Rubberised bitumen manufacturing assisted by rheological measurements

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Rubberised bitumen manufacturing assisted by rheological measurements

This paper investigates the effect of processing temperature and time on the rheological properties of Recycled Tyre Rubber Modified Bitumens (RTR-MBs) produced using two different base binders and an ambient ground crumb rubber modifier (CRM). The production of the RTR-MBs was accomplished by means of a standard Brookfield rotational viscometer together with a modified impeller Dual Helical Impeller (DHI) to allow mixing as well as real-time viscosity measurements of the produced RTR-MBs. The rheological properties of the final RTR-MBs were determined by means of standard Dynamic Mechanical Analysis (DMA) oscillatory and Multiple Stress Creep Recovery (MSCR) testing using a dynamic shear rheometer (DSR). The results indicate that the low processing conditions (160°C and 60 minutes) are not appropriate for developing RTR-MBs with enhanced physical and rheological properties. However, allowing the crumb rubber to interact with the base binder for longer mixing times (140 minutes) led to the development of an enhanced rubber (polymer) network structure within the blend (i.e. swelling of the CRM particles) and superior rheological properties. At the other extreme, using high processing conditions (200°C and 140 minutes) led to RTR-MBs in which the rubber network had been subjected to devulcanisation and depolymerisation with a subsequent reduction in modification.

Keywords: crumb rubber, rheological properties, viscosity, modified bitumen

1. Introduction:

The use of crumb rubber particles from recycled tyres in asphalt paving materials provides a solution to improve pavement mechanical performance as well as solve environmental problems associated with hazardous landfill of used tyres. The enhanced engineering properties imparted by adopting rubberized bitumen in different pavement applications are well recognized in many countries (Ruth and Roque 1995, Glover et al. 2000, Huang et al. 2002, Wang et al. 2012, Lo Presti 2013). However, if the material is not appropriately designed, produced and constructed, a counterproductive result could arise with pavement performance being inferior to conventional asphalt. An improved

product development procedure is therefore required to allow engineers to develop superior, rubber modified binders.

Rubberised bitumen is currently manufactured by means of a number of different bitumen–rubber interaction mechanisms to produce RTR-MBs with different mechanical properties. The interaction mechanism is traditionally considered to be a physical process with CRM particles being swollen by absorbing the lighter fractions (oily compounds) available in the bitumen into the bulk of the rubber particles with no chemical reaction (Heitzman 1992, Ghavibazoo and Abdelrahman 2012, Lo Presti 2013). The swelling mechanism and rubber dispersion are mainly controlled by temperature, time and CRM particle size (Attia and Abdelrahman 2009). As the processing conditions become more severe (increase in temperature/time), the rubber particles start to devulcanise or depolymerise and as they disintegrate will release the adsorbed oily compounds back into the bitumen (liquid) phase of the RTR-MB causing an overall reduction in viscosity (Ghavibazoo and Abdelrahman 2012). The amount and rate of dissolution of CRM components into the bitumen liquid phase can be regulated by changing the interaction parameters (temperature, mixing rate and mixing duration). The CRM can be fully digested into the bitumen by utilizing high-processing conditions and producing a product with no or minimised phase separation problems (good storage stability). However, the enhancement of the performance related properties (increased stiffness and elastic response as quantified by complex modulus and phase angle) through the modification process can be negatively affected (Lo Presti 2013).

The optimisation process of manufacturing RTR-MBs is normally done by monitoring the high temperature viscosity which indicates the state of the swelling mechanism over time, and then identifying the time at which the viscosity reaches its highest (peak)

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value. Although, viscosity is an important property especially in terms of binder pumpability, mixture workability and compaction, it cannot be solely used to predict the in-service performance of the binder within the asphalt mixture. Moreover, excessively high viscosity and the heterogeneity of RTR-MB products are two drawbacks that have in some cases led to detrimental effects on the compaction process and storage stability. Also, the high viscosity of RTR-MBs would require higher mixing and compaction temperature which raises concerns about workers' health due to possible hazardous fumes.

Specifying a generic recipe for the interaction variables of rubberised bitumen is almost impossible as the performance trend associated with these variables is not always clear due to the overlapping effects that include the base binder (physical and chemical properties), crumb rubber type, size, content and surface texture. All these factors play a key role in controlling the resultant product. Navarro and his co-workers demonstrated that a processing temperature of 210°C is the optimum temperature for RTR-MBs in terms of their rheological properties and storage stability with the processing device and impeller geometry having almost negligible influence at this temperature (Navarro et al. 2007). Furthermore, Ragab and his colleagues suggested that a combination of a very high mixing speed of 50 Hz and moderate temperature of 190°C had the best improvements on complex modulus |G*| and phase angle (δ) and provided improved cross linking by forming a 3D network structure within its matrix (Ragab et al. 2013).

In this study, the manufacture of RTR-MBs was carried out by utilising a simple laboratory tool consisting of a standard Brookfield viscometer with a modified Dual Helical Impeller (DHI) as shown in Figure 1 (Lo Presti et al. 2014). This configuration allows the practical investigation of a large number of variables associated with the

manufacture of RTR-MBs while measuring viscosity in real-time. The Brookfield viscometer with DHI has a number of benefits including the precise control of mixing and testing temperature, continuous monitoring of viscosity measurements, the ability to keep the rubber uniformly distributed within the blend by creating a convective-like flow and the need for small quantities (10 to 15 g) of material (Celauro et al. 2012, Presti and Airey 2013, Lo Presti et al. 2014). The results presented in the paper form part of a wider study looking at the development of rubberised bitumen materials that have improved mechanical properties while also being compatible and not prone to phase separation. This part of the study aims to understand the effects of processing conditions on the rheological properties of RTR-MBs produced using two different base binders. The blending variables (temperature and time) were investigated based on their influence on measurements of the linear and nonlinear viscoelastic properties of the RTR-MBs.
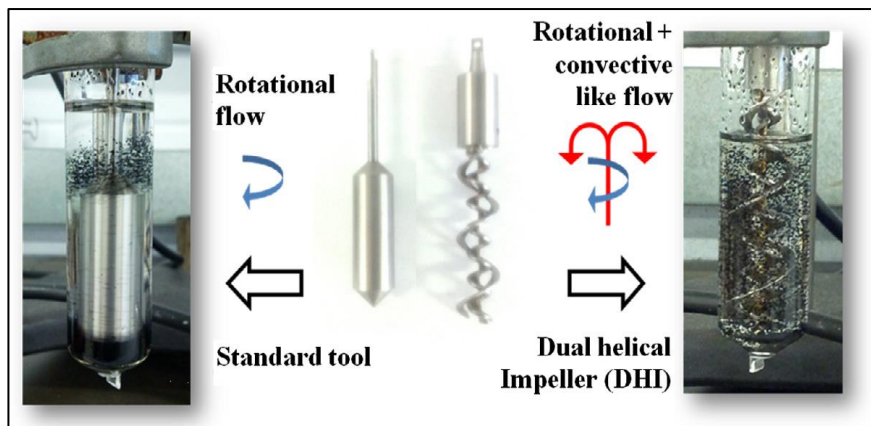

Figure 1: The modified Dual Helical Impeller (DHI) (Lo Presti et al. 2014)

2. Materials and experimental programme:

2.1 Materials

Two straight-run bituminous binders were used in this study, labelled "H" for "hard"

and "S" for "soft". Binder "H" has a penetration of 40 dmm and a softening point of

51.4°C, whereas binder "S" has a penetration of 200 dmm and a softening point of

37°C. Other physical and rheological properties are presented in Table 1. The two

binders were selected with large differences in their physical and rheological properties

in order to identify the effect of the base binder on the interaction mechanism and the

final RTR-MBs that are produced. In addition to binder "H" being considerably harder

than binder "S", it also has an asphaltenes content (determined according BS 2000-143:

2004) that is almost four times higher than binder "S" (15.2% compared to 4.2%).

The crumb rubber modifier (CRM) used in this study, labelled "N", is a powdered

rubber (nominal maximum size of 0.5 mm) produced by J. Allcock & Sons Ltd

(England) and derived from discarded truck and car tyres by ambient grinding followed

by the removal of all metallic and textile contaminants. Recycled tyre rubber particles

have a relatively higher density (1.15 ± 0.05 g/cm^3) than bitumen (1.02 g/cm^3). Figure 2

shows the percent passing gradation of rubber particles while Figure 3 shows SEM

images taken at different magnifications of the individual rubber particles. The SEM

images show that CRM produced by ambient grinding has very irregular shapes and

rough surface texture (large surface area), properties which are desirable for rubber-

bitumen interaction and hence better physical properties (Lee et al. 2008).

Table 1: The properties of base binders used in this study.

Ageing states	Index	Binder "S"	Binder "H"
Unaged binder	Penetration @25 °C, 0.1mm	200	40
	Softening point °C	37.0	51.4
	Rotational viscosity, Pa.s		
	@135 °C	0.192	0.474
	@160 °C	0.065	0.170
	@180 °C	0.025	0.075
	@200 °C	0.012	0.032
	Asphaltenes content	4.2%	15.2%

