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- popis výroby modifikovaných asfaltů
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- vliv dlouhodobého a krátkodobého stárnutí na vybrané mechanicko-fyzikální vlastnosti



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# **The Effect of Ageing on Selected Asphalt Binders**

Master's thesis

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I hereby declare on my honour that this master's thesis has been written only by the undersigned and without any assistance from third parties. Furthermore, I confirm that no sources have been used in the preparation of this document other than those indicated in the thesis itself.

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## **Abstract**

*This paper discuss an evaluation of data measured on asphalt binder with penetration 50/70 at several states of ageing (non aged binder, RTFO, RTFO3x, PAV and RTFO6x). Different modified binders (base binder, RET and SBS + RET modification) were tested at each state of ageing. To determine the rheological properties of asphalt, performance tests (stiffness complex shear modulus measuring  $G^*$ ) and empirical tests (penetration test, ring and ball test, kinematic viscosity, force ductility and elastic recovery test) were performed. The thesis discusses the effect of combining RET and SBS modification with PPA, so it's evaluates each test performed for each type of modification and for each state of ageing. The paper also discusses the possibility to replace one cycle of PAV ageing with three cycles of RTFO, referred in this paper as RTFO3x.*

### **Keywords:**

asphalt binder, asphalt ageing, RTFO, PAV, polymer bitumen modification

## **Abstrakt**

*Tato disertační práce je zaměřena na vyhodnocení dat naměřených na asfaltu s penetrací 50/70 mm. Byly zvoleny dvě typy modifikací, dohromady tedy tři typy zkušebních vzorků (nemodifikovaný asfalt, RET modifikace s PPA a kombinace RET + SBS a PPA modifikace) a každá z těchto modifikací byla podrobena různým typům stárnutí (nezestárlý asfalt, RTFO, RTFO3x, PAV a RTFO6x). Pro objasnění reologických vlastností těchto modifikací při různých typech stárnutí byly provedeny empirické (penetrace, bod měknutí, vratná a silová duktilita) i výkonostní (DSR a BBR měření) normované materiálové zkoušky. Práce je zaměřena na vyhodnocení vlastností pojiva při kombinaci RET a SBS modifikace. Dalším úkolem této práce je diskuse na téma, zda je možné nahradit PAV stárnutí třemi cykly RTFO.*

### **Klíčová slova:**

asfaltové pojivo, stárnutí asfaltu, RTFO, PAV, modifikace pojiva polymery

### **Překlad názvu:**

Vliv stárnutí na vybraná asfaltová pojiva



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# Introduction

Nowadays a major part of asphalt produced during crude oil distillation process is used for the paving industry. Other uses of the material are in roofing industry, waterproofing, protective coatings, etc.

There are many aspects that can be used to evaluate an asphalt road. It can be cheap to built, durable, easy and cheap to maintain, recyclable, the construction process can be environmental friendly, and so on. Some of these criteria can be met with the technology of polymer modification. The technology itself is very complex and (as usually) there is no single all purpose resolution, in other words there is no asphalt modifier that would create an universal binder to be used in every road.

Generally there are two criteria upon which we decide what behavior we want to achieve from the asphalt binder. There is the climate in which the pavement is built and there is the traffic volume, which tends to continually increases (especially heavy trucks) during the last decades. If those facts are not fully taken in an account it results in premature pavement deterioration.

In order to properly evaluate the asphalt binder there are several types of standardized testing. One of the methods has been developed in 1992 by American association Strategic Highway Research Program (SHRP) ,established by the Congress of United States in 1987, is called Superpave (SUperior PERforming Asphalt PAVEments). This method brought significant improvement to the research and business also as it shows how to effectively classify the binder according to it's properties.

There are other methods and tests that are employed all around the world to specify the binder, although some of them does not take in account the material's properties degradation during the pavement's service life (bellow zero temperatures, high traffic volume, material's oxidation). Another aspect of standardized testing is that it is hard to find the correlation between the result of some tests and the real field performance of the material.

Asphalt binder's physical properties are strongly effected by the temperature at which are the tests performed, the oxidation (ageing) of the material and also by the binder's chemistry. The chemical composition is closely related to the source of the crude oil. The chemistry changes with the oxidative ageing, which can be performed in a laboratory. Irreversible changes caused by the oxidation (and thus the change of chemistry) result in higher stiffness (which can reduce rutting) and brittleness of the material which strongly affects cracking resistance (thermal and fatigue) of the pavement. So if the life cycle of the road is to be maximized and the construction and maintenance costs are to be



minimized it is necessary for the material to preserve its initial properties for as long as possible.

Unfortunately the chemistry of binder (and its change caused by ageing) is very complex so many methods in this field of research are focused on material's fraction separation and then closely investigation of each fraction. For the future research it would be beneficial to closely establish the relationship between the change of asphalt's chemistry, its physical and empirical properties and the pavement's field performance.

# 1. | Background

## 1.1 Asphalt Binder

### 1.1.1 History of Use

As a material asphalt has been known to the human kind since prehistoric times. Evidence of use comes from Syrian desert near El Kown ( an archaeological site), where a bitumen covered flint implements uncovered dates as early as 40 000 BC. There are also proofs of using asphalt as a hafting tool by the Neanderthals. Bitumen was widely used in prehistoric and ancient era as a sealing material for boats, containers, baskets, crates, etc., in Mesopotamia there are evidence of using bitumen as mortar at constructions of palaces and temples. A medical use is also noticed by the ancient Egyptians when they used to embalm th corpses of their dead or by the Muslim physicians who prescribed asphalt for skin ailments and wounds. [5], [3]

The first evidence of asphalt use as a road construction material is also from the ancient times from the Babylonia Empire, the asphalt was probably used as a stick between three layers of brick road. [5] The ancient Greeks were also familiar with this material (word asphalt comes from the Greek asphaltos). Also the Romans used asphalt to seal their baths and aequeducts. [10]

From ancient times there are many known natural deposits of crude oil, mainly in Middle East area. Not everywhere was the material prized or used though. In Mesopotamia the material was highly prized but not from every deposit though. Sometimes the quality of material could not compare, mainly due to its highly flammability and the bitumen could not be thickened with evaporation. This led the ancient civilization to invent the word *naphthu* (forerunner of *naphth* or *naft* in Arabic), useless flammable crude oil. The opposite was (highly prized) was *iddu* - the name means "the product from Id", which was one of the ancient cities on the south bank of Euphrates, where rich and quality natural asphalt springs were located. [3]

### 1.1.2 Asphalt chemistry

Asphalt binder, also known as bitumen, is a residue obtained from the distillation of crude oil. There is more than one way to produce an asphalt binder (e.g. blending binders from different crude stocks, using specific refining processes such as, air blowing, and using chemical or polymer modifiers) and it mostly depends on the economics of

the production. [22] The chemistry of bitumen is a complex and difficult issue and it is strongly effected by the place of origin of the crude binder and refining process used. The material mostly comprise carbon (82–88%) and hydrogen atoms (8–11%) and one or more heteroatoms of nitrogen, sulfur, and oxygen. The chemical makeup of the binder also dictates it's rheological and mechanical properties. Base binder can be divided into four fractions, saturates, aromatics, resins and asphaltenes, which is referred as SARA fractions.[7]

The relation ship between an exact chemistry of the asphalt and it's rheological performance can be indicates by chemical attributes such as polarity, molecular size or ionic character (acid, base, amphoteric). The most sufficient one, in order to describe the relationship between asphalt's chemistry and it's performance, is the polarity. The polar fractions in any given asphalt binder are typically classified into two groups, asphaltenes and maltenes. Further more, maltenes are separated into saturates, aromatics, and resins. So together with the asphaltenes they are referred to as SARA.[14] Each of these fractions have different polarity, the highest polarity have asphaltenes, the least have saturates, the other two fractions are between them. The polarity extremes (saturates and asphatenes) impacts plasticizing and softening of the material, whereas resins and asphaltenes contribute to the stiffness of asphalt.[22] A different approach to the chemistry's influence on the engineering properties of asphalt showed Robertson [13], he divides the chemistry into two parts, the molecular level and the chemistry of interaction among all molecular species in asphalt. Thus are the fractions divided to the polar ones and non-polar molecules. Polar molecules contributed to the elastic part of the binders' viscoelastic response while the non-polar contributed to the viscous part of the viscoelastic response.[22] The temperature is also a major aspect to consider, an asphalt with lower asphaltenes content is to be more stiff and brittle at lower temperatures. [9]

## 1.2 Polymer modification

Polymers are large molecules made by monomers (small molecules) which chemically reacts together. How a polymer behaves is based on sequence of monomers and on the distribution of theirs molecular weights .[2] Modifying bitumen by polymer increases the cost by 60 to 100 %, so the question is, why to do that and whether it is cost effective. There are several basic reasons for use of this technology:

- To obtain softer blends at low temperatures, which should leads to reduction of cracking
- To reach stiffer blends at high temperatures, which should enhance rutting resistance
- To reduce viscosity at layout temperatures
- To increase stability of binder Becker, Méndez, and Rodríguez [2]

To evaluate whether the technology pays for itself, the United States Federal Highway Administration (FHWA) has come up with a life cycle cost analysis of asphalt roads

containing rubber binders and other treatments. In other research, done in Ohio Department of Transportation in 2001, three binder (two of them were polymer modified) were compared. Both, fatigue and rutting resistance were enhanced by modification (SBS and SBR), according to this survey. [26]

According to their properties, polymers used to modify asphalt are elastomers (polyethylene, polypropylene or ethylene-vinyl acetate) or thermo plastic elastomers (SBS, SBES or SIS), although none of these are originally designed for asphalt modification. The first group (elastomers), began to be produced commercially before 1930s (firstly used in roof industry). They have little or no elastic component, which results in quick permanent deformation under load and in brittleness. On the other hand they show good high temperature properties and enhance the rutting resistance. The cost also is not that high when compare to other polymers (SBS and other elastomers). The phase separation problem also occurred. As for the second group, thermo plastic elastomers, they soften on heating and harden on cooling. Better resist to permanent deformation is also reported when stretching under load and elastically recovering once the load is removed. Another advantage of this kind of polymers is high resistance to heat, oxidation and ultra violet radiation. The compatibility problems occurred in some bitumens (ones with low asphaltene content) and the storage ability is another issue. The price is also high when compared with elastomers. [27]

There are two ways of incorporating polymer into crude binder - mechanical mixing and chemical reaction. [27] In order to achieve one phase where polymer is dispersed into the binder the polymer content have to be low - approximately less than 4% (it varies according to the polymer). As polymer content increases, phase separation may occur. The chemical composition of the actual binder is also very important - high asphaltene content decreases the compatibility between the binder and polymer and leads to asphalt gelation. [2], [27]

### 1.2.1 Adding PPA

Polyphosphoric acid ( $H_n + 2P_nO_{3n+1}$ ) is commercially offered acid with many applications throughout the industry, such as: water treatment, pharmaceutical synthesis, pigment production, flame proofing, metals finishing and one of it's major uses, asphalt modification. In 1973 there was a first patent of PPA as an asphalt modifier and there have been more since that. As a modifier, PPA increases binder's viscosity and high temperature stiffness, without affecting asphalt's penetration and with only a minor effect on low and intermediate properties., although it's real effect highly depends on the crude oil's source. The more highly polar fractions (mostly asphaltenes) asphalt contents the more PPA effects its stiffness. PPA also chemically reacts with a polymer (SBS) and positively effects binder's elastic response. The issue with using PPA as a modifier is, that the acid is hydrophilic material and easily absorbs water, so the content of the modifier needs to be less than 1%. [25]



## 1.3 Asphalt Ageing

In order to properly evaluate the material it is necessary to work with its correct form. It is not possible to determine the properties (p.e. rutting resistance, brittleness, etc.) of the asphalt pavement, in its first few years or at the end of the pavement's life cycle, by performing the tests with crude asphalt sample. As the material is exposed to the mixing and layout process during the construction works and as it is exposed to the weather and the traffic for 20 or more years, the chemistry of the binder changes and with it its rheological properties and field performance. For that reason there are two basic types of laboratory ageing introduced and standardized by American Association of State Highway and Transportation Officials (AASHTO). Both types of laboratory ageing were performed in the empirical part of this thesis.

### 1.3.1 RTFO

Short term laboratory ageing RTFO (Roll Thin Film Oven) simulates the changes that occur in chemistry of the binder during the process of mixing asphalt and gravel and the changes caused by the layout process during the construction works.

The test is performed by rotating a thin film of an asphalt sample ( $35\text{g} \pm 0.1\text{ g}$ ) in a double walled preheated electrical oven ( $163.0^\circ\text{C} \pm 1.0^\circ\text{C}$ ) for 75 minutes. Thus the material changes its physical properties and it can be evaluated as it will perform in a newly constructed road. [18]

### 1.3.2 PAV

Long term oxidative ageing of asphalt binder (Pressure Ageing Vessel - PAV) is also performed is by means of pressurized air and elevated temperature. The test is designed to simulate the in-service oxidative aging that occurs in asphalt binders during pavement service. The 'in-service' term refers to aging of the asphalt binder that occurs in the pavement as a result of the combined effects of time, traffic, and the environment.

An asphalt sample is placed in stainless steel pans and aged at the specified aging temperature for 20 h in a vessel pressurized with air to 2.10 MPa. The temperature varies according to the sample's grade. In this paper the temperature was set to  $100^\circ\text{C}$ . After the PAV process, the asphalt binder residue is then vacuum degassed. "Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)" [20]

## 1.4 Material Behavior

Flow and deformation properties of asphalt binder are unique due to material's high sensitivity to temperature and loading rate, the material behaves like a Newtonian fluid only at very high temperatures (above the softening point) or at very low shear rates. The behavior of bitumen is described by mechanical properties and by its durability. To describe asphalt's mechanical properties there are many standardized tests that could

be divided into two groups. First, there are index tests (older methods), they are still widely used although presently the newer methods are coming to use more and more. The main common index tests are:

- Penetration: In Europe, Australia and Japan this index is used to classify the binder, although it's rheological importance is questionable. The test is performed at intermediate temperature by needle penetration and the depth in mm is measured.
- Ring and Ball: This test is widely used all around the world for measuring the consistency of binder at very high temperature range. The measured value is softening point, which is a temperature at which a small metal ball falls through a flat asphalt sample.
- Rotational Viscosity: A measure of resistance to flow at production and construction temperatures. The test is also use for defying the temperature at which is a crude binder being mixed with a polymer.
- Elastic Recovery: The sample is stretched with a ductilometr and one the strain is released the sample is left for a time to relax and then the elastic part of deformation is measured in %.
- Force Ductility: Also measured with a ductilometr, a strength and energy required for a complete failure of asphalt sample from tensile strength applied. An effect of modifier can be calculated from two peaks given by the chart of applied strength vs deformation.

Newer methods of defying binder behavior involve (among others) using dynamic shear rheometr (DSR) to measure binder's shear behavior, for low temperature behavior measuring of stiffness is performed by bending beam rheometr (BBR). The shear properties are described by two main values: the total resistance to deformation and the relative distribution of that resistance between an elastic part and a viscous part. The first value is measured by complex shear modulus  $G^*$  [MPa], the second one by phase angle  $\delta$  [°]. Those values can vary according to the temperature - p.e.  $\delta$  by as much as 85°, between peak summer and peak winter conditions.

