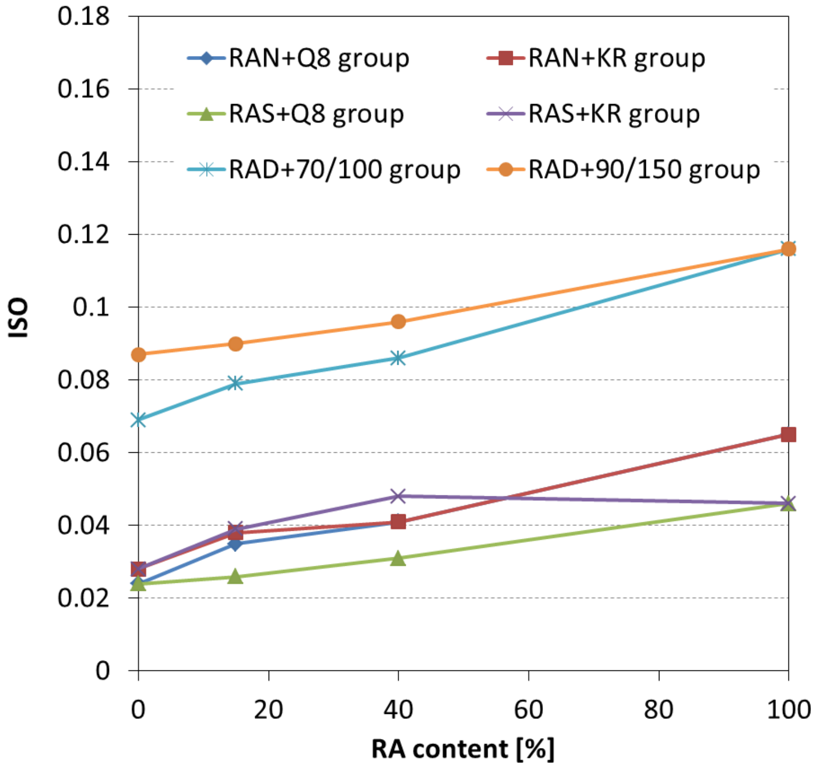


Figure 4.41 ISO as a function of RA content

Table 4.6 Rough estimates of SBS content by DRD, based on a calibration curve

Original of RAD (Caribit B85 Plus)	4,5	%
0%RAD+70/100	No SBS present	
15%RAD+70/100	0,6	%
40%RAD+70/100	1,8	%
100%RAD+70/100	4,4	%
90/150-75	4,2	%
15%RAD+90/150-75	4,9	%
40%RAD+90/150-75	5,1	%

5 Conclusions

- Although the polymer in a modified bitumen (PMB) can degrade during the service life of an asphalt pavement, the results of this report indicate that part of the characteristics of the polymer is still available in the PMB reclaimed from a milled old asphalt surface-layer. These characteristics can be manifested when blending with virgin Pen. grade bitumen or with virgin PMB binder. It means that the polymer from the reclaimed binder can function in a new mixture when recycled.

- It is possible to restore the rheological properties of the reclaimed PMB binder to its original state by mixing it with a soft virgin PMB binder..

- As a first step in mixture design for the industry, the logPen. model and the SP model together can be used to approximately predict the penetration value at 25 ºC and the S.P. of the blended binder consisting of reclaimed PMB binder plus virgin Pen. grade binder or plus virgin PMB binder.

- A linear correlation between $\log(G^*_{0.4Hz;\ 25ºC;\ [MPa]})$ and $\log(Pen._{25ºC;[dmm]})$ makes it possible to use the G* to predict the Pen. value for the purpose of evaluating the effect of recycling when a small amount of binder is obtained.
- The Grunberg-Nissan model is an option to describe some fundamentally rheological properties of the blended binder, like viscosity at different temperatures and complex modulus at a wide frequency range.

- Based on the viscosity data, temperatures for mixing and compaction are recommended for work package 4 (WP4) in this project. The used method is also very useful for mix design in industry. Due to the polymer modification and aging of the binder, the required mixing temperatures for the blended binder are high, in some cases above 180°C. Such high temperatures should be avoided to prevent degradation of the polymer.

- The S=O index and SBS index from FTIR can describe the chemical properties of a blended binder; the SBS index value only helps in the case of reclaimed PMB plus virgin Pen. grade bitumen. The SBS index can only reflect the relative SBS content but hardly characterize its degradation behaviour; the GPC test can directly describe this behaviour when original binder is available as a reference.

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