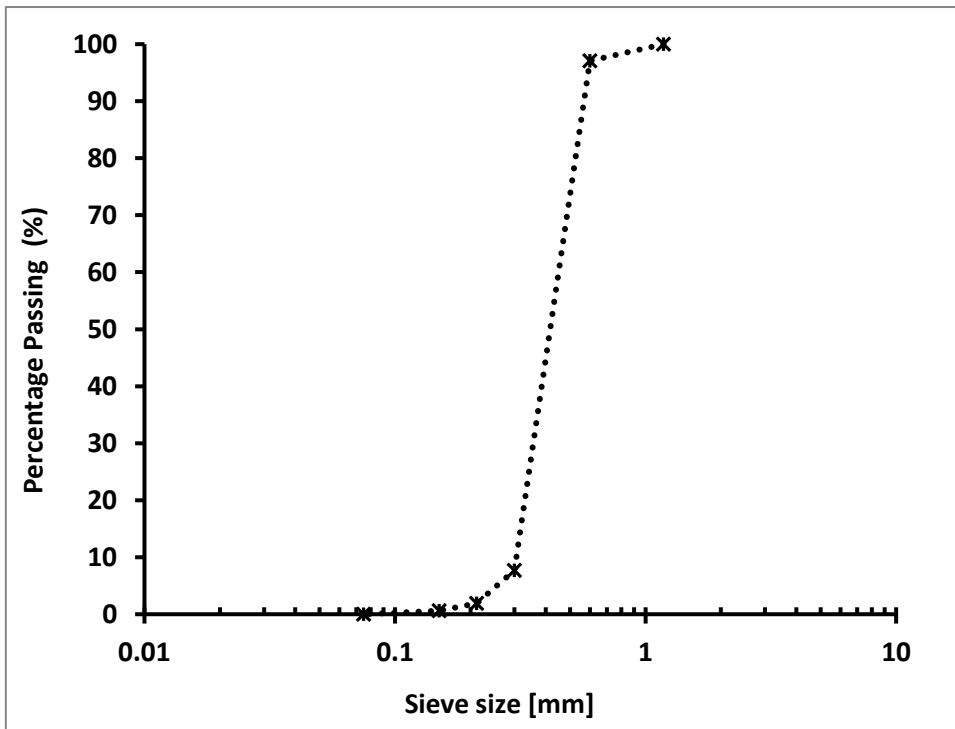|	|G*|/sinδ @ 60 ºC & 1.59Hz, kPa	0.615	1.95
RTFOT aged residue	|G*|/sinδ @ 60 ºC & 1.59Hz, kPa	1.256	7.70
RTFOT + PAV aged residue	|G*|.sinδ @ 20 ºC & 1.59Hz, kPa	1050	10027

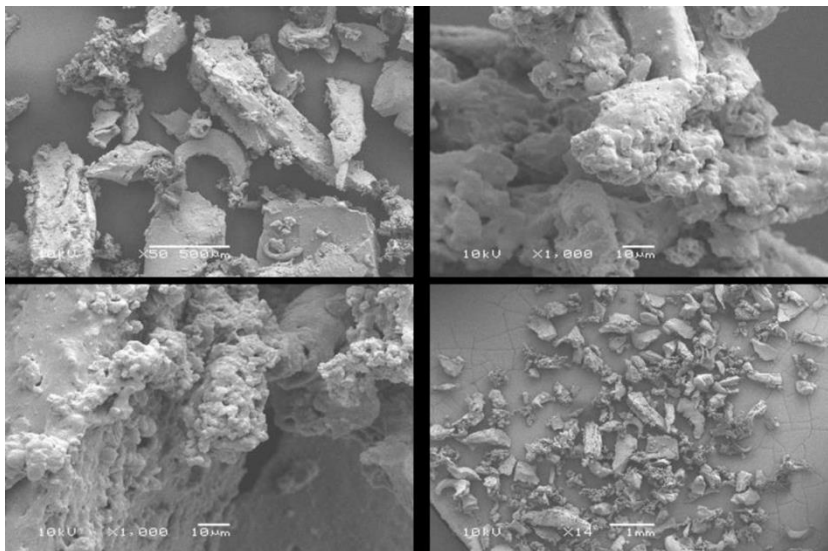Figure 2: The passing percent gradation of Crumb Rubber

Figure 3: SEM images for the CRM

2.2 RTR-MBs production

The RTR-MBs were blended at three different temperatures (160ºC, 180ºC and 200ºC), and two mixing times (60 and 140 minutes). The time at 200ºC required to reach the maximum viscosity for binders "S" and "H" (15 and 25 minutes respectively as shown in the results) were also used to produce RTR-MBs at 200ºC. The rubber percentage mass was kept constant for all RTR-MBs combinations, being 18% by bitumen weight which is equal to 15.25% by weight of total blend. This concentration was chosen based on previous studies (Celauro et al. 2012, Wang et al. 2012, Presti and Airey 2013) which showed that increasing the CRM content from 20% to 25% (by weight of bitumen) has resulted in only minor changes of high temperature viscosity and low temperature stiffness. The processing conditions and rubber concentration were selected to match the commonly used specifications; ASTM D6114, CalTrans Bitumen Rubber User Guide, SABITA Manuel 19, VicRoads and APRG Report No. 19 and Austroads User Guide and previous literature (Memon 2011).

The following protocol was used for each blend:

(1) About 200g of neat bitumen (contained in a tin) was heated at 160ºC in the oven for 45 minutes. The fluid test sample was then stirred and 10g of bitumen transferred into separate sample containers (Brookfield viscometer cylinders/tubes). The sample containers (tubes) were then placed in a sealed container to protect them against any unwanted oxidation and then left to cool down to room temperature.

(2) Each of the sample containers (tubes) was then placed into the preheated temperature control unit of the Brookfield viscometer (preheated to the selected mixing temperature) and given 15 minutes to obtain equilibrium temperature throughout the sample.

(3) The designed rubber quantity (1.8g to achieve the 18% rubber content by weight of bitumen) was gradually added while manually stirring the blend with a thin spatula. All the rubber was fed into the sample container (cylinder) within 5 minutes.

(4) After that, the preheated DHI was lowered into the blend of bitumen and rubber and rotated at a constant speed of 100 rpm. Viscosity was constantly monitored throughout the mixing time. The mixing time was taken as the time from when the impeller started rotating.

(5) Once the designed blending time was reached, the sample container was taken out of the temperature control unit and the RTR-MB poured directly into a 10 ml vial. The vial was left to cool down to room temperature before being sealed and stored in a cold store at 5°C for future DSR testing. All RTR-MBs combinations were produced using these identical conditions in order to eliminate any unwanted side effects.

(6) The different RTR-MBs were labelled in such a way to give information about the processing conditions and materials. For example, the code of "S18TR-N-180-60" means, soft bitumen "S" blended with "18" percentage of normal tyre rubber "TR-N" at processing temperature of "180" °C and mixing time of "60" minutes.

(7) At least two replicates of each RTR-MB blend were produced and the average values are reported.

2.3 Rubber dissolution test

A gravimetric procedure was used to determine the CRM particles that dissolve into the bitumen at the different processing conditions. As about 98% of CRM particles are

larger than 212µm, they can be extracted using a #200 mesh (75 µm) sieve. Using a #200 sieve (75µm) to determine the dissolution state of CRM particles has been proving to be a good method with high repeatability (Ghavibazoo and Abdelrahman 2012). The assumption is that particles less than 75µm can be considered to be dissolved in the bitumen rather than present in the bitumen as solid intrusions. Increasing solubility of the CRM particles is usually associated with good storage stability with the test being undertaken to identify the final storage stability of the RTR-MB product and the overall state of the material (Leite et al. 2001). The details of the procedure are as follows:

(1) Approximately 3g of RTR-MB was transferred into an Erlenmeyer flask and the mass of the sample determined to the nearest 1 mg.

(2) About 100ml of toluene was then added to the flask with continuous agitation until most lumps disappear and the flask was then place into a steam bath for 30 minutes.

(3) The solution was then strained through a pre-weighed #200 (75 µm) mesh and the retained insoluble rubber particles were washed with extra toluene until the filtrate flow was substantially colourless.

(4) The #200 mesh was then heated in an oven at 110°C for 30 minutes, removed from the oven and placed in a desiccator for 30 minutes and the mass determined to the nearest 0.1mg. The drying and weighing were repeated until constant mass is attained.

(5) The rubber that did not dissolve into the bitumen (rubber particles > 75 µm) was calculated by taking the difference in mass between the final (containing insoluble rubber particles) and initial (clean) #200 mesh. The percent of rubber dissolution was then determined based on the initial rubber content.

(6) Three replicates were made for each blend.

2.4 Dynamic Shear Rheometer (DSR)

The dynamic mechanical analysis (DMA) of the RTR-MBs was undertaken by means of a Kinexus Model Dynamic Shear Rheometer (DSR) supplied by Malvern Instruments Ltd. The RTR-MBs samples were tested under the following settings with at least two replicates:

- Oscillatory sweep frequency (0.1 – 10 Hz).

- Strain control mode within the LVE region (less than 1% strain), amplitude sweep strain controlled tests were done to check the LVE region.

- Multiple temperatures (30˚C - 80˚C at 10˚C intervals).

- Parallel plate geometry with 25mm diameter and 2mm gap to minimise the effect of rubber particles on the viscoelastic measurements. An investigation was done to check the effect of using different gaps and using 2mm gap was proved to give repeatable and reliable results

- All tests were conducted on unaged samples.

In addition to the oscillatory DMA tests, the Multiple Stress Creep Recovery (MSCR) test was also conducted on the RTR-MBs using a Malvern DSR CVO Model. The test consists of applying repeated creep-recovery cycles with 1 second applied creep shear stress followed by 9 seconds recovery period. At least two replicates were tested for each of the RMR-MBs. The test methodology follows the standard ASTM D 7405 procedure but instead of only using two shear stresses (0.1 kPa and 3.2 kPa), multiple stress levels are used to examine the stress sensitivity of RTR-MBs. The following sequence was used for the MSCR test:

- Isothermal temperature of 60˚C.

- Seven stress levels were used (100, 400, 1600, 3200, 6400, 12800 and 25600 Pa). The sequence was designed so that there were no rest periods between creep and recovery cycles or changes in stress level.

- Applying 10 cycles at each stress level.

- Plate geometry was 25mm diameter parallel plates with 2mm gap.

- All tests were conducted on unaged samples.

3. Results and discussion

3.1 Viscosity monitoring

Monitoring the viscosity of RTR-MBs constantly as a function of processing time and temperature is very beneficial in order to understand the actual physical change throughout the processing (production) of RTR-MBs. The increase in viscosity by adding the rubber is attributed to the rubber particles swelling which results in a reduction in the inter-particle distance as well as stiffening of the binder by reducing the oily fractions in the bitumen (adsorbed by the rubber particles).

Figure 4 shows the viscosity progression over time for both base binders "S" and "H" when interacted with the rubber at different temperatures. The viscosity readings from the Brookfield viscometer were recorded every 5 minutes for the first 60 minutes and then every 10 minutes for the next 80 minutes. The viscosity values for the base bitumen (binders "S" and "H") at the three processing temperatures (values given in Table 1) have also been included in the plots at a time of -5 minutes which corresponds to the 5 minute period required to manually add the rubber particles to the blend. Three parameters corresponding to the swelling rate (increasing viscosity with time), swelling extent (time to reach maximum viscosity) and dispersion/dissolution rate (decreasing

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viscosity with time) are quantitatively evaluated from the viscosity progression displayed by each binder in Figure 4 and are listed in Table 2. The swelling rate is defined here as the rate of viscosity gain with respect to time, and determined by taking the arithmetic average of tangents ($\partial v/\partial \tau$) of the viscosity progression curves (Figure 4) from the point of adding all the rubber up to the peak viscosity. The dissolution rate represents the decrease in viscosity with respect to the time and is derived by taking the slope of viscosity progression curves after reaching the peak viscosity.