To express the rheological properties of the binder, complex shear modulus  $G^*$  is represented as a function of either  $\delta$  or of the frequency rate at which the sample is being stressed (commonly referred to as a master curve). This characteristic is very depended on temperature, as the temperature increases or as the frequency decreases,  $G^*$  decreases while  $\delta$  increases continuously. The higher the complex shear modulus gets, the more is the binder resistant to deformation, the lower the phase angle gets, the less it is elastic and the ability to store an energy declines. At high temperatures, the binder gets more viscous, phase angle values are close to 90°, in the same time, complex shear modulus values vary according to a consistency properties of the sample. Using these values two parameters can help to categorize the binder, for rutting resistance we use  $G^*/\sin\delta$  while for understanding the fatigue cracking resistance of binder we use  $G^* \times \sin\delta$ . [6]

At low temperature due to the material's stiffness, it is not possible to reliably measure properties using two parallel plate geometry of DSR. At very low temperatures, bending beam rheometer (BBR) is used to properly measure binder's behavior. The test sample is a small asphalt beam and a constant force at a constant temperature is applied. By three point bending of the sample, engineering beam theory is used to measure the stiffness. There are two parameters evaluated with this test. Creep stiffness is a measure of how the asphalt resists constant loading and the m-value is a measure of how the asphalt stiffness changes as loads are applied at constant temperature. A creep load is used to simulate the stresses that gradually build up in a pavement when temperature drops and the asphalt binder acts more like an elastic solid.[23]

## 1.5 Tests Performed in This Thesis

### 1.5.1 Penetration Test

Penetration test is described by standard AASHTO T 49. The test is useful for grading the material, basic assumption is that the less viscous the asphalt, the deeper the needle will penetrate. The test results correlate (more or less) with the actual performance of the material. Therefore, asphalt binders with high penetration numbers (called "soft") are used for cold climates while asphalt binders with low penetration numbers (called "hard") are used for warm climates. An advantage of this method is that the test is quick and cheap, so it can be performed in a field, typical disadvantage (as for all the empirical tests) is that it does not measure fundamental engineering parameter.[11], [18]

### 1.5.2 Ring and Ball Test

This empirical test (described in standard AASHTO T 53) is performed in order to gain the material's softening point, which is a temperature at which a bitumen sample can no longer support the weight of a 3.5-g steel ball. In other words a temperature point, at which the material does not behave like an elastic solid any more and behaves like a liquid. Again, as for penetration test, the higher the softening point is, the more the binder is suited for the colder climates.[15]

### 1.5.3 Viscosity

Apparent viscosity of the binder was measured at two temperatures, 135° and 165°, according to the standard AASHTO T316-13. The viscosity at elevated temperatures is a useful parameter to determine whether the asphalt can be handled and at the refinery and it also determines the temperature of the mixing process for the polymer to incorporate properly.[19]

### 1.5.4 Force Ductility

To evaluate cracking properties of asphalt binder, direct tension tests were performed at temperature 10°. A standard ductilometer was used to measure the strength of

the asphalt binder at the critical cracking temperature. The asphalt binder has limited ability to resist stress without cracking and with this test stress at failure and strain at failure in an asphalt binder test specimen pulled at a constant rate can be obtained.

### 1.5.5 Elastic Recovery

Elastic recovery test indicates the presence of polymer in the binder and show asphalt's elastic properties. The test is performed at temperature of 25° using standard ductilometer, according to the standard AASTHO T 301-13. The specimens are pulled to a specified distance using constant force and after 200 mm they are cut in the middle. After a fix period of time a residual strain is measured and percent of elastic recovery is calculated.[18]

### 1.5.6 MSCR

The MSCR test is one of the newest test methods, performed with DSR, that can show us the recoverable and non-recoverable creep compliance. It also identify the change of elastic response for two different stress levels (0.1 and 3.2 kPa), tests specimen being subjected to ten cycles of creep and stress recovery for each loading level. The test indicates the asphalt binder's resistance to the permanent deformation under repeated loads.[21]

### 1.5.7 DSR - Frequency Sweep

In order to evaluate the binders resistance to deformation ( $G^*$ ) and it's the amount of recoverable and non-recoverable deformation ( $\delta$ ), frequency sweep was performed for each sample using dynamic shear rheometer (DSR). Those two characteristic are highly dependable on a temperature, so in this thesis the tests were performed at 60° and 70° and tests were performed with 25 mm geometry and the frequency range was from 0.1 Hz to 10 Hz, including 1.59 Hz (10 rad).[23]

### 1.5.8 BBR

In order to evaluate a low performance of the binder, BBR test was performed on each sample at temperature of -12° using Bending Beam Rheometer according to the standard AASTHO T313-12. With the BBR test, two parameters are obtained. Stiffness [MPa] and m-value [-], which is a change of stiffness with time at constant temperature and load. A low temperature thermal cracking of the pavement is related to the creep stiffness. [17]



## 2. Theoretical Part

### 2.1 Superpave Specification

In order to understand the properties of each type of binder and to correctly predict its behavior in the field, it is necessary to characterize the binder by its behavior relevant to temperature. This behavior - temperature based system was introduced Strategic Highway Research Program (SHRP). The grading is based on specified criteria that the binder has to meet for different temperatures. Based on material's performance, two numbers are assigned to each binder, it is called PG grading. For example the Superpave classifies the binder as PG 64-40, the first number stands for the temperature for which the binder met the physical criteria according to the grading system. The same applies for the second number, only this is the lower temperature. These numbers represent the temperatures of the pavement for which the binder should perform satisfactorily.

The idea of the PG grading is to test the binder at the conditions which simulates the three stages during its lifetime. In the table 2.1, the PG grading is displayed.

The first set of tests is performed on original (non aged) binder, that represents the transport, storage and handling of asphalt. It is necessary to ensure that it is possible to handle the binder at the hot-mixing facility, the tasks such as pumping the binder or mixing it with the aggregate. That is why the Superpave specification contains the criteria of maximum rotatory viscosity 3 000 Pa at 135°C.[16] Due to the safety reasons during the asphalt handling and the construction the flashpoint of binder needs to be determined, the required minimum is according to the specification 230°C.

The second stage of binder's lifetime represents hot-mixing of binder and aggregate

**Table 2.1:** My caption

High Temperature Grades [°C]	Low Temperature Grades [°C]
PG 46	-34, -40, -46
PG 52	-10, -16, -22, -28, -34, -40, -46
PG 58	-16, -22, -28, -34, 40
PG 64	-10, -16, -22, -28, -34, -40
PG 70	-10, -16, -22, -28, -34, -40
PG 76	-10, -16, -22, -28, -34
PG 82	-10, -16, -22, -28, -34

in the production plant and layout process during the concoction works. To work with the correct form of binder, RTFO ageing is performed (8 bottles, each contains 35 grams of asphalt) in rolling thin film oven for 85 minutes at the temperature of  $160^{\circ}\text{C}$ , the thin film of binder (it's surface) is continually exposed to the temperature and the airflow. By this type of ageing it is also possible (and required by the specifications) to determine the mass loss from the ageing process, it must not exceed the maximum given by the standard, which is 1,00 %. [24]

The last stage of asphalt binder is it's life period in pavement. During this time the changes occurs due to the influence of traffic and climate, these changes are represented by the PAV ageing, which was first introduced by the Superpave specification. The RTFO sample (50 grams) is exposed to the pressure of 2070 kPa and the temperature according to the standard met by previous Superpave testing ( $90^{\circ}\text{C}$ ,  $100^{\circ}\text{C}$  or  $110^{\circ}\text{C}$ ) for period of 20 hours.

Each sample (original binder, RTFO aged and PAV aged asphalt) is tested with DSR to evaluate it's rutting (permanent deformation) potential. This potential is calculated simple by dividing the complex shear modulus by the phase angle, both determined with a single DSR test ( $|G^*|/\sin(\delta)$ ). Per standard this number must be minimum of 1.0 kPa for original binder and 2.2 for RTFO aged sample. Therefor high values of the complex shear modulus and low values of the phase angle are desirable in order to achieve good rutting resistance.

Another parameter in the Superpave standard, also measured with DSR, is the evaluation of fatigue cracking resistance. Per the standard this can be simply calculated by multiplying the complex shear modulus and the phase angle ( $|G^*| * \sin(\delta)$ ). This parameter is obtained for PAV aged sample and the limit given by the standard is 5 000 kPa. In order to prevent the fatigue resistance, low values of both, the complex shear modulus and phase angle, are desirable.

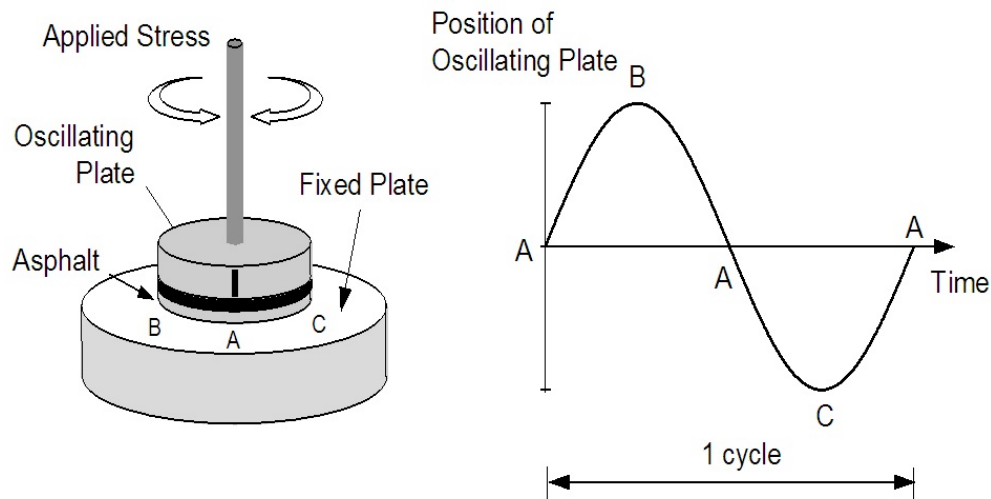


Figure 2.1: Dynamic shear rheometer [4]

The last common issue of asphalt roads is (low) thermal cracking. It is caused by the weather condition rather than just by the traffic volume. At low temperatures the binder shrinks and thus it builds up tensile stresses in the road. When these build up stresses exceed the tensile stresses of the binder, the low thermal cracking occurs. For addressing this issue the Superpave specification came up with a standard for bending beam evaluation (BBR) and thus determining the low temperature properties of the binder. The test is performed by applying a constant load on the sample beam at the constant (sub zero) temperature.

During this test BBR measure creep stiffness of the beam and change of the creep stiffness in time (60 seconds), this parameter is called the m-value. The higher the creep stiffness is the higher the probability of the sample to crack is. The maximum limit given by the standard is 300 MPa and the minimum m-value is 0.3 for PAV aged sample. In order to prevent the low thermal cracking the low creep stiffness and the high m-value is desirable.

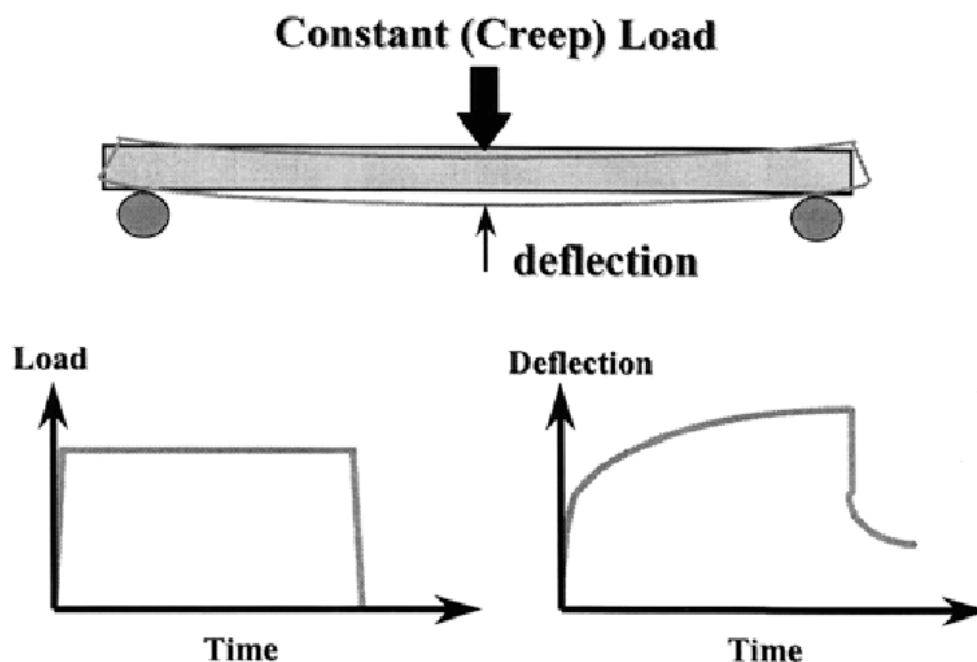


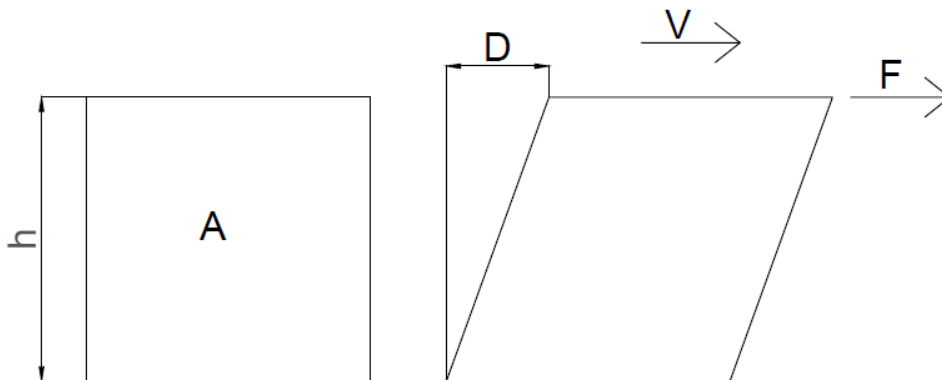
Figure 2.2: Bending beam rheometer [1]

For certain binders there can be situation that the m-value is higher than 0.3 and the creep stiffness is within a range between 300 and 600 MPa, in such situations, another test is required. A tensile tension applied on asphalt sample which is thus deformed. The amount of strain that occurs just before the sample breaks is measured. Per standard a minimum strain of 1.0 % must be achieved.

## 2.2 Rheology

In asphalt rheology two basic point of views (theories) come together. First, there is the classical theory of elasticity, which defines an elastic solid body as a material in which the stress is always directly proportional to strain. Stress does not depend on the rate of strain, such elastic body is defined by Hooke's law. The second point of view (second theory) is classical hydrodynamics. Here, a viscous liquid is defined as a matter in which the stress is directly proportional to the rate of strain and not to strain itself, such a matter is called Newtonian liquid. Both theories can be applied only in idealized experiments and of course the deviations appear when the strain or the rate of strain are not infinitesimal. Some materials during stress more or less exhibit a behavior that combines solid like and liquid like behavior, these materials are called visco-elastic. Often, stress strain behavior of these materials are time depended and linear, then such behavior is called linear visco-elasticity. For linear visco-elastic bodies, the ratio of stress to strain is a function of frequency and is not depended on the magnitudes of neither of them.