It can be seen that all the RTR-MBs followed the same trend in terms of viscosity profile regardless of the type of base binder. The results also show that as the temperature increases, the rate of swelling increases (36 mPa.s/min for S18TR-N-200 compared to 17 mPa.s/min for S18TR-N-180) but the extent of swelling (maximum viscosity) decreases (Green and Tolonen 1977, Abdelrahman 2006). In addition, the RTR-MBs processed with binder "S" swelled and devulcanised at a faster rate than those produced with binder "H". This was more pronounced at 200°C where the swelling rate for binder "S" was almost doubled that for binder "H" and the time needed to reach the peak viscosity was 15 minutes compared to 25 minutes. The explanation for this is that the softer base binder (lower viscosity) with higher aromatic content has a higher rate of penetration (diffusion) into the rubber particles. Also the elevated temperatures lead to more rapid mass transfer and chemical reaction rates and would reduce the cross-link density of the rubber making the solvent diffuse into the rubber network more readily (Green and Tolonen 1977, Rahman 2004). Generally, the time needed to achieve the desirable swelling state and/or digestion state is significantly reduced by increasing the processing temperature. However, production at 160°C was shown to be too low to have a significant effect on the devulcanisation and depolymerisation of the rubber particles regardless of the base bitumen.

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The viscosity of all the RTR-MBs, blended using bitumen "S" at the end of mixing time (140 minute) for each mixing temperature, was measured at three temperatures (160, 180 and 200°C) in order to evaluate the influence of a constant test temperature on the final viscosity of the RTR-MBs as shown in Table 3. The viscosity results in Table 3 show, at each of the three test temperatures that the binders produced at 180°C and 200°C have a lower viscosity than those produced at 160°C due to the devulcanisation and depolymerisation of the rubber particles at these higher processing temperatures.

The effect of the devulcanisation and depolymerisation of the rubber particles on the overall viscosity of RTR-MBs can be explained qualitatively by applying the equation derived by Einstein for the viscosity of a dilute suspension of rigid spheres (Glover et al. 2000):

$$\eta = \eta_{(s)} (1 + 2.5 \, \Phi) \tag{1}$$

Where η is the bulk viscosity of the matrix, $\eta_{(s)}$ is the viscosity of the solvent, and φ is the volume fraction of the spheres. For CRM processed at 200°C there is a reduction in rubber particle size as demonstrated by the dissolution test results presented in the following section. This leads to a lowering of the effective volume fraction φ and therefore a decrease in the matrix viscosity η. Although, the liquid phase viscosity $\eta_{(s)}$ would definitely increase due to the polymeric components (<75μm) being released from the CRM and becoming dissolved in the base binder, their relative effect is very small compared to the particulate effect. Support for this conclusion can be found in work undertaken by Thodesen and his co-workers which revealed that the effect of rubber particles on viscosity when considered as inert filler is 12 times greater than the effect of rubber dissolved in the base bitumen (rubber-bitumen interaction) (Thodesen et al. 2009). It should be mentioned that the Einstein equation is able to accordingly

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represent suspensions with low concentrations where the distance between particles is much bigger than the filler radius, while the Frankel equation is able to predict the viscosity behaviour of suspensions with high concentrations (Hesami et al., 2012).

Although, increasing the binder viscosity at high in-service temperature is favourable to improve rutting resistance, high viscosity at mixing and compaction temperatures imposes large difficulties in the production of asphalt mixtures. Controlling the volumetric properties of these asphalt mixtures becomes extremely challenging resulting in high air voids, or to counter this, excessively high mixing temperatures are required which could cause emission problems and further harden the bitumen. While the reduced viscosity of RTR-MBs processed at (200°C-140min) would be beneficial at mixing and compaction temperatures, the lower degree of modification of the final product would be concern in the final asphalt mixture.

Many researchers have demonstrated that the optimum blending time to give the most desirable material (good rutting resistance) is the time at which the viscosity reaches its peak (Kandhal 1992, Memon 2011, Celauro et al. 2012, Presti and Airey 2013). However, in the following sections of this study, a more detailed rheological assessment of the final RTR-MBs will be undertaken to prove or disprove this assumption.
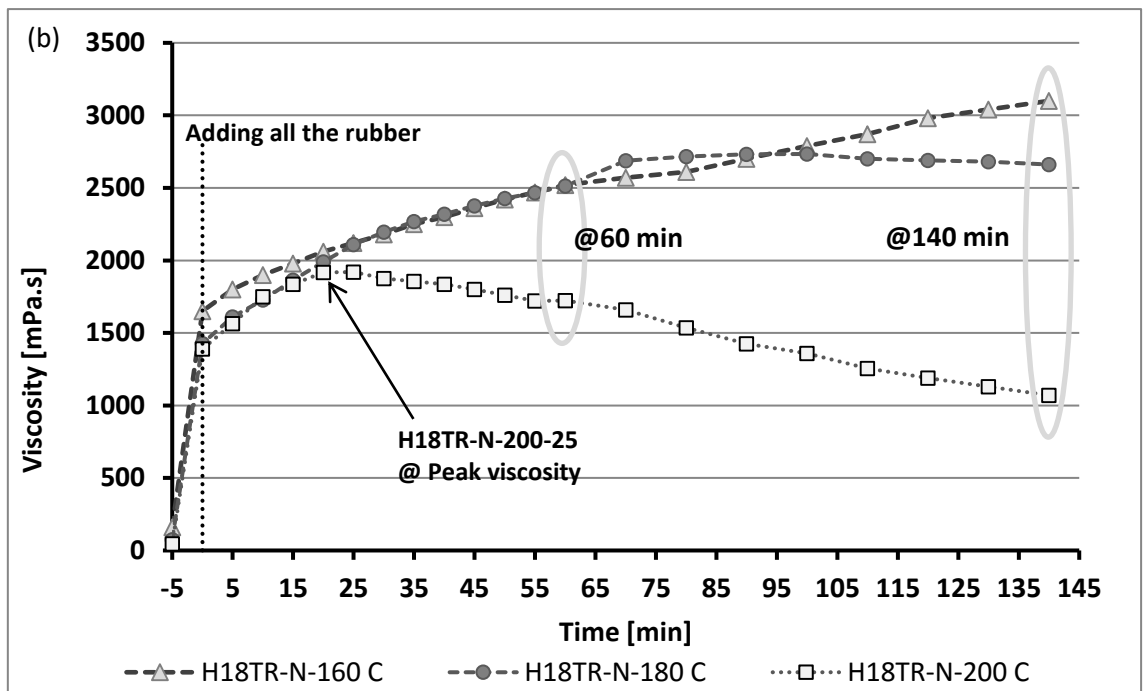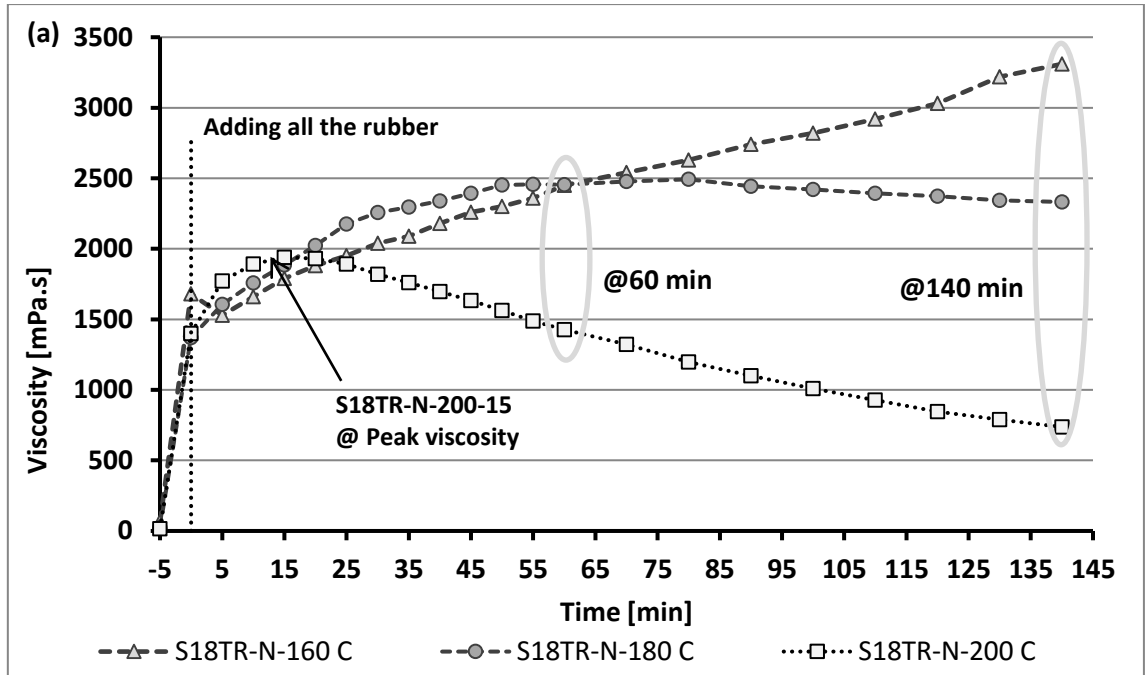
Figure 4: Viscosity progression over time (a) RTR-MBs produced using bitumen "S" and (b) RTR-MBs produced using bitumen "H"

Table 2: Quantitative parameters associated with the interaction process

Code	Swelling rate (mPa.s/min)	Swelling extent (min)	Dissolution rate (mPa.s/min)	Peak viscosity mPa.s	Final viscosity mPa.s @140min

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S18TR-N-160°	14	----	----	3310	3310
S18TR-N-180°	17	80	2.7	2492	2331
S18TR-N-200°	36	15	9.6	1940	737
H18TR-N-160°	12	----	----	3100	3100
H18TR-N-180°	16	90	1.8	2730	2660
H18TR-N-200°	21	25	7.4	1920	1070

Table 3: The viscosity of RTR-MBs produced using bitumen "S" measured at different temperatures using the modified impeller (Dual Helical Impeller DHI).