According to the classical hydrodynamics the perfect viscous liquid has no shape and the matter has no memory. The stress depends on the current rate of strain only and previous deformations are not taken in account. When the flow is produced, the mechanical work is instantaneously dissipated. On the other hand, following the theory of classical elasticity, the elastic body has a preference of a shape and spontaneously returns to it, when no force is applied. In this case the mechanical work (needed for the deformation) is stored as an elastic energy. Visco-elastic body dissipates but also store the mechanical work needed for the deformation. Again these two cases are idealized experiments and in most materials some from both theories is applied.



**Figure 2.3:** Simple shear experiment

The stress strain behavior can be measured by various experiment, most basic is simple shear, displayed in figure 2.3. Here we can express the shear stress  $\tau$  as a force

per unit area of sheared surface of the body,

$$\tau = \frac{F}{A} \quad (2.1)$$

also the shear strain  $\gamma$  as a displacement per unit distance

$$\gamma = \frac{D}{h} \quad (2.2)$$

and the shear rate  $\dot{\gamma}$ , which is the rate of change of the shear strain in time.

$$\dot{\gamma} = \frac{V}{h} \quad (2.3)$$

For perfectly elastic solid body also applies that

$$\tau(t) = G\gamma(t) \quad (2.4)$$

where  $G$  is the shear modulus, which is a constant. Similarly for perfectly viscous body, following the theory of hydrodynamics, applies that

$$\tau(t) = \eta\dot{\gamma}(t) \quad (2.5)$$

where  $\eta$  is shear viscosity, that is also a constant in this case.

Visco-elastic materials combine the two theories, so the equations are of course different. In short time applied stress the response is solid like, than at long time responses the liquid behavior dominates. Also, the history of deformation is taken in account. An easy way to demonstrate this kind of behavior is by performing creep and recovery experiment.

In such experiment a constant shear strain is applied at time  $t = 0$ . After a certain time period, during which a stress is monitored the strain is stopped being applied. In elastic solid body, the stress would be constant, for a Newtonian liquid the strain rate would be zero and so would be the stress. For visco-elastic body stress decreases in time and stress strain ratio is a function of time (that applies for small strain only). This behavior can be described by equation 2.6.

$$G(t) = \frac{\tau(t)}{\gamma} \quad (2.6)$$

Notice, that  $G(t)$  is not a constant any more (as it is for an elastic solid body) but it is a function of time. This value is called the stress relaxation modulus and it characterizes a visco-elastic body. If the applied step of strain is not small, the relaxation modulus is not only the function of time but of strain as well, so  $G(t, \gamma)$ .

Unlike in elastic materials or in viscous liquids, the strain rate decreases with time and the strain rate is constant, when reaching the creep state. In the relaxation part of the experiment (sudden unload of the strain) the strain rate  $\dot{\gamma}$  is negative and the liquid recoils, reaching an equilibrium state of strain. This value of strain is smaller than the

strain at the time of removing the strain at the beginning of the relaxation part. A ratio of strain to stress (time depended) in the creep part of the experiment (before the relaxation) is called the creep compliance and is the function of time,  $J(t)$ . For visco-elastic body, the history of creep and recovery experiment is taken in account and according to the Boltzmann superposition principle the effects of mechanical history are linearly additive when the stress is a function of the rate of strain history or alternatively the strain is given as a function of the history of rate of change of stress. This principle can be expressed by the equations 2.7 and 2.8, which are the two forms of linear visco-elastic constitutive equation:

$$\tau(t) = \int_{\text{inf}}^t G(t-t')\dot{\gamma}(t')dt' \quad (2.7)$$

$$\gamma(t) = \int_{\text{inf}}^t J(t-t')\dot{\tau}(t')dt' \quad (2.8)$$

To obtain the relaxation modulus  $G(t)$ , stress relaxation experiment is performed. To obtain the creep compliance  $J(t)$ , the creep and recovery experiment is performed.

For a visco-elastic body, there are the four basic regions of behavior, that are time depended. In figure 2.4 the glassy, transition, rubber plateau and flow region are displayed. Those regions (material behavior) are time depended. At very short time period, the material responds in glassy region, relaxation modulus value is very high (thousand mega pascals). If the time period is longer, the molecular chains locally relax, relaxation modulus rapidly falls and material exhibits transition region behavior. If there are small chains in material, means low molecular weights, from this region, relaxation slowly drops to zero. For molecules with bigger molecular weight, material with longer chains, as the time progresses, the relaxation modulus remains more or less the same, this behavior is called rubber plateau region. The final region is the flow state (terminal region). Here, molecular weights and its distribution play major effect. The length molecular chains strongly effect the length of the rubber plateau. The same chart and the same rules also apply for the creep compliance  $J(t)$ .

For determining the relaxation modulus and the creep compliance, the most common way is to perform periodic experiments with frequency of loading  $\omega$ . A sinusoidal strain with the amplitude  $\gamma^0$ , so the shear strain can be expressed as:

$$\gamma = \gamma^0 \sin \omega t \quad (2.9)$$

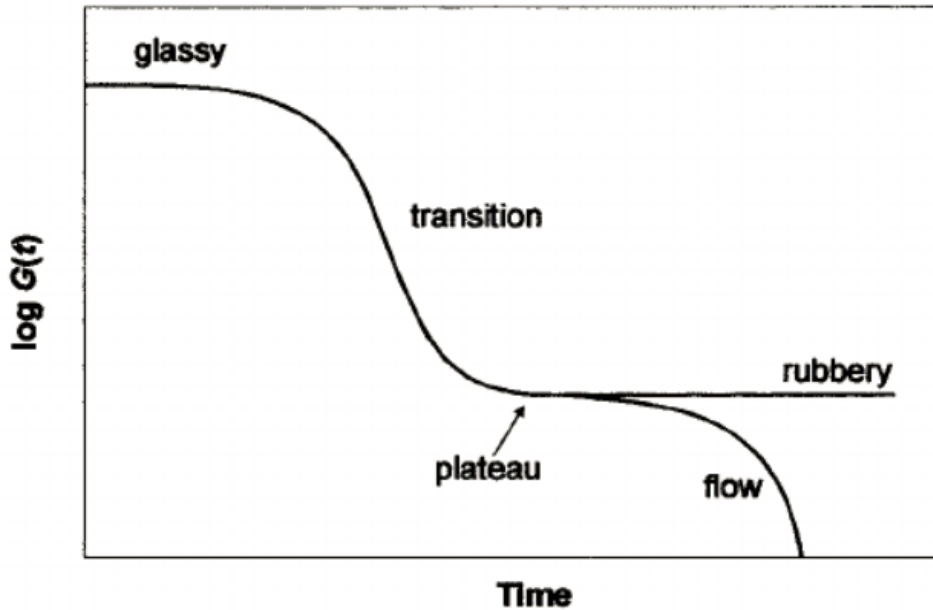
by time derivative we can get the rate of strain as:

$$\dot{\gamma} = \gamma^0 \omega \cos \omega t \quad (2.10)$$

The constitutive equation 2.7 can be expressed as:

$$\tau(t) = \gamma^0 [G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)] \quad (2.11)$$

$G'$  is the storage modulus. It determines the mechanical energy stored (and recovered) by each cycle of loading.  $G''$  is the loss modulus, which is the measure of dissipated



**Figure 2.4:** Stress relaxation in a visco-elastic body

energy as heat per cycle of loading. These two values ( $G'$  and  $G''$ ) together determine the complex shear modulus  $G^*$  in equation:

$$G^*(\omega) = G'(\omega) + iG''(\omega) \quad (2.12)$$

The storage modulus is defined as the stress in the phase with sinusoidal shear deformation divided by the strain. The loss modulus  $G''$  is  $\frac{\pi}{2}$  out of the phase. The phase shift between the sinusoidal strain and thus resulting stress is called the phase angle  $\delta$ , which is also a function of frequency of loading:

$$\delta = \frac{G''(\omega)}{G'(\omega)} \quad (2.13)$$

This phase angle define the energy loss per the energy recovered per a cycle of loading. There is also a relationship between the complex shear modulus and the creep compliance simple given by equation:

$$J_* = \frac{1}{G_*} \quad (2.14)$$

At lower frequencies of loading (which correspond to the longer time) the storage modulus  $G'$  is smaller than the loss modulus  $G''$ , which means that the viscous response to applied strain is dominating. At intermediate frequencies the storage modulus  $G'$  slowly becomes more dominating than the loss modulus, and in this range of time the  $G'$  is relatively constant (flat), when the loss modulus decreases a bit. In the flow (transition) region, the loss modulus reaching it's maximum and then drops rapidly. The situation is displayed in figure 2.6.



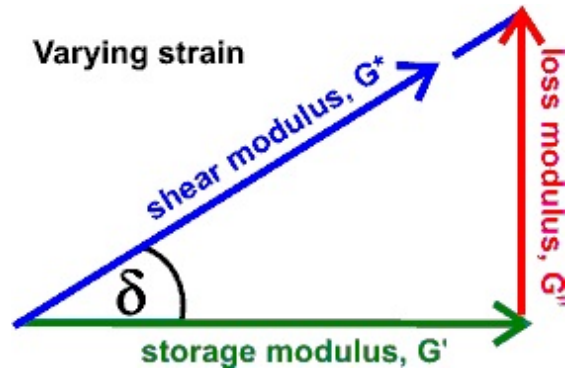


Figure 2.5: Relationship between the phase angle and the complex shear modulus[12]

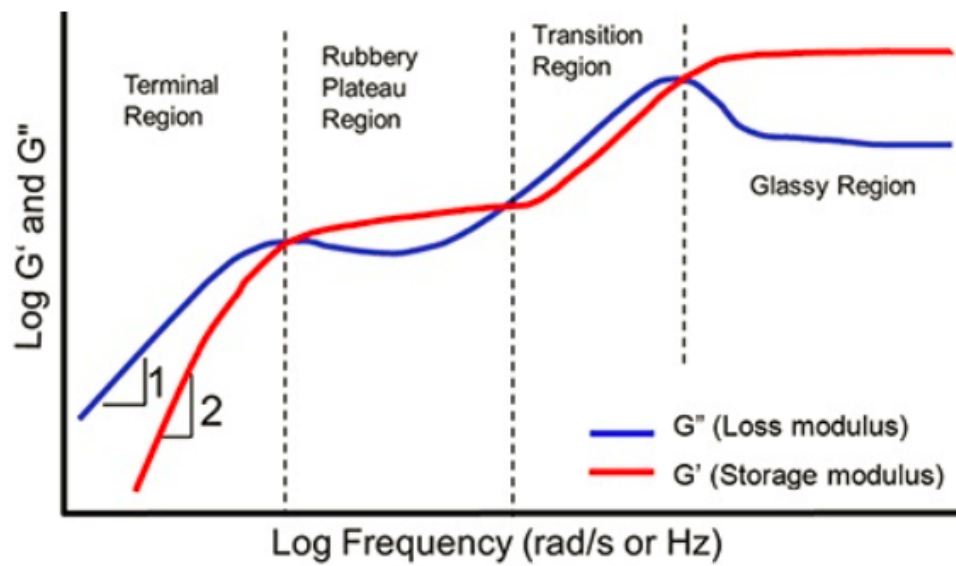


Figure 2.6: Relationship between storage and loss modulus[8]

## 3. | Empirical Part

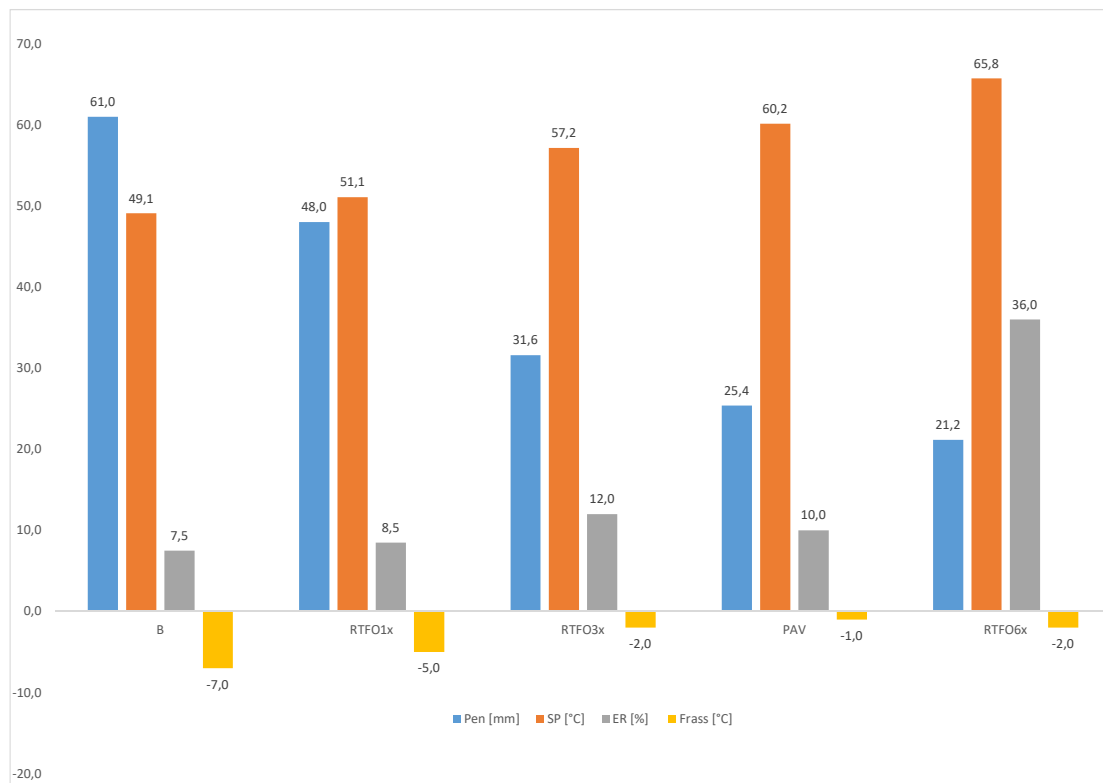
The second part of this paper shows an evaluation of data measured on asphalt binder Total 50/70 at several states of ageing and two types of polymer modification plus neat (non modified) binder. Testing samples were non aged binder, RTFO, RTFO3x, PAV and RTFO6x. In the first section there is data measured for non modified binder. In the second section the the data shows PMB with Elvaloy™5160 and polyphosphoric acid. In the third part of this chapter the binder was modified with SBS + Elvaloy™ and polyphosphoric acid. The focus of this study is to determine the change in visco-elastic behavior of non modified and of modified bitumen in different states of ageing. Another point of the discussion is whether or not it is possible to replace PAV ageing by RTFO ageing performed three times in the row (samples labeled as RTFO3x).

### 3.1 Non Modified Binder

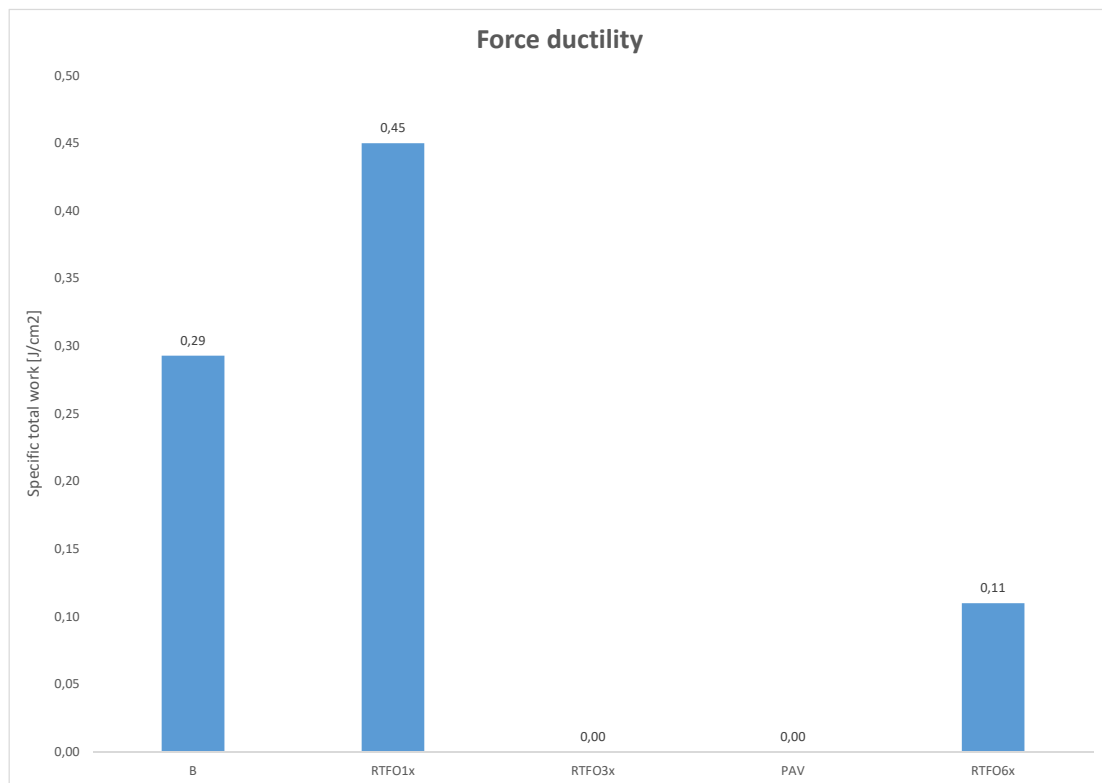
Figure 3.1 shows data from Penetration (blue bar) test, measuring of softening point SP with Ring and Ball test (orange bar), Elastic Recovery Ductility test (grey bar) and measuring of Frass breaking point (yellow bar).

The same increasing/decreasing trend (with the ageing of binder) can be observed for Penetration and Ring and Ball tests, which is to be expected. For Penetration almost three times the value difference can be observed between non aged binder and RTFO6x aged one. For Ring and Ball test the difference is not so transparent, linear increasing trend can be still observed - with the ageing the binder gets much harder (penetration value decreases, but the change in softening point is not so substantial). The Elastic Recovery Ductility test (ER) on the other hand, where sample aged with RTFO method, done three times in a row (RTFO3x), had 12% of recovery when PAV aged sample had only 10% and then again for RTFO6x there can be observed an elevation of value to 36%, does not follow this increasing trend. Same trend in values (higher values for RTFO3x than for PAV ageing) can be seen in DSR or BBR testing.

Force ductility tests were performed as well, displayed in figure 3.2, the results are not complete though due to the cracking of samples aged RTFO3x and RTFO6x. From results that could be obtained the linear trend can not be determined though. Interestingly enough, sample aged RTFO6x could withstand the deformation of 400 mm, when PAV and RTFO3x samples could not.

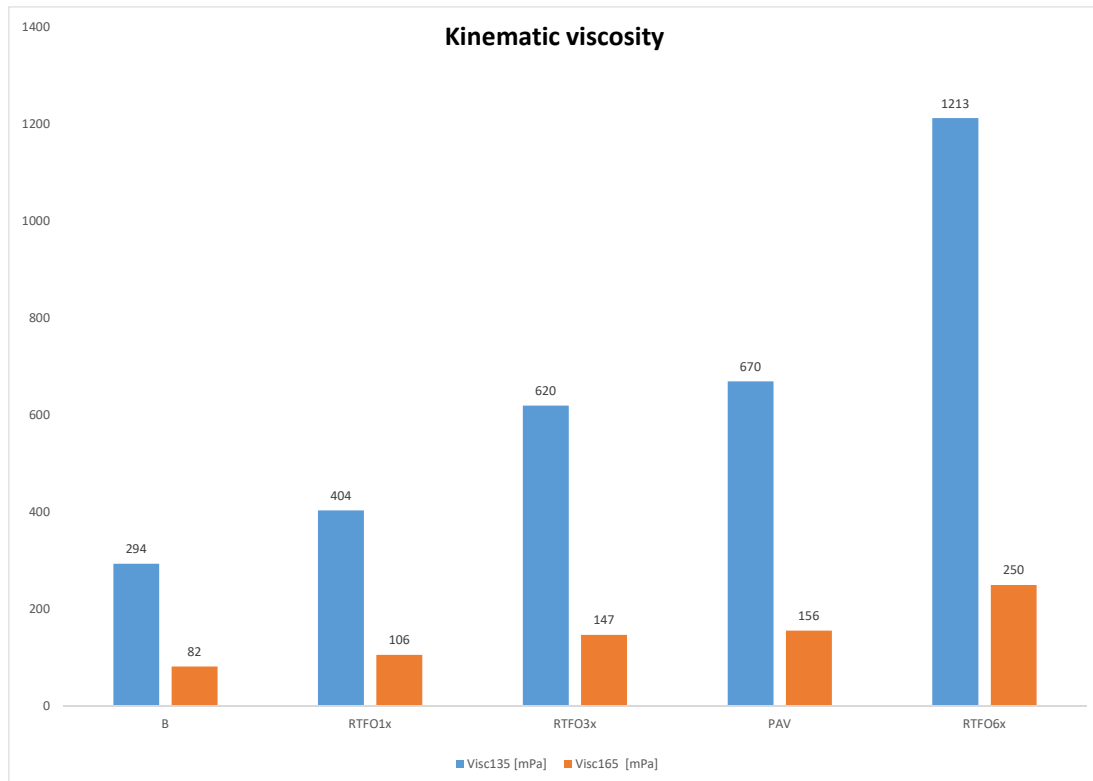


**Figure 3.1:** Basic data evaluation, non modified binder



**Figure 3.2:** Froce Ductility, non modified binder

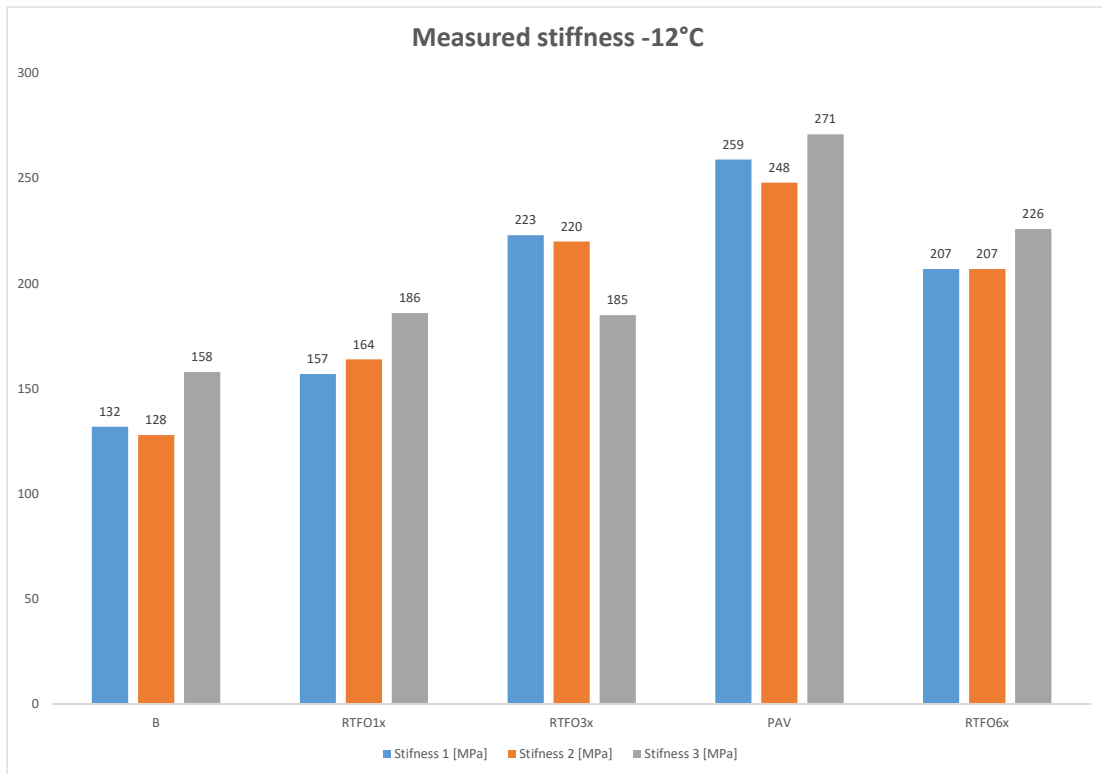
Figure 3.3 shows kinematic viscosity for each state of aging (x axis) with temperatures of 135°C (blue bars) and 165°C (orange bars). For all states of aging and for both temperatures an increasing trend in values can be observed. The difference in values at lower temperature (135°C) between PAV and RTFO6x is greater than the difference at 165°C, which means that the ageing of binder effects high temperature behavior (165°C) less than it effects the viscosity at lower temperatures.



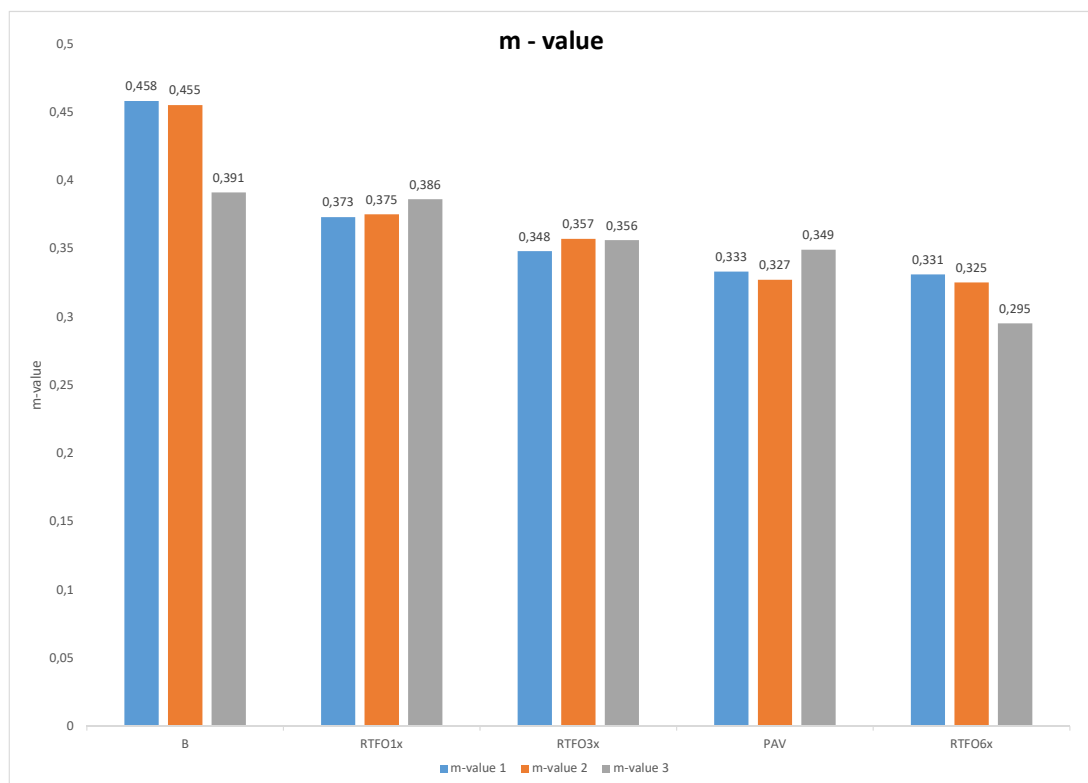
**Figure 3.3:** Kinematic Viscosity, non modified binder

Figure 3.4 provides an evaluation of low temperature properties of asphalt binders at -12°C. Always three measurements for each state of ageing were performed and at least two of them must differentiate in 5 % of value at most so the experiment is valid, this condition applies always for blue and red bars for each state of ageing. There is an increasing trend in creep stiffness with increasing ageing of binder. Contrary to the empirical tests in 3.1, PAV shows lower values (stiffness and m-value) than RTFO3x aged sample.

The rate of change in creep stiffness in time is represented by the m-value, which is shown in figure 3.49, the trend is decreasing value with increasing ageing of binder with an exception of RTFO6x aged sample, which shows greater values than PAV aged one, the same applies to measured stiffness. Blue, orange and grey values from figure 3.49 corresponds to those from figure 3.4.

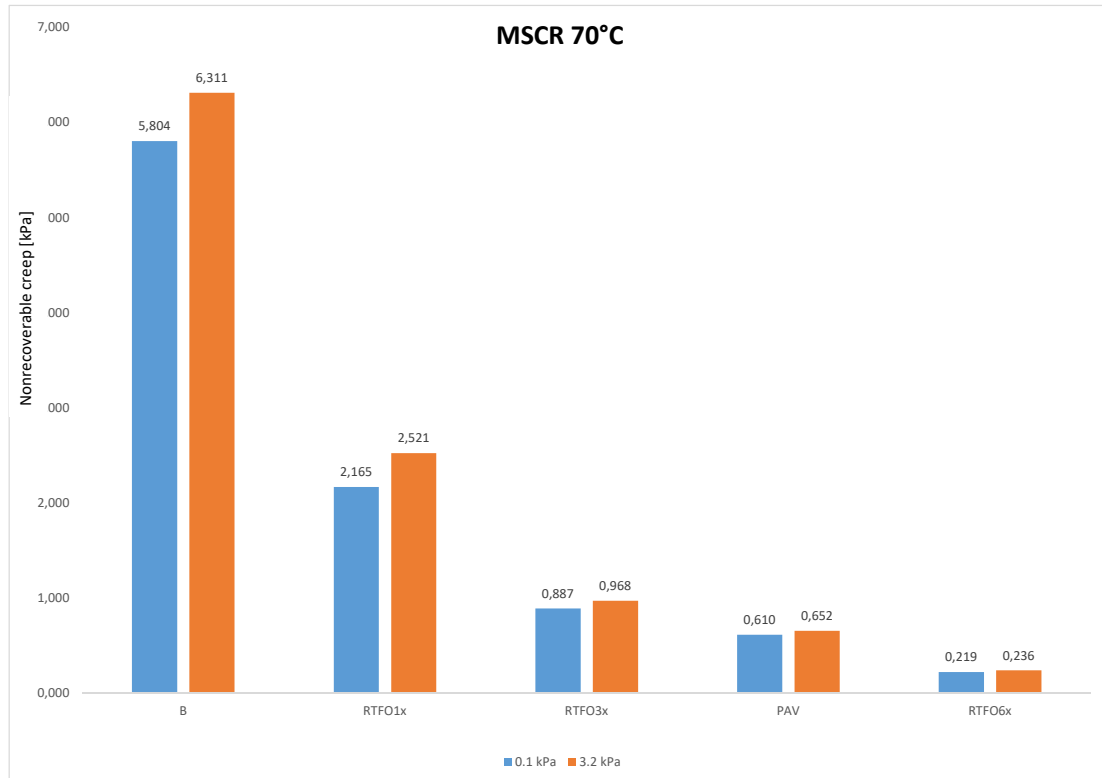


**Figure 3.4:** Measured stiffness, non modified binder



**Figure 3.5:** m-value at -12°C, non modified binder

The multiple stress creep recovery test MSCR was performed and the non-recoverable creep compliance  $J_{nr}$  for 0.1 kPa and for 3.2 kPa is shown in figure 3.6, as the ageing of binder increase the amount of residual strain left in the specimen after repeated creep and recovery decreases. Measuring was performed with 25 mm geometry at 70°C. The difference in  $J_{nr}$  for 0.1 kPa and for 3.2 kPa is not so great as is expected for a non modified binder. There is a big gap between values for non aged samples and for RTFO1x aged ones, than the difference between other states of ageing is not that great, for RTFO6x aged samples the results are almost the same.