Test temperature	Rotational viscosity (mPa.s)		
	S18TR-N-160-140	S18TR-N-180-140	S18TR-N-200-140
160 °C	3220	2950	1810
180 °C	2520	2270	1190
200 °C	1940	1480	740

3.2 Rubber dissolution

The amount of rubber dissolution is proportional to the amount of rubber passing through mesh #200 (75 μm). It should be mentioned here that the analysis of "dissolution percentage" is more for qualitative purposes rather than quantitative purposes because there may be some rubber particles passing the sieve that have been reduced in size to less than 75 μm but are not completely dissolved in the bitumen. Figure 5 shows the average CRM dissolution results for the six processing combinations of 3 temperatures and 2 mixing times. The range bars represent the maximum and minimum values for the replicates. It can be seen that rubber dissolved into the bitumen is strongly dependent on the processing temperature. As the processing temperature increases, the dissolution percent of CRM increases. The results also show that increasing the processing time results in an increase in the dissolved percentage of CRM. Increasing the processing time from 60 to 140 minutes at 200°C led to a considerable amount of rubber being dissolved into the bitumen. The difference

between the two base binders "S" and "H" on the dissolution percentages is apparent at lower processing conditions. Softer bitumen "S" is better at dissolving the rubber than stiffer bitumen "H" due to its higher rate of diffusion into the CRM (seen with the swelling phase). However, at higher processing conditions (200°C-140min), the effect of base binders on dissolution percentage was significantly reduced as the influence of temperature and extended processing time (reduced cross-link density of the rubber and thereby greater solvent diffusion into the rubber network) is far greater than the viscosity of the base binders.
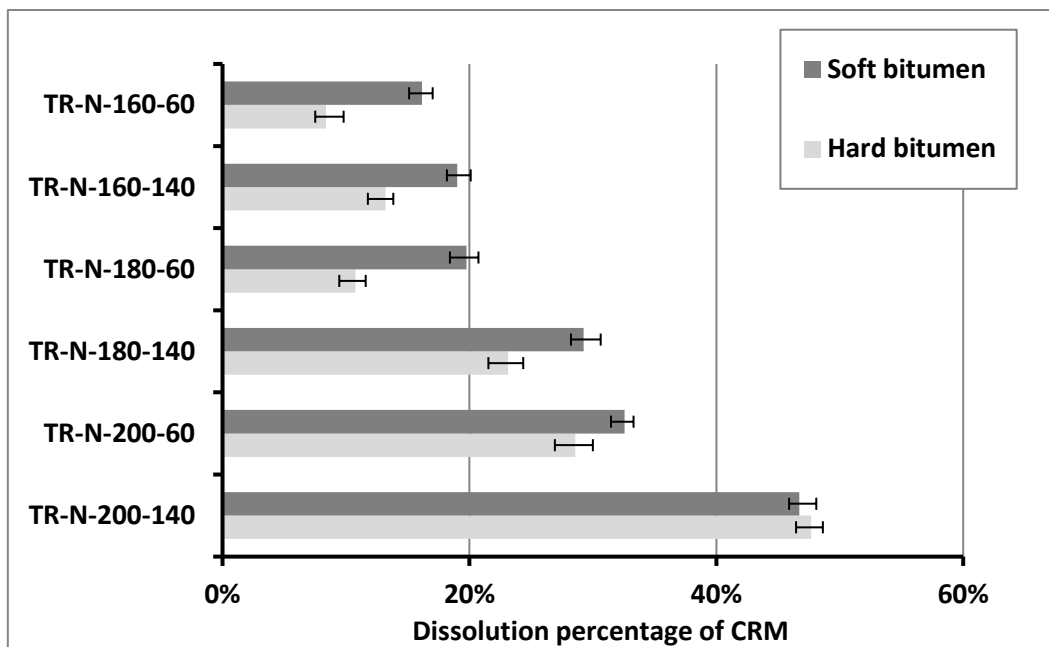
Figure 5: Rubber dissolution percentage

3.3 Dynamic Mechanical Analysis (DMA)

3.3.1 Master Curves

It is important to evaluate the rheology and viscoelastic properties of the final RTR-MBs under different loading times and temperatures. This has been achieved by means of DMA to define the stress-strain-time-temperature response of the binders. Master curves of complex modulus |G*| at a reference temperature of 30°C were produced for

the RTR-MBs using the Time Temperature Superposition Principle (TTSP) and William, Landel and Ferry (WLF) equation. Figure 6 shows the master curves for the RTR-MBs produced using binder S while Figure 7 shows the data for binder H.

It is clear from Figures 6 and 7 that the processing (mixing) conditions have influenced the final properties of the RTR-MBs. The master curves show that rubber modification has resulted in a significant increase in the complex modulus at low frequencies (equivalent to high temperature response) and consequently the RTR-MBs can be expected to have enhanced rutting behaviour. This increased stiffness can be attributed to the prevalence of the rubber (polymer) network formation which is stiffer and more elastic than the viscous phase of the base binders (Airey, Singleton et al. 2002, Navarro et al. 2005). However, the rubber modification is less effective within the base bitumen dominant areas (low temperatures and high frequencies) and the curves tend to coincide at high frequencies, particularly for the RTR-MBs processed with "H" bitumen.

In terms of the effect of production conditions, it can be observed that the higher processing condition (200ºC-140min) has led to a substantial reduction in complex modulus within the rubber dominant areas (high temperatures and low frequencies) due to the partial degradation of the polymer network by the means of depolymerisation and devulcanization (Abdelrahman and Carpenter 1999, Attia and Abdelrahman 2009). These binders can be considered to be over processed. However, these processing (mixing) conditions have reduced the complex modulus at low temperatures and high frequencies relative to the other RTR-MBs which may be desirable for fatigue and low temperature cracking resistance. The higher processing conditions would normally cause oxidative age hardening of base bitumen and increase complex modulus but this effect is not as dominant as the depolymerisation and devulcanization of the rubber

particles and the subsequent reduction in complex modulus. Additionally, the lighter

components which were absorbed by the rubber during the swelling process would be

released back into the liquid phase of the bitumen during the

depolymerisation/devulcanization process further decreasing complex modulus

(Abdelrahman and Carpenter 1999).

The results also show that the RTR-MBs processed at 160°C and 60 minutes have lower

complex modulus demonstrating a lower degree of swelling (under processed). There is

no significant difference for the other processing (mixing) conditions in terms of the

|G*| master curves.
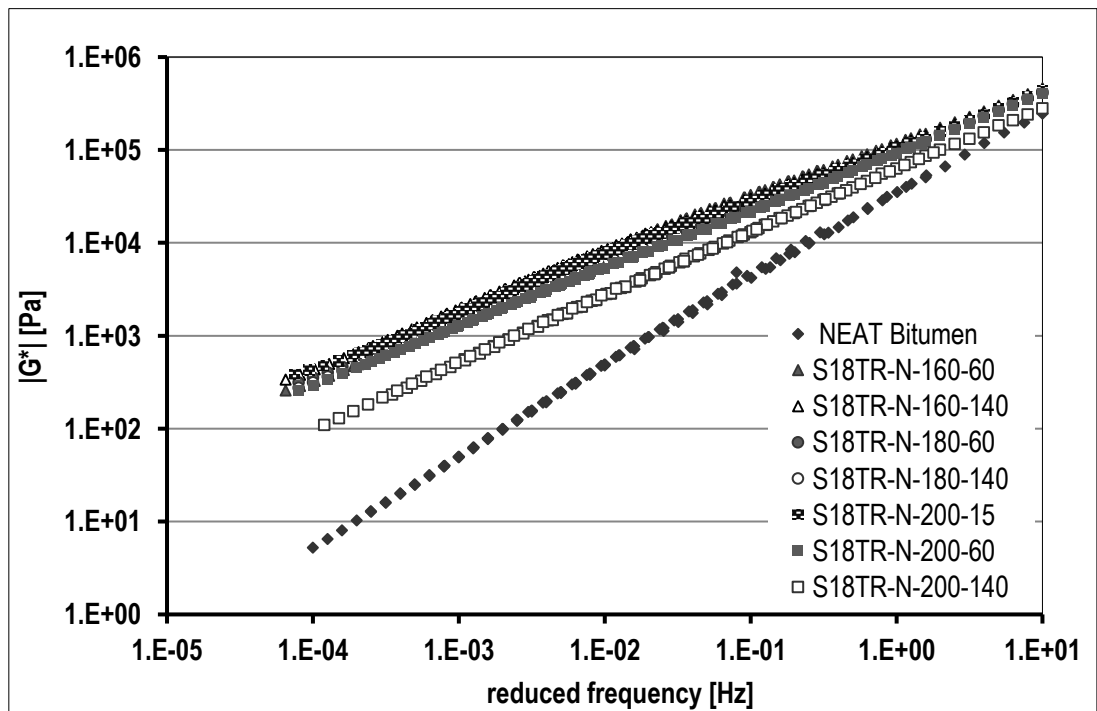
Figure 6: Master curve at 30 °C of RTR-MBs produced using bitumen "S"
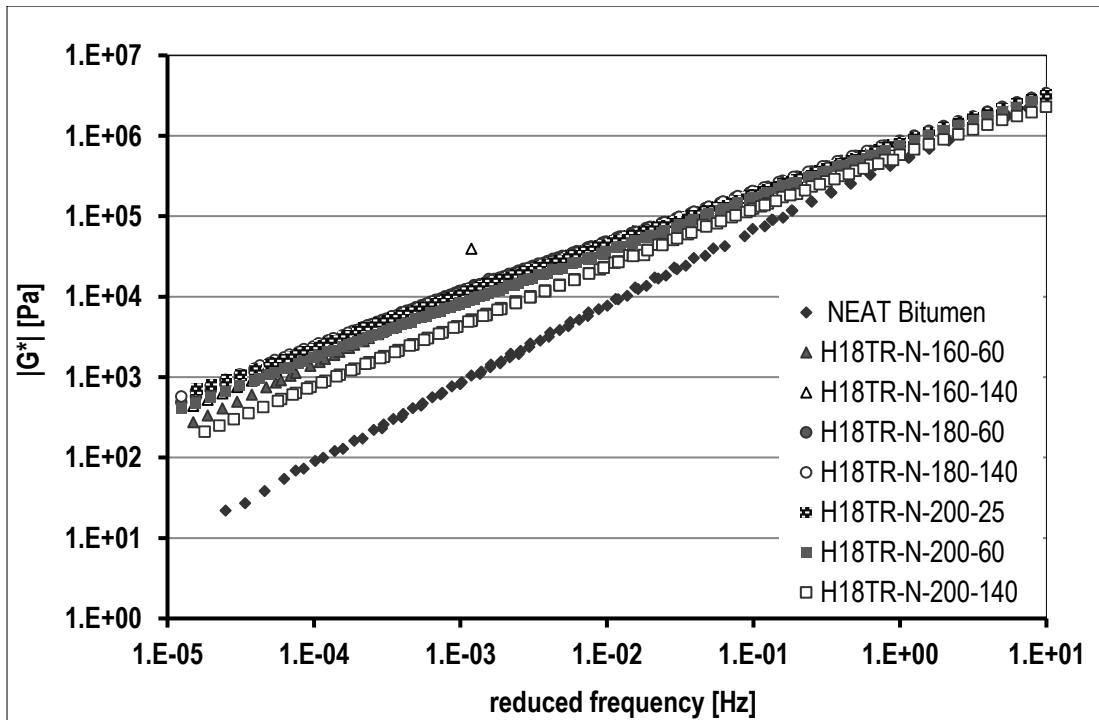
Figure 7: Master curve at 30 °C of RTR-MBs produced using bitumen "H"