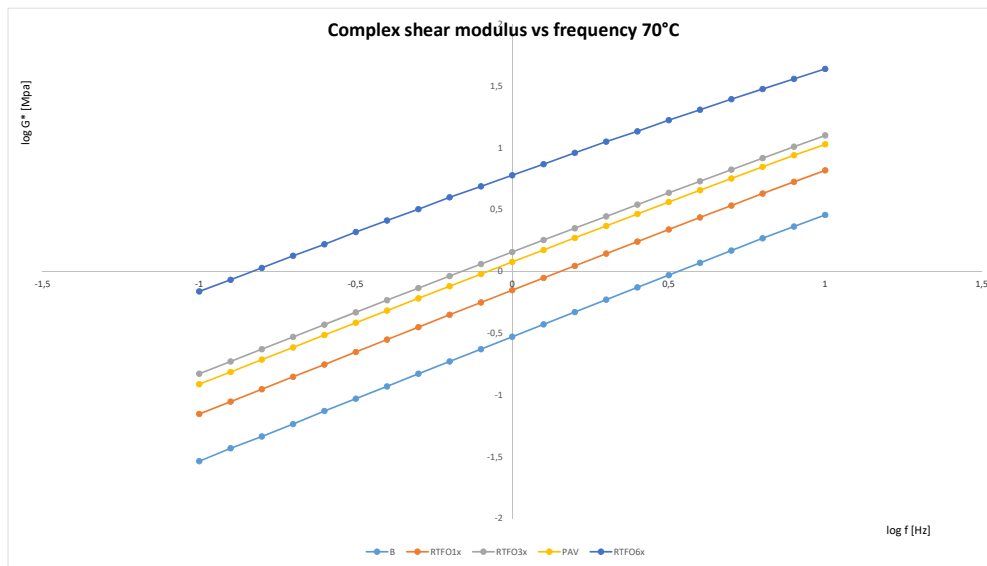


**Figure 3.6:**  $J_{nr}$  values for 0.1 kPa and 3.2 kPa at 70°C, non modified binder

Figure 3.7 shows Complex shear modulus  $G^*$ [Mpa] versus Frequency [Hz] measured at 70°C with 25 mm geometry. Increasing trend in stiffness of binder can be observed for all the samples. A substantial difference in stiffness in higher frequency can be observed when comparing RTFO6x with any other aged sample. Only a little difference in values for RTFO3x sample and PAV aged sample can be observed. The slopping of the curves is not influenced by ageing, although the values differentiate substantially.

Complex shear modulus  $G^*$ [Mpa] versus Frequency [Hz] measured at 60°C is shown in figure 3.8. Again only a small difference in values between PAV and RTFO3x. When comparing figures 3.7 or 3.8 with figure 3.4 not only the difference between values is different but the order of values for each state of ageing is not the same neither. BBR tests show stiffness of material when applied three-point bending for sub zero

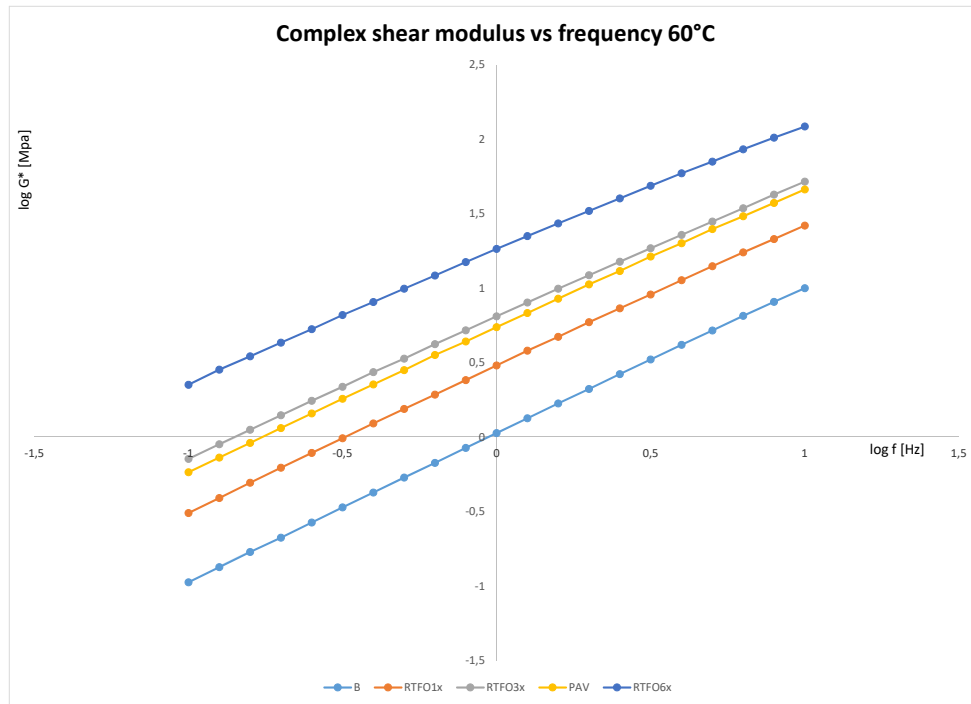




**Figure 3.7:** Isotermic plot at 70°C of Complex shear modulus vs Frequency in logarithmic scale, non modified binder

temperatures (-12°C), DSR shows shear stiffness by complex shear modulus.  $G^*$  (shear properties) is influenced a lot by ageing of material for both temperatures, for measured stiffness measured by bending of sample (BBR tests) the difference between ageing is not so great, so for temperatures below zero, the ageing of the binder makes much less a difference than for high (DSR) temperatures.

For better understanding the difference between values in high frequencies, figure 3.10 shows  $G^*$  [MPa] vs  $f$  [Hz] at 60°C and figure 3.46 at 70°C without the logarithmic scale of axis.



**Figure 3.8:** Isothermic plot at 60°C of Complex shear modulus vs Frequency in logarithmic scale, non modified binder

For the highest frequency (10 Hz) a great difference can be observed, between non aged binder (B) and RTFO6x it is 15,5 times the value for 70°C and for 60°C it is 12 times. The smallest difference is between RTFO3x and PAV aged sample, it is only 1,1 the value.

The difference at high frequencies between non aged and 6xRTFo aged sample for 60°C is about twelve times the value, for 70°C it is about 15 times the value, so more or less the same, which means that the effect of temperature is not so great (which is contrarily to the viscosity behavior in figure 3.3). Also now it can be seen that the sloping of the curves is different for each state of ageing. For RTFO6x the trend is much less linear than it is for other states of ageing.

Logarithmic reliance of complex shear modulus and phase angle Delta is shown in figure 3.44 measured at 70°C with 25mm geometry. Phase angle delta is a measure of the ability of an asphalt binder to recover from a given deformation, the lower the  $\delta$ , the more it behaves like an elastic solid (less like a liquid) and is therefore able to recover from the deformation.

The effect of ageing is shown in stiffness shifting towards greater values and lowering of phase angle Delta in the same time. The greatest difference is shown between non aged binder (base) and RTFO6x aged binder. The same difference between non aged binder (B) and 6xRTFo aged sample can be observed as for all the former testing. There is very slightly difference between PAV (yellow) and RTFO (orange) values though.

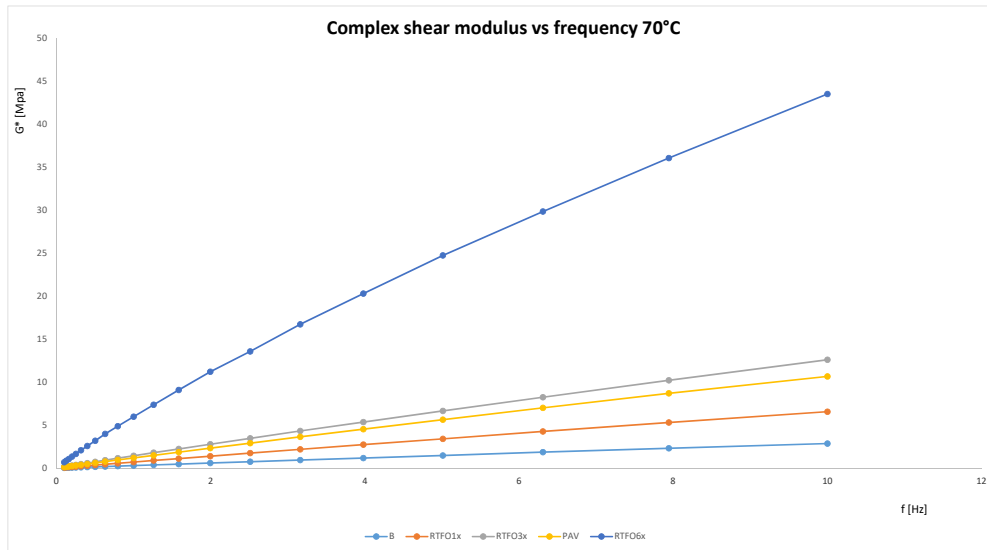


Figure 3.9: Isothermic plot at 70°C of Complex shear modulus vs Frequency, non modified binder

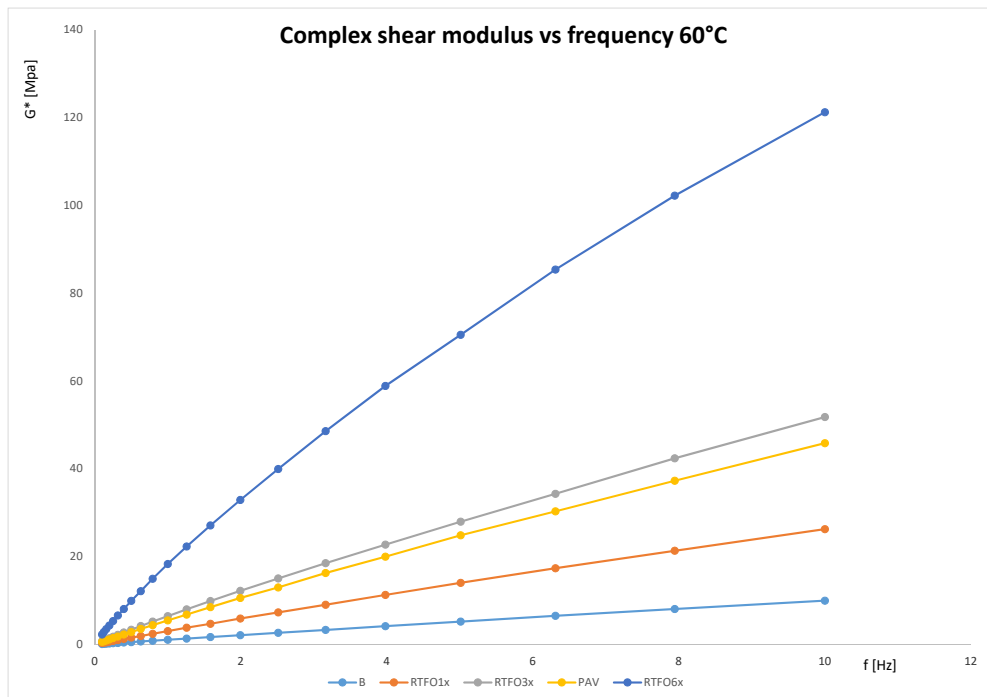
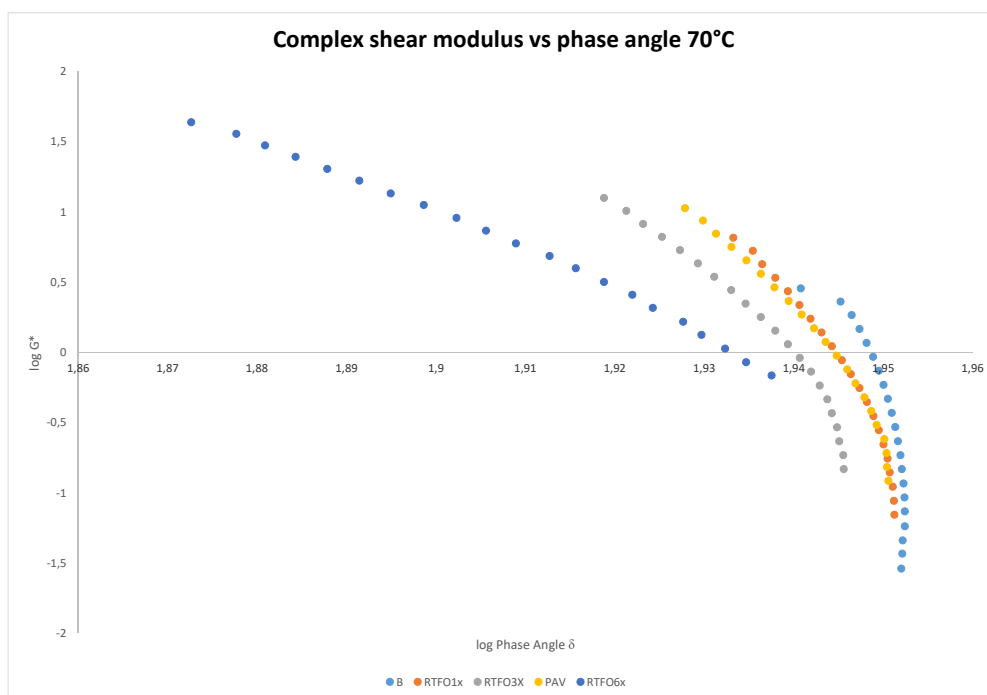


Figure 3.10: Isothermic plot at 60°C of Complex shear modulus vs Frequency, non modified binder

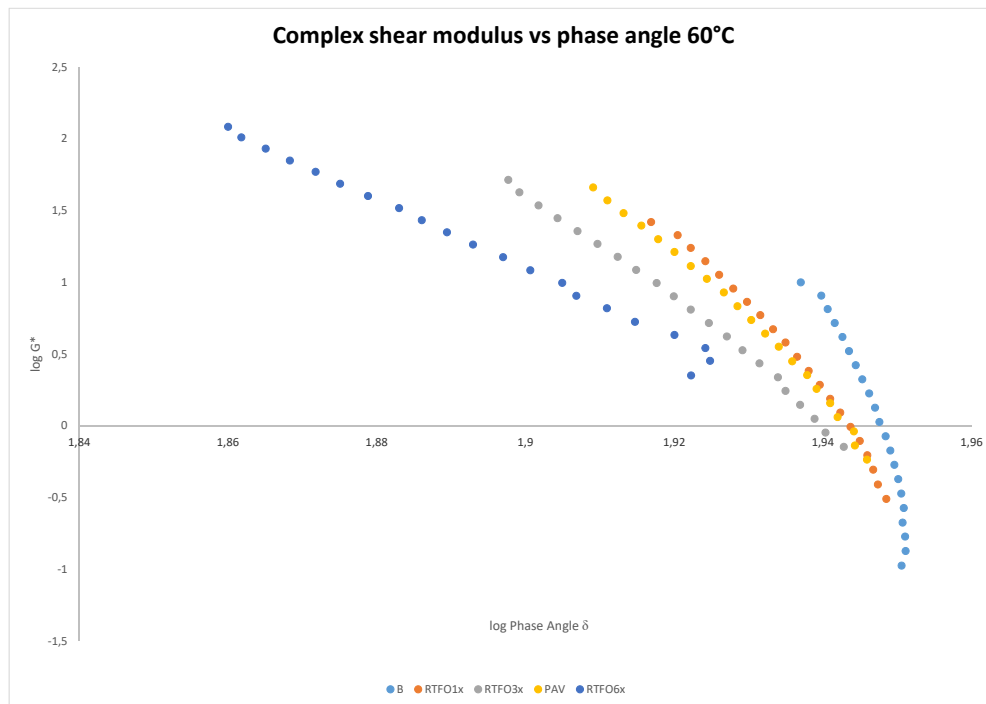
Also RTFO6x aged specimen showed much greater range of values than other states of ageing, that means - with binder that stiff (RTFO6x) it depends much more on the frequency of loading.

High values of  $G^*$  and low values for  $\delta$  are desirable from the standpoint of rutting resistance, low values of  $G^*$  and low values of  $\delta$  are desirable from the standpoint of resistance of fatigue cracking.



**Figure 3.11:** Log  $G^*$  vs log Delta at 70°C, non modified binder

For comparison the same data measured at 60°C logarithmic reliance of  $G^*$  and Delta is shown in figure 3.45. All values of  $G^*$  are lower, due to lower testing temperature. Complex shear modulus shift in values for 60°C and for 70°C is about from half to quarter the value. Again only a little difference can be observed between PAV and RTFO aged samples and a difference between PAV and RTFO3x is not marginal.



**Figure 3.12:** Log  $G^*$  vs log Delta at 60°C, non modified binder

### 3.1.1 Summary of non modified binder

It is obvious that with the state of ageing of asphalt binder measured values are increasing (decreasing) it becomes stiffer and less elastic.

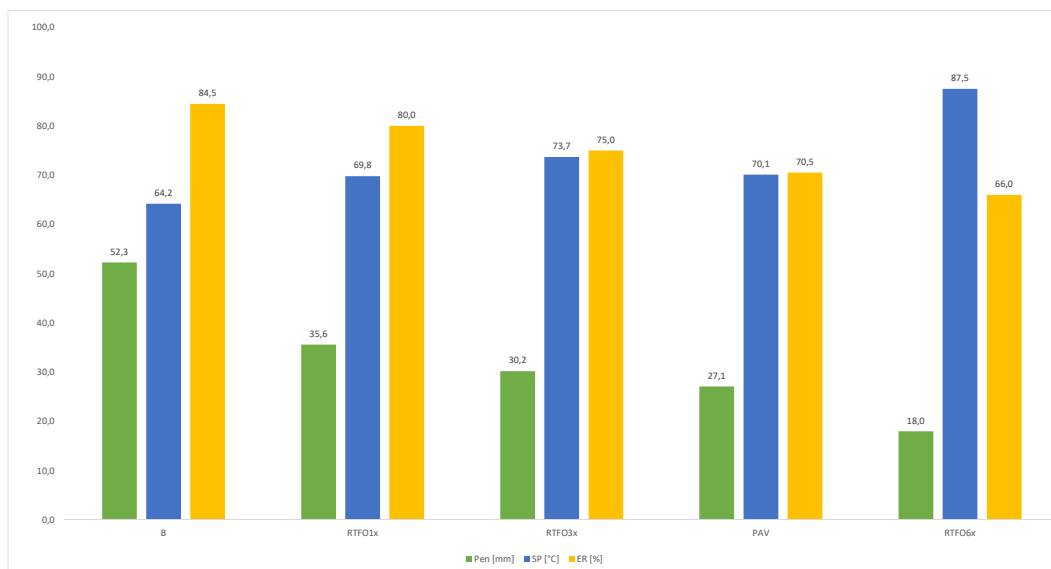
For penetration, softening point and Frass point shown in figure 3.1 and for kinematic viscosity shown in figure 3.3 always the same increasing or decreasing trend can be observed in the same order: non aged binder (B), RTFO1x, RTFO3x, PAV and RTFO6x. The situation is not the same for all tests though, for BBR stiffness values in figure 3.4, and for DSR data like  $J_{nr}$  measuring, figure 3.6,  $G^*$  vs frequency for both temperatures, figures 3.7, 3.8 and for  $G^*$  vs Phase Angle Delta in figures 3.44 and 3.45 the trend of increasing in values is in order: non modified, RTFO1x, PAV, RTFO3x and RTFO6x, so the PAV and RTFO3x are switched, the same applies for elastic recovery ductility in figure 3.1 (grey color bar).

For some tests (DSR frequency sweep, MSCR, kinematic viscosity or force ductility) it could be assumed that it is possible to consider RTFO3x (three times RTFO for 75 minutes) values almost the same as for PAV ageing. RTFO six times done in the row shows completely different values though, when comparing the tests performed.

## 3.2 Elvaloy™ Modified Binder

The same tests as for non modified asphalt were performed for binder modified by Elvaloy™ and polyphosphoric acid and for all five states of ageing: non aged (B), RTFO1x, RTFO3x, PAV and RTFO6x.

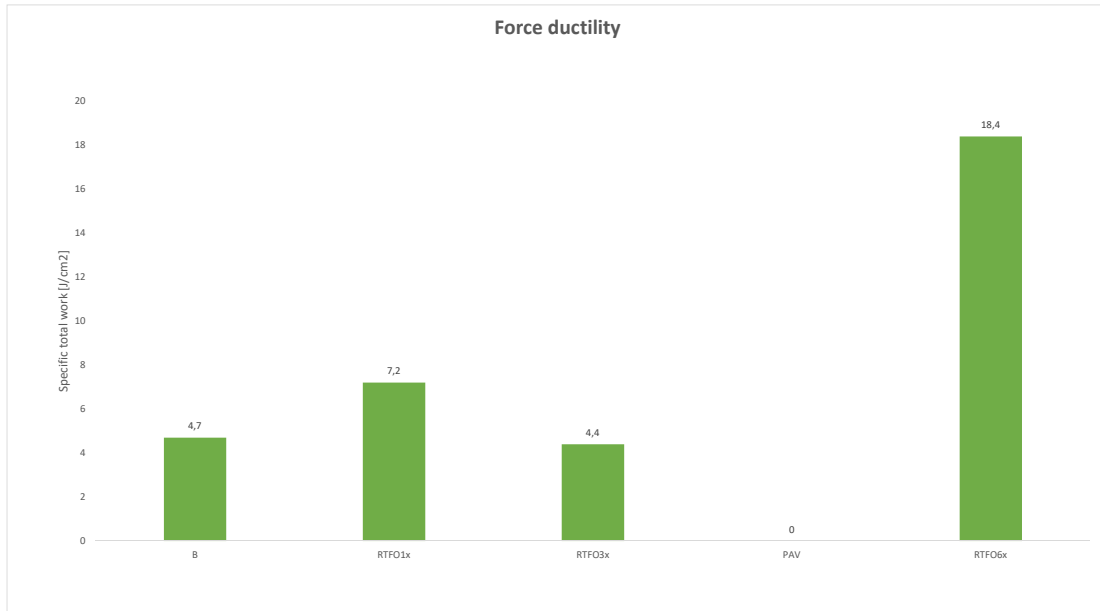
In figure 3.13 data for penetration (green bar), softening point (blue bar) and elastic recovery test (yellow bar) is shown. For penetration and elastic recovery test the same order of values as for non modified binder in figure 3.1 according to states of ageing of bitumen (B, RTFO1x, RTFO3x, PAV, RTFO6x). For softening point the PAV value is lesser than RTFO3x though which does not correspond with non modified binder in figure 3.1, where RTFO3x sample has lesser value than PAV aged one. Also here, ER results indicates a presence of polymer (Elvaloy™) and where a major change in penetration and softening point with aging can be observed not such a transparent difference in values for ER results.



**Figure 3.13:** Basic data evaluation, Elvaloy™

Results for force ductility test are shown in figure 3.14, although the results are not complete due to cracking of samples for PAV ageing, the same trend as for non modified binder (figure 3.2) can be observed in order of values, but only visa versa (PMB values are increasing). Another change is, that for non modified binder the RTFO3x aged

sample kept crackng during the test, for PMB it was able to perform the procedure and only PAV sample cracked.



**Figure 3.14:** Froce Ductility, Elvaloy™

Kinematic viscosity of non modified binder (figure 3.3) shows 4 and 3 times the value (for both temperatures) between non aged and RTFO6x aged bitumen.

The same trend can be observed when comparing the states of ageing for the Elvaloy™ modified binder, for temperature of 135°C the difference is 5 times the value and for 165°C there is a difference 3,5 times the value, so for both lower and higher temperatures the difference is little bit more transparent but it could be said that the effect of ageing (hence times the values) was almost the same for viscosity behavior for non modified samples and PMB.

Bending beam rheometer data evaluation for Elvaloy™ modified binder is shown in figures 3.16 and 3.17. Measured stiffness, contrary to non modified samples (figure 3.4), shows linear trend, according to the states of ageing, although the values for PAV and RTFO6x are close. It is obvious that Elvaloy™ modification of binder did not enhance the low temperature cracking behavior of binder, as the values are almost the same as for non modified samples, for PAV ageing the values decreased when compared with non modified asphalt. As for m-value, non modified binder showed linear trend (figure 3.49) although it's measured stiffness did no. For Elvaloy™ modification the case is actually the opposite, m-value does not show linear trend with ageing (figure 3.17 when

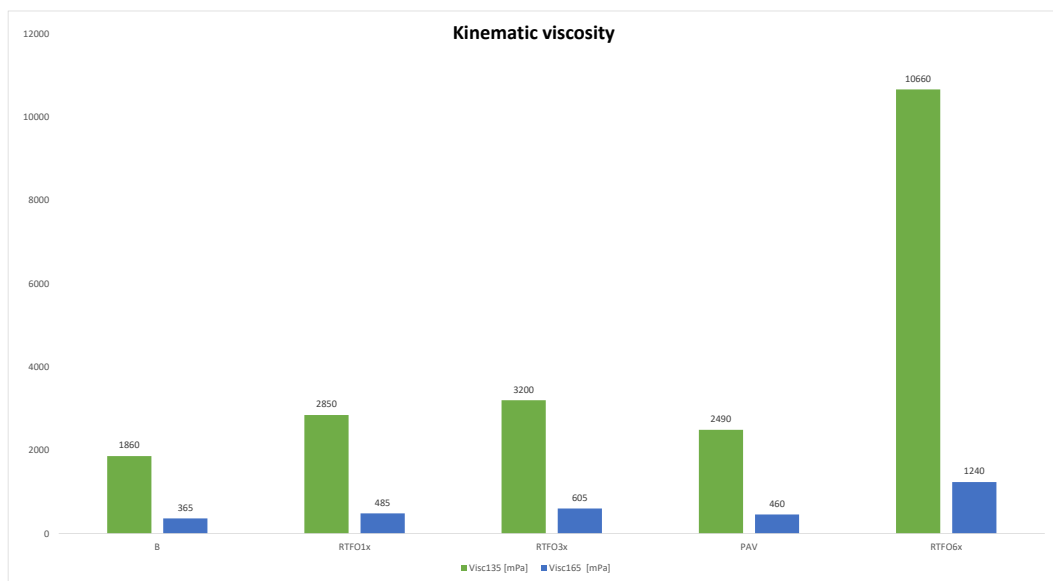
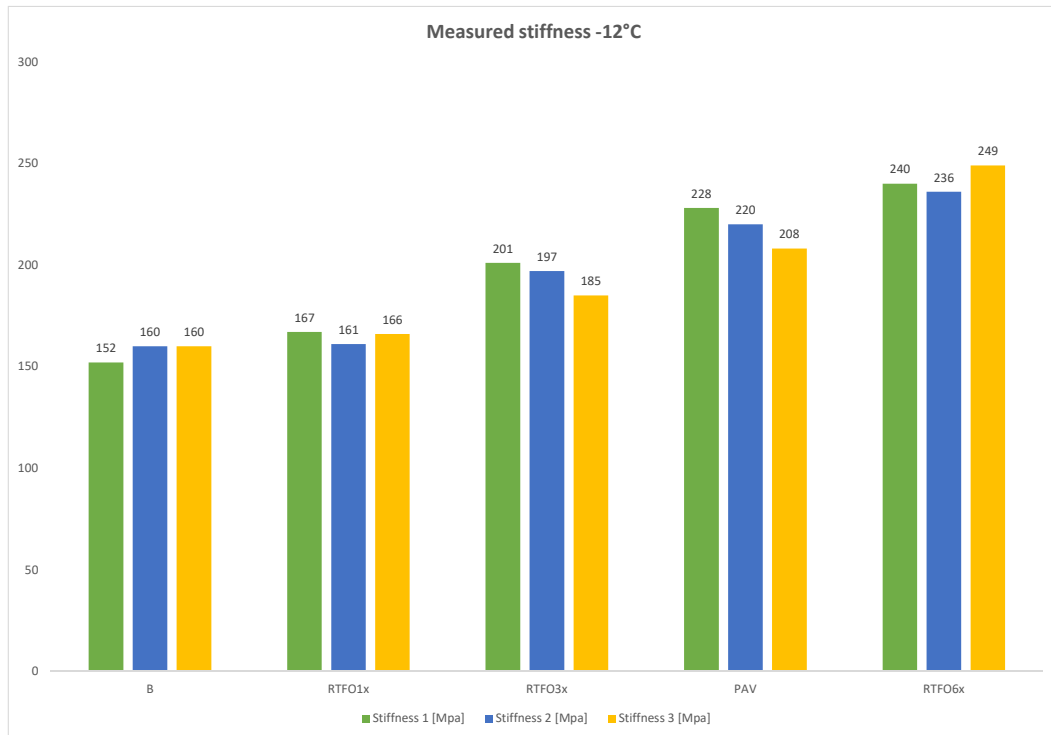


Figure 3.15: Kinematic Viscosity, Elvaloy™



measured stiffness does. So for PAV ageing changed the time response to stiffness at constant temperature (m-value) more for Elvaloy™ modification than for non modified samples. PAV shows higher values of m-value than RTFO3x and RTFO6x aged samples, for Elvaloy™PMB.