3.3.2 Black Diagrams

Black diagrams can be used to show the relation between stiffness and viscoelasticity of materials without the need to apply shift factors to the raw data as required for master curves (Airey 2002). Therefore, the presence of the polymer structure within the RTR-MBs and their thermo-rheological properties can be conveniently distinguished in one plot. Figures 8 and 9 show a shift for the RTR-MBs to lower phase angles and slightly higher complex modulus compared to the base bitumens. The increased complex modulus with decreased phase angle at higher temperatures can be attributed to the addition of CRM and the establishment of a rubber (polymer) rich phase. The complexity of RTR-MB Black curves suggests microstructural modifications due to the addition of rubber.

The Black curves for RTR-MBs produced at higher processing conditions (200°C-140min) for both base binders show a significant change in shape with less curvature

and higher phase angles. This suggests that processing the RTR-MBs at higher temperatures and extended times results in a certain amount of rubber being dissolved/dispersed into the base bitumen (as shown in the dissolution tests) leading to the production of a more compatible material that has a smoother transition from solid-like to liquid-like behaviour. The results also show that materials processed at blending times corresponding to the maximum swelling extent (200°C-15min and 200°C-25min) have the lowest phase angles within the rubber dominant areas (high temperatures and low frequencies). On the other hand, the Black curves associated with RTR-MBs produced at low processing conditions (160°C-60min) are more complex and also have higher phase angles. The higher phase angles of these products in comparison to other conditions can be attributed to the higher amount of light fractions still within the bitumen as the undissolved rubber particles were not completely swelled.

When the effects of different base binders are compared, it can be seen that the degree of complexity in the curvature is somewhat higher for CRM processed using soft bitumen "S" than "H". Also, when the data inside the highlighted ellipses in Figures 8 and 9 are examined, the black diagram of "S" has phase angles which extend to lower values in comparison to base binder "H". According to the literature, bitumen with higher aromatic content is more compatible with CRM and better at devulcanising the rubber during the interaction process while bitumen with higher molecular weight fractions or asphaltenes is better at depolymerising the rubber (Billiter et al. 1997). As depolymerisation can result in the degradation of the internal rubber network, the higher phase angles associated with the binder "H" RTR-MBs is to be expected.
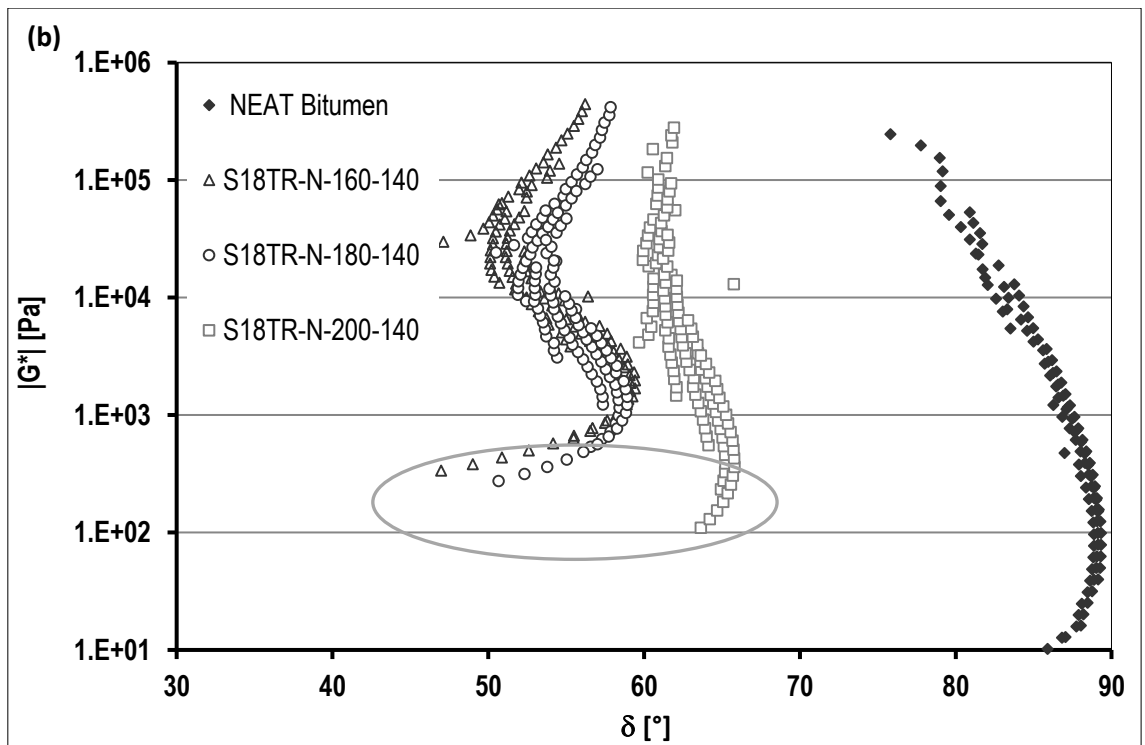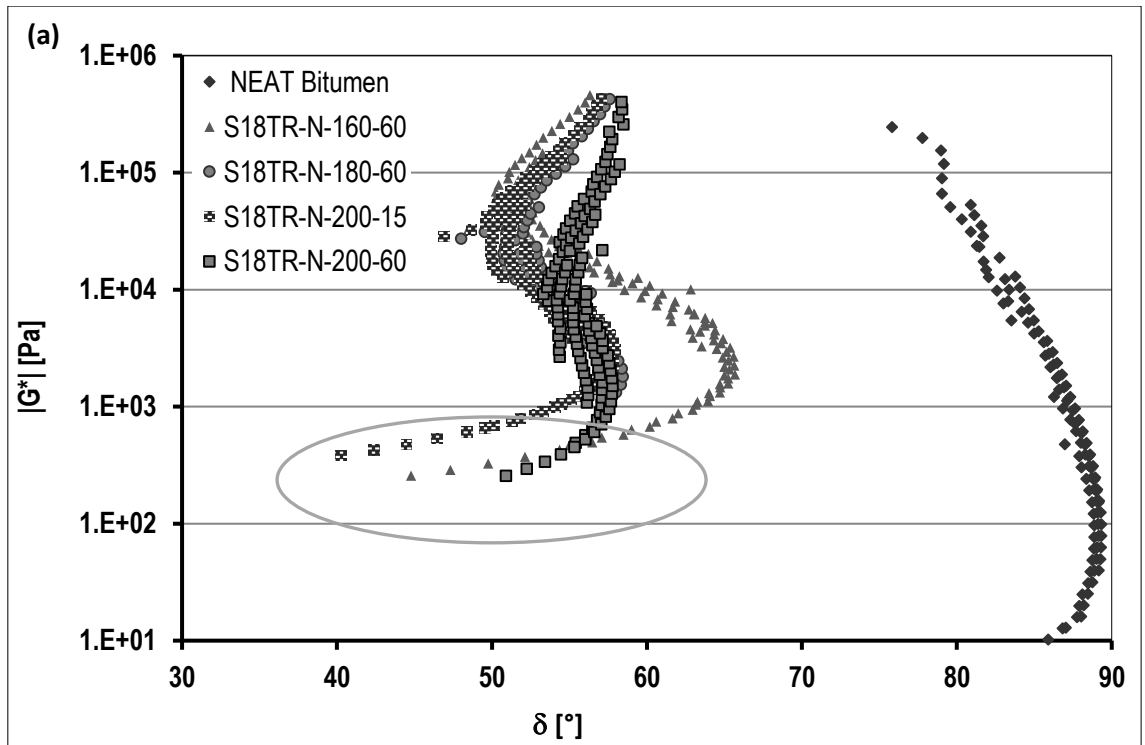
Figure 8: Black diagram of RTR-MBs produced using bitumen "S", (a) at 60min and
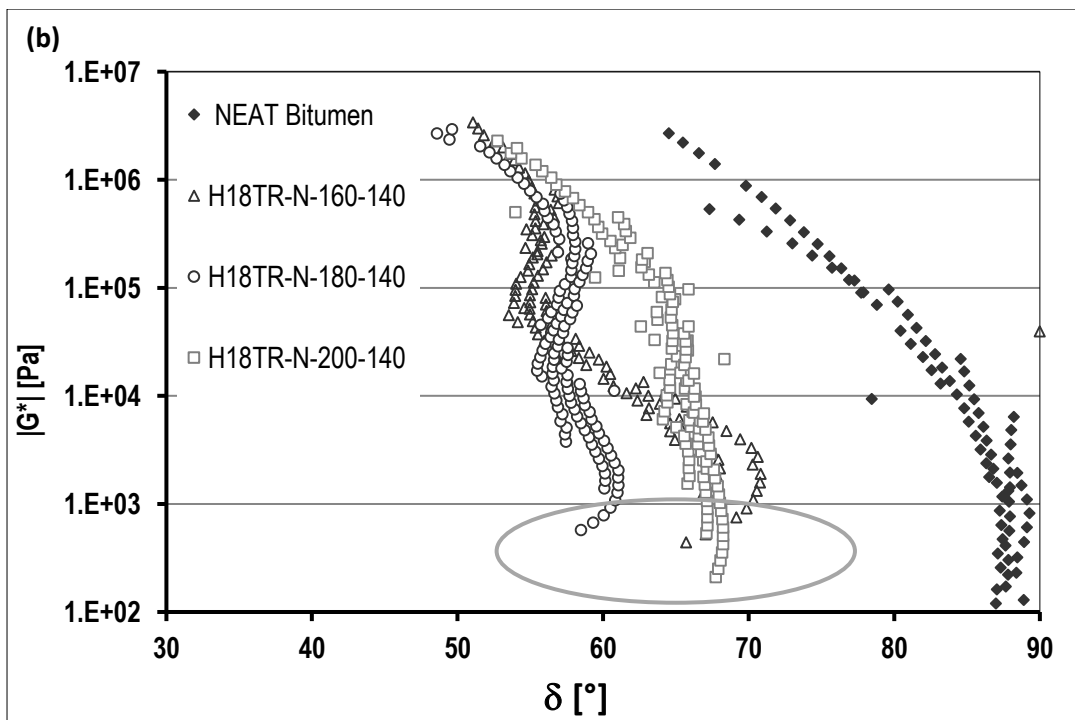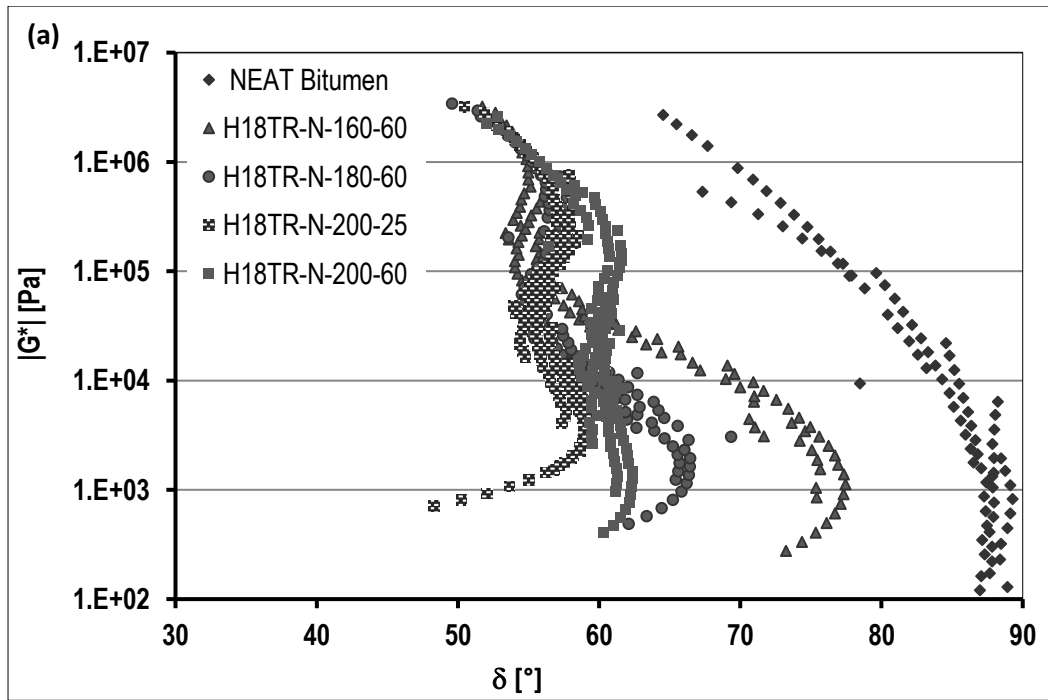15min processing time and (b) at 140min processing time