**Figure 3.16:** Measured stiffness, Elvaloy™

Figure 3.18 shows the non-recoverable creep compliance  $J_{nr}$  for 0.1 kPa and for 3.2 kPa measured with MSCR test at temperature of 70°C. The same trend as for non modified binder in figure 3.6 can be observed, the values for PAV aged sample are higher than for RTFO3x, although for PMB the difference is much more transparent and the value is even greater than for RTFO1x, which is opposite than for non modified samples, which means that due to the presence of polymer the elastic behavior of binder is influenced by PAV ageing more than for non modified samples. The rutting resistance actually increased by adding Elvaloy™ to asphalt.

Complex shear modulus  $G^*$  versus frequency at temperatures 60°C and 70°C, measured with 25 mm geometry, is shown in figures 3.19 and 3.20 in logarithmic scale. There is an interesting shift in values between these two temperatures for RTFO3x aged sample and for PAV aged one. And again a great difference in measured values between RTFO6x and all other states of ageing can be observed, the same as applies for non modified samples in figures 3.8 and 3.7. There is also a substantial difference in values between the two temperatures, much greater than for non modified samples.

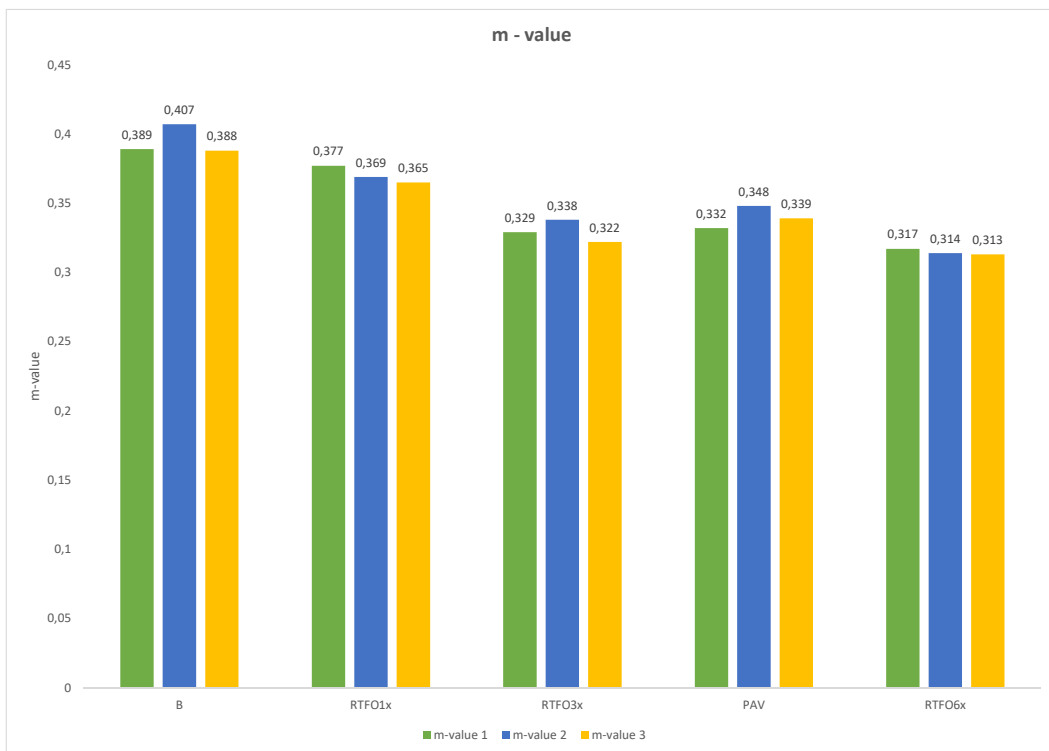
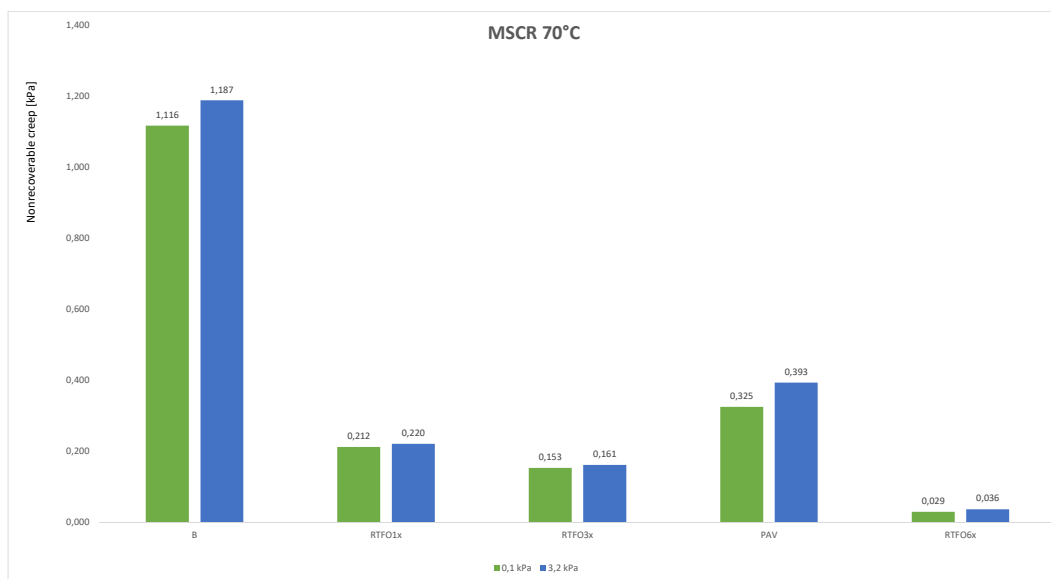
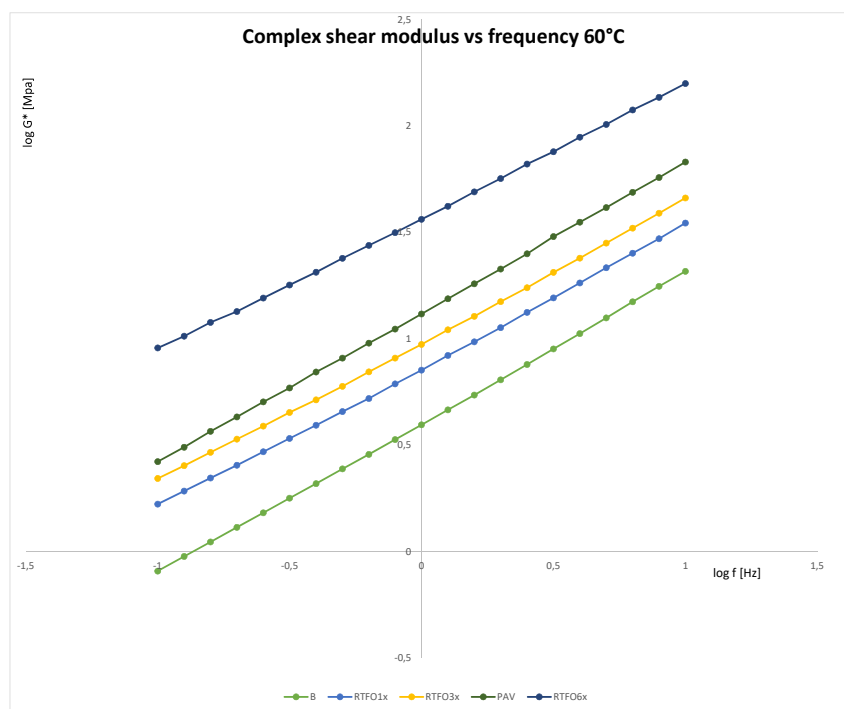


Figure 3.17: m-value at -12°C, Elvaloy™



**Figure 3.18:** Jnr values for 0.1 kPa and 3.2 kPa at 70°C, Elvaloy™

It means that the difference in stiffness is more influenced by the temperature (70°C or 60°C) for PMB than for non modified sample.



**Figure 3.19:** Isotermic plot at 60°C of Complex shear modulus vs Frequency in logarithmic scale, Elvaloy™

For better understanding the great difference between non aged binder (B) and RTFO6x aged sample (especially at higher frequencies), figures 3.21 and 3.22 shows reliance between complex shear modulus and frequency without logarithmic scale. For temperature of 60°C it is about 7,5times the value (between B and RTFO6x at highest frequency) and for 70°C it is 8,5 times, so the difference is almost the same for both temperatures (which is the same trend as for non modified asphalt, although for PMB the difference is even lesser). The smallest difference for temperature of 70°C is between RTFO3x and PAV, it is 1,2 times the value, which is almost the same as for non modified binder. For temperature of 60°C the situation is different though. The smallest difference in values is between RTFO1x and RTFO3X and it is 1,3 times the value, which does not correspond with non modified asphalt, where the smallest difference was between RTFO3x and PAV. So it could be said that the modification of binder (Elvaloy™ and polyphosphoric acid) influenced the shear properties in the way that PAV ageing effects the binder less then RTFO ageing done more three times in a row.

In figures 3.23 and 3.24 there is again another change in order of values according to the state of ageing of bitumen. PAV aged sample shows higher values than RTFO3x and RTFO aged samples for both temperature. This trend in order of values can not

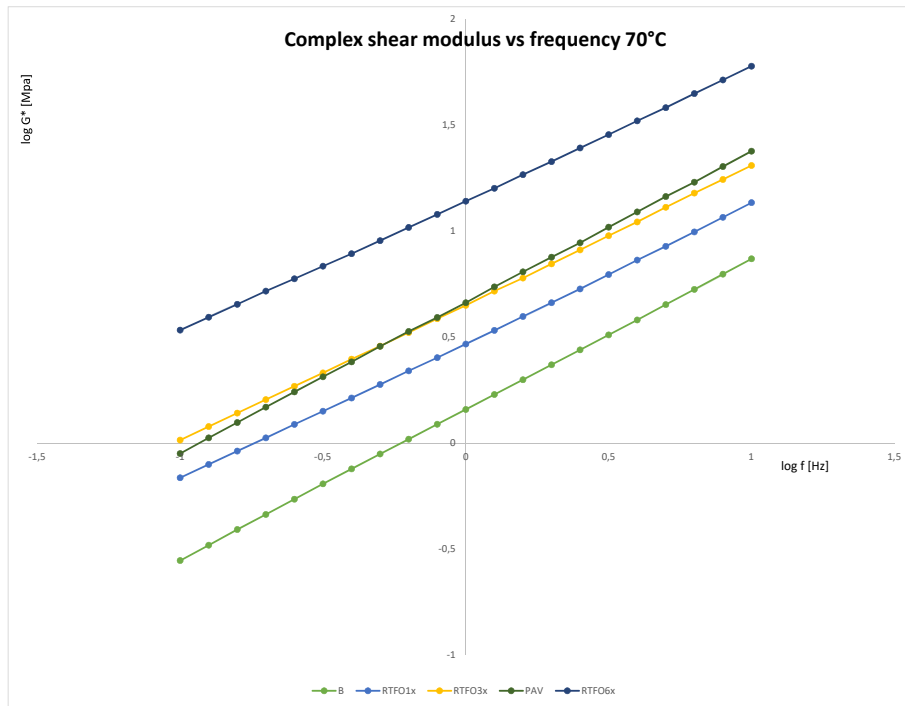


Figure 3.20: Isotermic plot at 60°C of Complex shear modulus vs Frequency in logarithmic scale, Elvaloy™

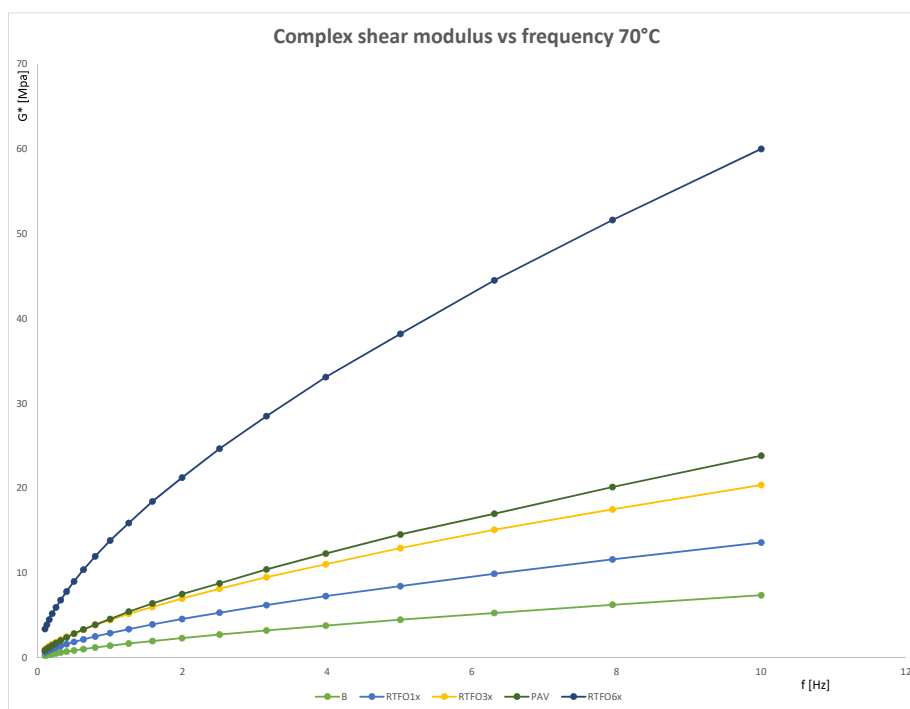
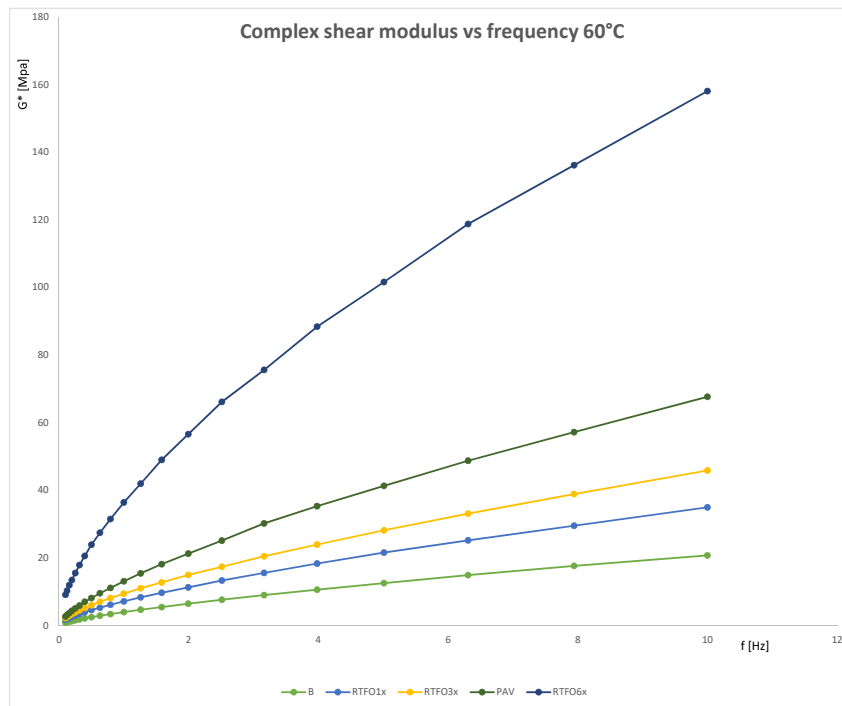
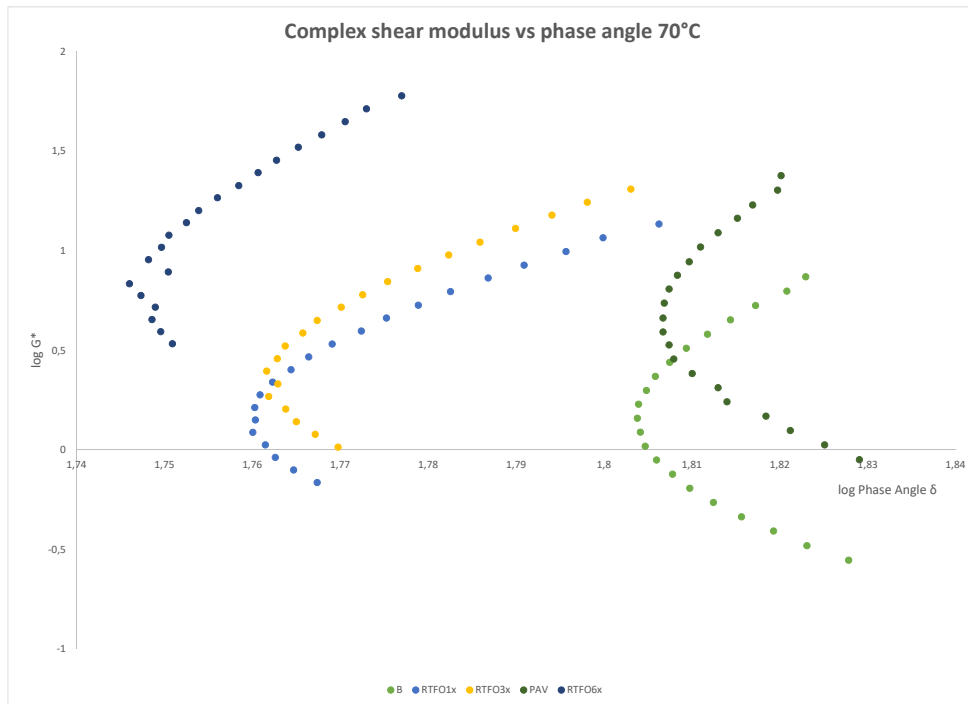