Figure 9: Black diagram of RTR-MBs produced using bitumen "H", (a) at 60min and 25min processing time and (b) at 140min processing time.

3.4 Temperature Susceptibility

The evolution of the loss tangent with temperature is used here as a viscoelastic

function to examine the temperature susceptibility of the RTR-MB materials. An extended plateau region or flattening of the tan δ curves over a wide range of intermediate temperatures is desirable for better temperature susceptibility (González et al. 2006, Navarro et al. 2009, Nejad et al. 2012). A reduction in temperature susceptibility is important to produce a material that is able to resist rutting at high temperatures while maintaining good fatigue cracking resistance (González et al. 2006). Figures 10 and 11 show the tan δ values over a range of temperatures between 30 and 80°C at a constant frequency of 1Hz. The range bars represent the maximum and minimum of values of tan δ for different replicates.

It can be seen that processing conditions of (180°C-140min), (200°C-60min) and (200°C-15, 25min) have produced RTR-MBs with the lowest temperature susceptibility as indicating by their flat curves. Although, higher processing (200°C-140min) resulted in comparatively higher tan δ values, these RTR-MBs still demonstrated good temperature resistance properties as shown by the low slope of their tan δ versus temperature relationship. The RTR-MBs produced at the low temperature processing condition of 160°C showed the largest change in tan δ over the temperature range presented in Figures 10 and 11 and therefore the highest temperature susceptibility of all the binders. Even though the base binder "H" is stiffer and more elastic than "S", the RTR-MBs produced using the soft bitumen "S" generally had lower tan δ values than RTR-MBs produced using the hard bitumen "H". This can be attributed to the difference in swelling and dissolution mechanisms of CRM with the "S" binder being more compatible with the CRM particles and the modification being more dominant.
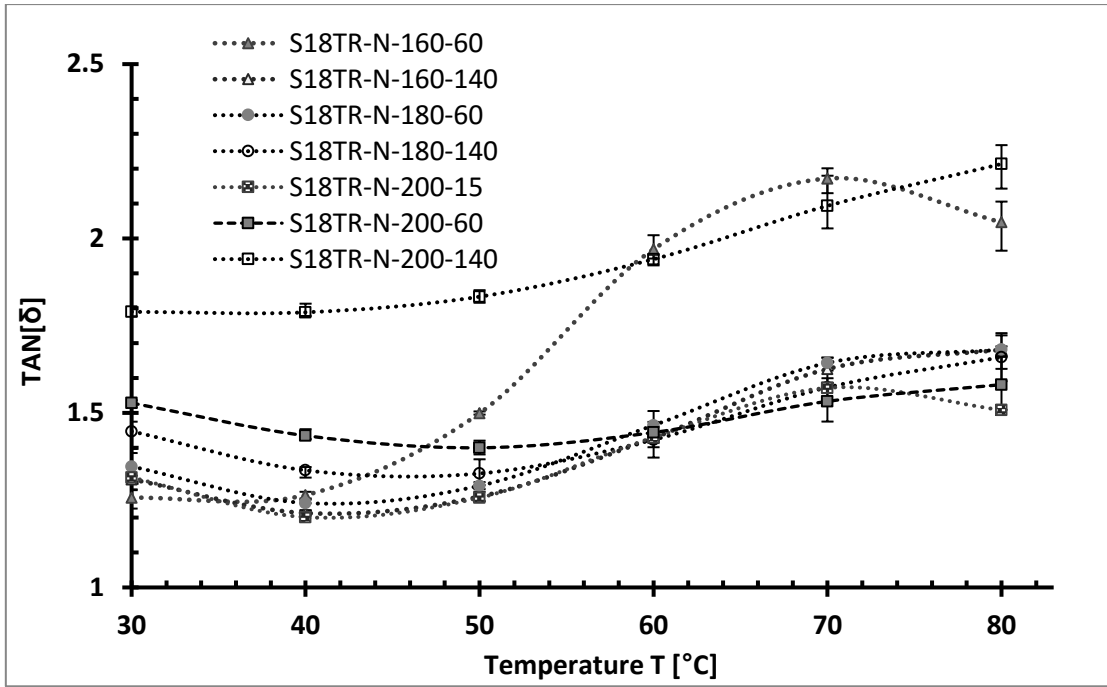
Figure 10: Tan(δ) at 1Hz of RTR-MBs produced using bitumen "S"
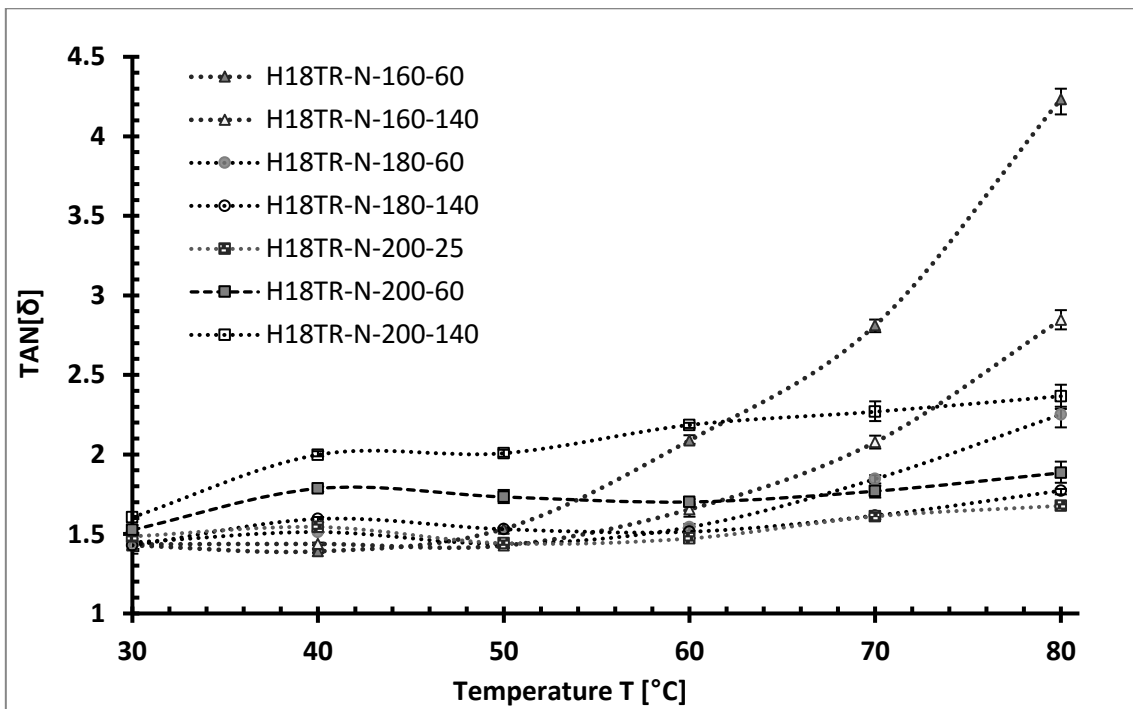

Figure 11: Tan (δ) at 1Hz of RTR-MBs produced using bitumen "H"

3.5 Multiple Stress Creep and Recovery (MSCR)

3.5.1 Non-recoverable compliance

Non-recoverable creep compliance (Jnr) has been recommended as an alternative to the current SHRP parameter $|G^*|/\sin \delta$ when assessing the permanent deformation performance of different bitumens (D'Angelo et al. 2007). Jnr has the ability to predict the improvement that is imparted by modification, and it is also more sensitive to the stress dependence of modified binders making it suitable for specification purposes for both neat and modified bitumen (D'Angelo 2009, Tabatabaee and Tabatabaee 2010). Measuring the Jnr of binders at high stresses and outside the linear viscoelastic region is also conceivably more appropriate when considering the rutting behaviour of asphalt mixtures as the strains in binder films on aggregate surfaces can be several hundred times greater than the overall average strain of the mixture.

Figures 12 and 13 show the results of Jnr (average value for the 10 creep and recovery cycles) over a wide range of stresses between 100 Pa and 25,600 Pa at a test temperature of 60ºC. The results clearly highlight the significance of stress dependency in RTR-MBs with stress dependency over all stress levels being more apparent in RTR-MBs processed using the soft bitumen "S". The RTR-MBs processed using the hard bitumen "H" were less dependent on the stress with values of Jnr being relatively stable up to a stress level of approximately 1.60 kPa after which there is evidence of an inflection point in the material response and the presence of non-linearity at the higher stress levels.

The Jnr values also captured the effects of processing conditions with the materials produced at (180ºC-140min), (200ºC-15min) and (200ºC-25min) all performing very well as indicated by their low Jnr values. Good results were also seen for the soft

bitumen "S" for RTR-MBs produced at (180°C-60min) and (160°C-140min). The higher Jnr values of the RTR-MBs produced at high processing conditions (200°C-140min) indicated that these conditions lead to some breaking of the cross-linking rubber (polymer) network by means of devulcanization and depolymerisation. At the other extreme, higher Jnr values at low processing conditions of (160°C-60min) suggest incompleted interaction (insufficient swelling) between CRM and base binder.
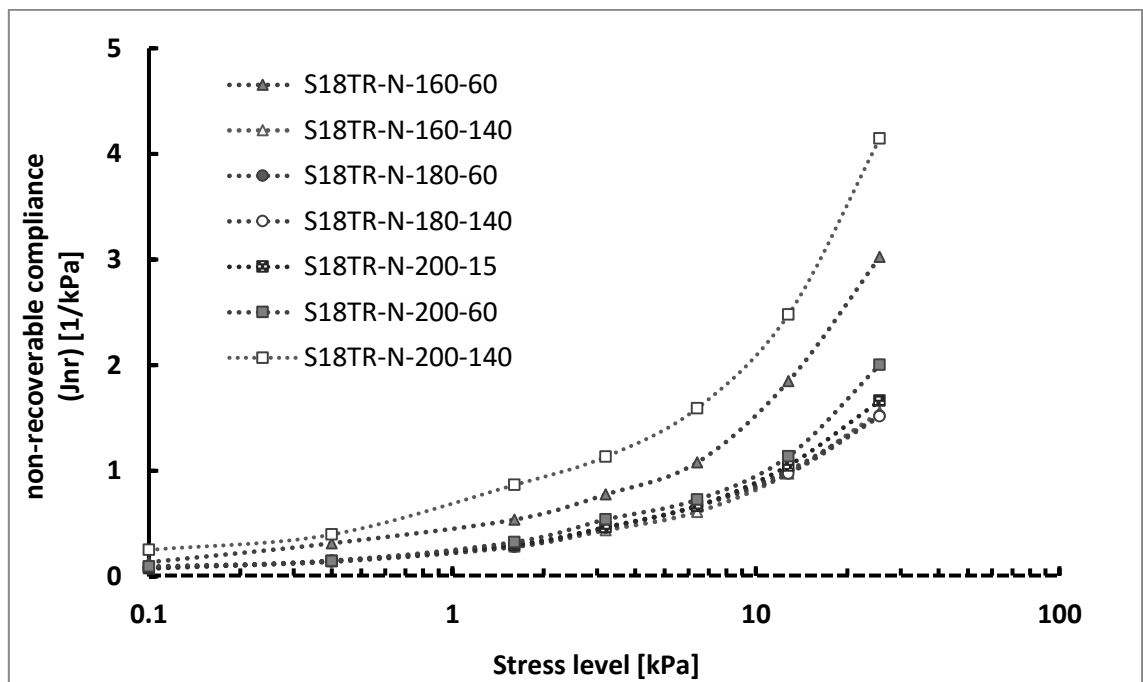

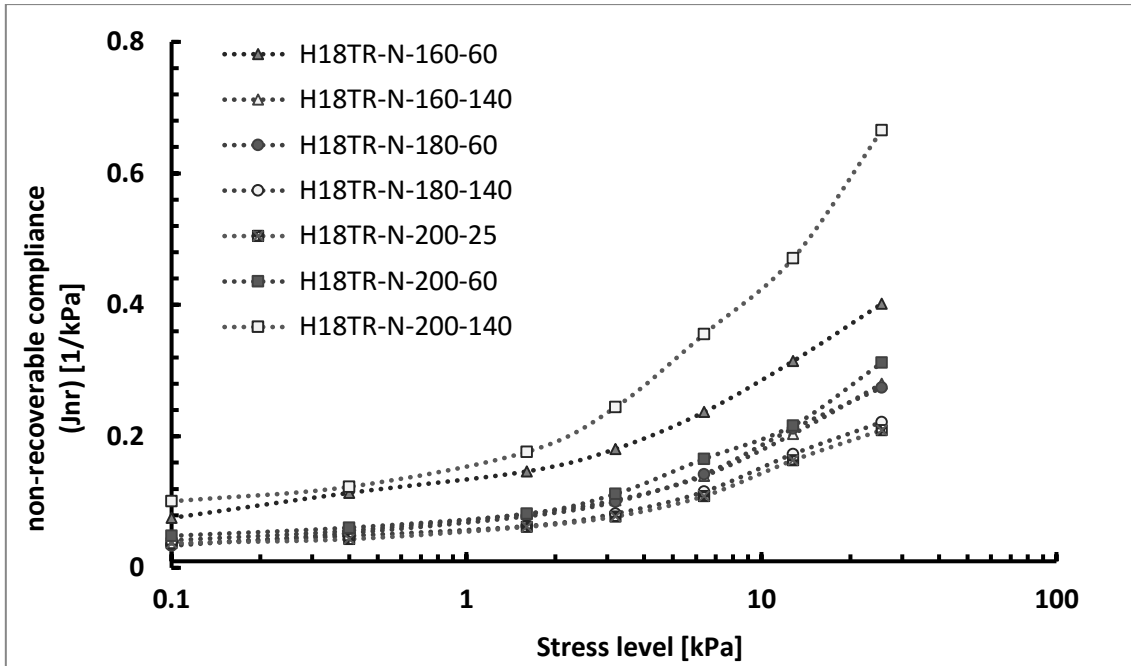Figure 12: Jnr of RTR-MBs produced using bitumen "S"

Figure 13: Jnr of RTR-MBs produced using bitumen "H"

3.5.2 Percentage recovery

Providing information about elastic recovery in addition to the non-recoverable compliance, stress sensitivity and non-linearity behaviour of modified bitumens is another advantage of performing the MSCR test. The average percentage recovery of 10 cycles at three stress levels (0.1, 3.2 and 6.4 kPa) is presented in Figures 14 and 15 with the error bars denoting the standard deviation of the 10 cycles. The results show that RTR-MBs processed at (180°C-140min) and (200°C-60min) have the highest elastic response compared to the other RTR-MBs produced at the other conditions. Additionally, these conditions maintained a high elastic recovery across all the stress levels. It can be seen that as the stress level increases, the difference in recovery response of the different RTR-MBs becomes more significant.

In terms of the effect of base binder, the different processing conditions modified the RTR-MBs in the same trend with the only difference being that the RTR-MBs produced using soft bitumen failed to maintain high elastic response at the higher stresses in comparison to the "H" bitumen. A limit of 15% reduction in percentage of recovery from 0.1 to 3.2 kPa is considered acceptable for modified bitumen that has good elastomeric response (Morea et al. 2012). Thus, only the RTR-MBs processed using bitumen "H" at (180°C-140min) and (200°C-60min) fulfilled the 15% maximum specification which could be translated into a better rutting resistance. The results also highlight that characterising the material within only the linear viscoelastic region is not enough for an appropriate material ranking. Figure 16 is used by AASHTO TP 70-13 as an indicator of the presence of an acceptable elastomeric polymer. The average percent recovery at 3.2 kPa, versus the average non-recoverable creep compliance at 3.2 kPa was plotted on the graph. All the RTR-MBs fell above the line indicating an acceptable elastomeric polymer apart from those produced at (160°C-60min).
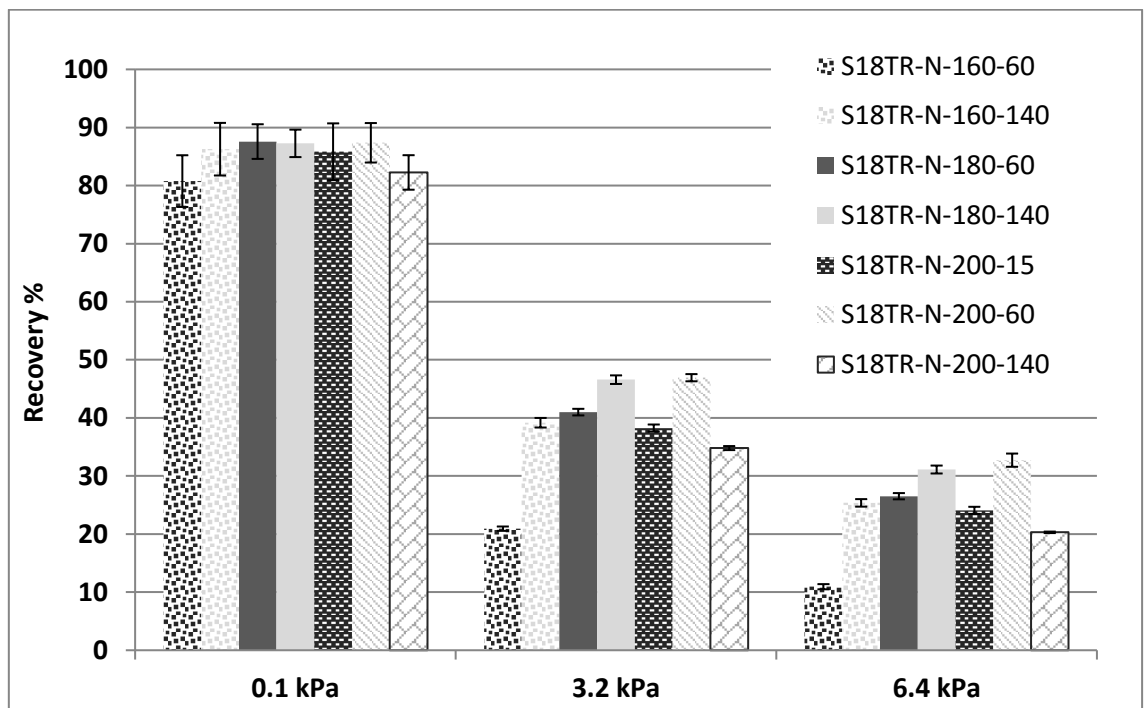

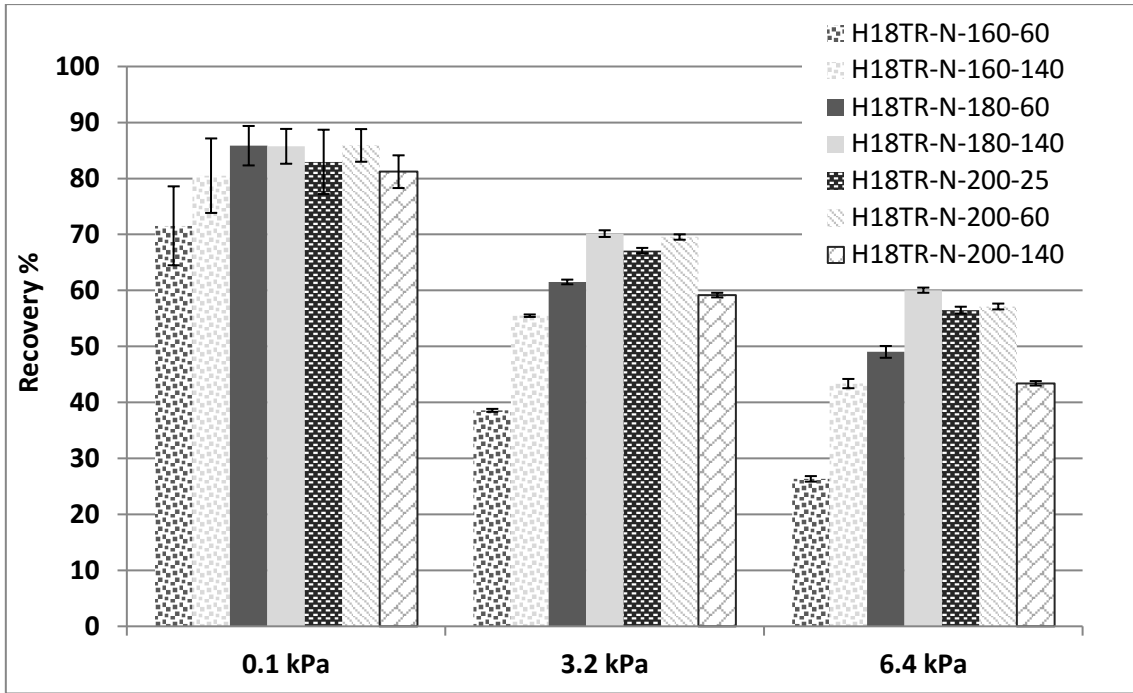Figure 14: Recovery of RTR-MBs produced using bitumen "S"

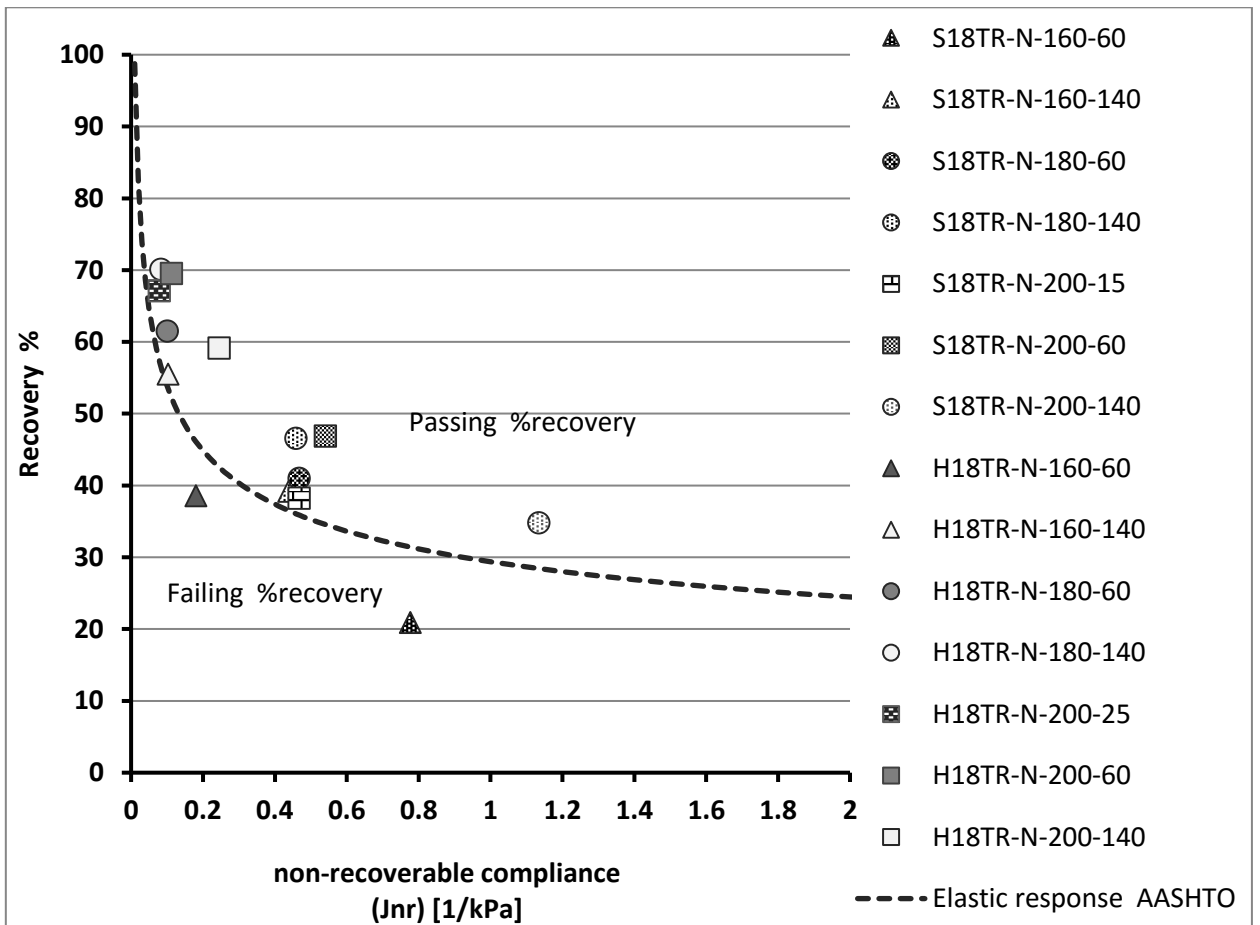Figure 15: Recovery of RTR-MBs produced using bitumen "H"

Figure 16: The elastic response of RTR-MBs produced using bitumen "S" and "H"

4. Conclusions

RTR-MBs were successfully produced in the laboratory by using the Brookfield rotational viscometer and a modified impeller (Dual Helical Impeller (DHI)) that allowed a reliably control of the blending temperature as well as keeping the rubber particles evenly dispersed throughout the production process. Three mixing temperatures ($160^{o}C$, $180^{o}C$ and $200^{o}C$) and two mixing times (60 and 140 minutes) were used to produce the different RTR-MBs which all consisted of 18% CRM by bitumen mass. Two additional mixing times (15 and 25 minutes) were also included at $200^{o}C$ as these times were associated with the peak viscosities for RTR-MBs produced at this temperature. The rheological properties of the final RTR-MBs were determined by means of standard Dynamic Mechanical Analysis (DMA) oscillatory and Multiple Stress Creep Recovery (MSCR) testing using a dynamic shear rheometer (DSR). The main conclusions that could be drawn based on the laboratory investigations in this research are:

(1) The tools used to produce RTR-MBs give an excellent opportunity to effectively investigate the many variables associated with the manufacturing of RTR-MBs using minimum material consumption for laboratory needs.

(2) RTR-MBs properties are largely dependent on their manufacturing conditions; therefore, carefully assessing these variables is essential to develop better materials. Based on the findings of this study, RTR-MBs manufactured at processing conditions of ($180^{o}C$-140min), ($200^{o}C$-15, and 25min) and ($200^{o}C$-60min) had the most desirable properties.

(3) Selecting higher mixing temperature ($200^{o}C$) can significantly reduce the time needed to reach the maximum swelling extent. This also develops superior rheological properties and potential saving in energy consumption.

(4) The results also highlight that selecting materials based only on the linear viscoelastic region properties is not sufficient and in some cases might be misleading. Therefore, characterising the non-linear behaviour in addition to linear is essential for an appropriate materials selection.

(5) Optimising the blending variables based only on the highest viscosity does not always guarantee best performance materials. Using rheological testing within and outside the LVE region would help increase understanding of the material and hence optimise effectively the processing conditions.

(6) The results have revealed that developing satisfactory performance characteristics in terms of percentage of recovery and temperature susceptibility can also result in the RTR-MBs being less sensitive to non-linear behaviour. This suggests that the interaction parameters of (180°C-140min) and (200°C-60min) led to the formation of an enhanced internal rubber (polymer) network structure within the RTR-MBs.

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