Figure 3.21: Isotermic plot at 70°C of Complex shear modulus vs Frequency, Elvaloy™

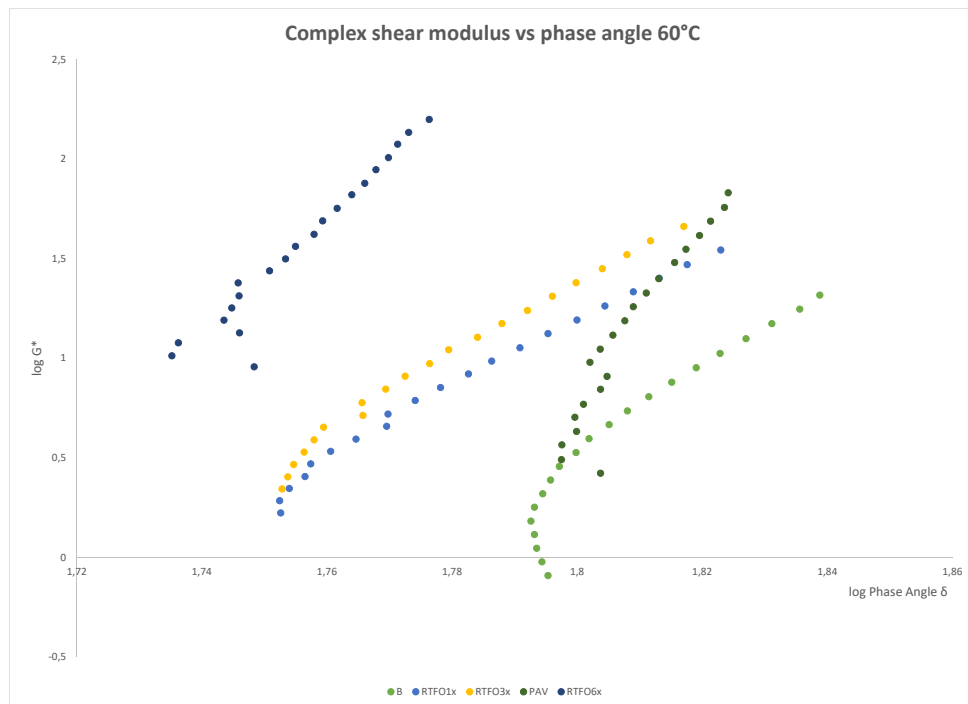


**Figure 3.22:** Isothermic plot at 60°C of Complex shear modulus vs Frequency, Elvaloy™

be observed at non modified samples in figures 3.44 and 3.45 though.



**Figure 3.23:** Log  $G^*$  vs log Delta at 70°C, Elvaloy™



**Figure 3.24:** Log  $G^*$  vs log Delta at 60°C, Elvaloy™

### 3.2.1 Summary of Elvaloy™ modified binder

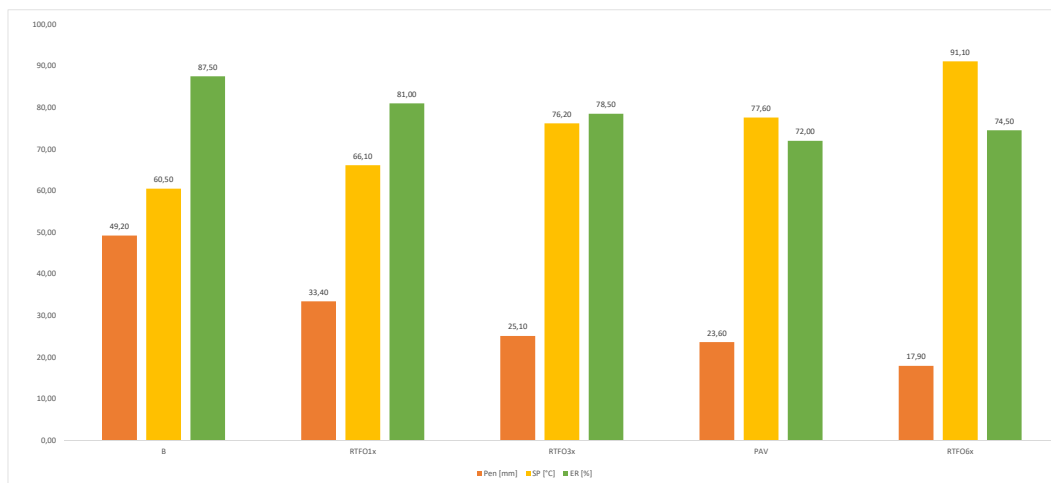
It is obvious that with the state of ageing the measured values gets higher in more or less linear trend, the binder gets stiffer and less elastic. Also by adding Elvaloy™ to asphalt, it became more elastic and its properties are less influenced by ageing. There is the same pattern for order of values according to the ageing of samples. For penetration, elastic recovery test and for complex shear modulus versus frequency (although depending on temperature) the order is the same (B, RTFO, RTFO3x, PAV, RTFO6x), this also corresponds with non aged samples. The situation is different for softening point, kinematic viscosity, for those tests the same order as for MSCR can be observed. The Black's diagrams for both temperatures show different trend than for non modified binder, for PMB the values for PAV and B (non aged sample) are very similar.

None of tests performed for both, PMB and non modified binder, suggested that it would be possible to replace PAV ageing by RTFO ageing done three times in a row (RTFO3x) - although for some tests the results are very similar (complex shear modulus versus frequency at 70°C or kinematic viscosity at higher temperature), the case is most transparent in figures 3.23 and 3.24, in which not even a linear trend could be observed.



### 3.3 SBS + Elvaloy™ Modified Binder

For the third part of the assignment the samples were modified by SBS + Elvaloy™ and the polyphosphoric acid. Again, the samples were aged in order: B (non aged), RTFO1x, RTFO3x, PAV and RTFO6x. The same test as for non modified and for Elvaloy™ modified bitumen were performed.

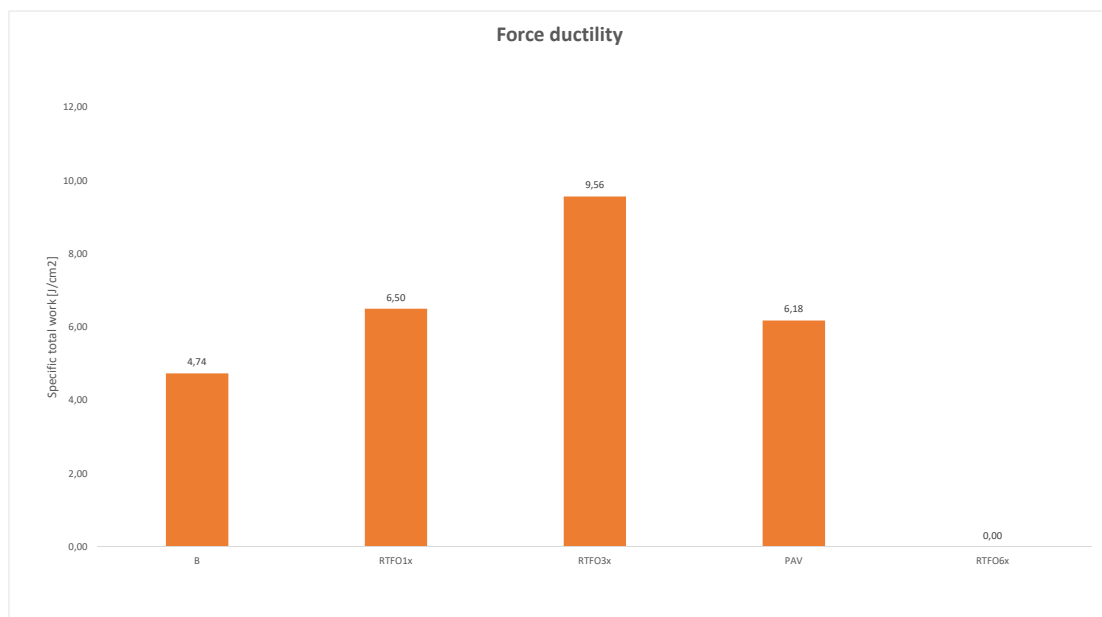


**Figure 3.25:** Basic data evaluation, SBS + Elvaloy™

Figure 3.25 shows penetration (orange bar), softening point (yellow bar) and elastic recovery test (green bar) for third modification of binder (SBS + Elvaloy™). The results are ordered from left to right in order: B (non aged sample), RTFO1x, RTFO3x, PAV and RTFO6x aged asphalt.

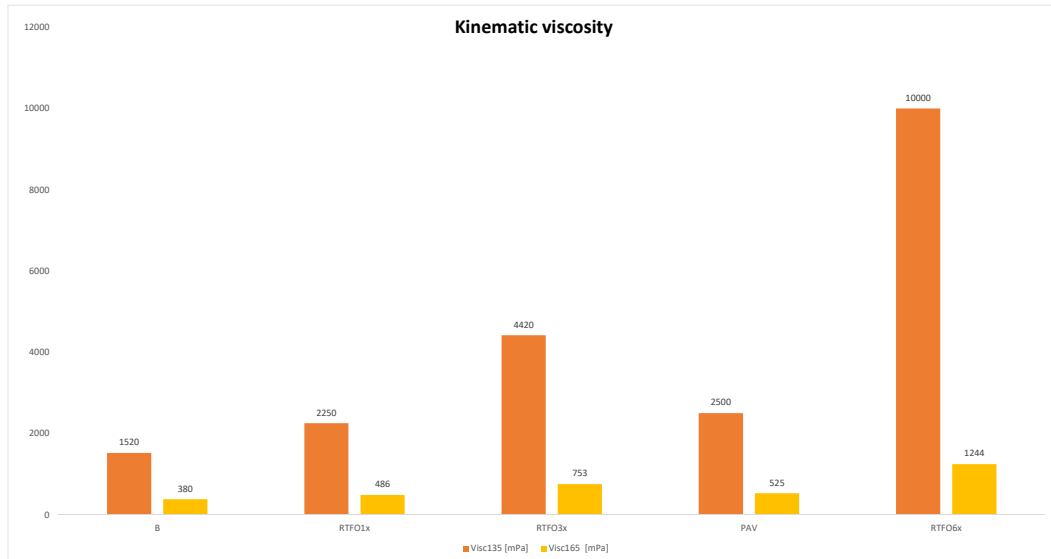
For penetration and softening point it is obvious that PAV aged sample is out of order again, which is contrary to the Elvaloy™ and non modified samples (figure 3.13 and figure 3.1), for elastic recovery (PAV ageing) the case of order is the same as for non modified binder (figure 3.1). So the hardening of the binder is influenced differently when modified by Elvaloy™ and when SBS is added, it hardens less after PAV ageing.

Force ductility test is shown in figure 3.26. When comparing the data with Elvaloy™ modified binder and non modified binder it is obvious that binder gets less inclined to brittle (is more ductile) by adding SBS to Elvaloy™ modified asphalt. Com-



**Figure 3.26:** Froce Ductility, SBS + Elvaloy™

paring figures 3.2, 3.14 and 3.26 (non modified, Elvaloy<sup>TM</sup> and SBS + Elvaloy<sup>TM</sup>) it is obvious that modification enhanced the visco-elastic properties for force ductility test.



**Figure 3.27:** Kinematic Viscosity, SBS + Elvaloy<sup>TM</sup>

By modifying the binder its rotatory viscosity was enhanced mainly for lower temperature (135°C). It is obvious that adding SBS to the Elvaloy<sup>TM</sup> mixture (figure 3.27) did not make much of a change (for Elvaloy<sup>TM</sup> see figure 3.15). The order of values according to the states of ageing follows the same trend with almost the same results for only Elvaloy<sup>TM</sup> and for Elvaloy<sup>TM</sup> combined with SBS modifier. So the effect of ageing is very similar.

Adding SBS to Elvaloy<sup>TM</sup> modified asphalt caused a difference in order of values (B, RTFO1x, RTFO3x, PAV and RTFO6x) when comparing stiffness of Elvaloy PMB (figure 3.16) with SBS + Elvaloy<sup>TM</sup> PMB and non modified samples (figures 3.28 and 3.4), the value for RTFO6x aged sample has different order to PAV and for non modified sample even to RTFO3x. For Elvaloy<sup>TM</sup> PMB the trend is increasing with ageing of binder, adding SBS caused the RTFO6x aged sample to lesser the stiffness and the trend shows inclination to non modified samples.

As in order to prevent the temperature (and fatigue) cracking the lower values of stiffness are desirable, it could be said, when comparing non modified asphalt, Elvaloy<sup>TM</sup> modified binder and SBS + Elvaloy<sup>TM</sup> modified samples (figures 3.4, 3.16 and 3.28), that adding Elvaloy<sup>TM</sup> caused the bitumen to be more inclined to temperature

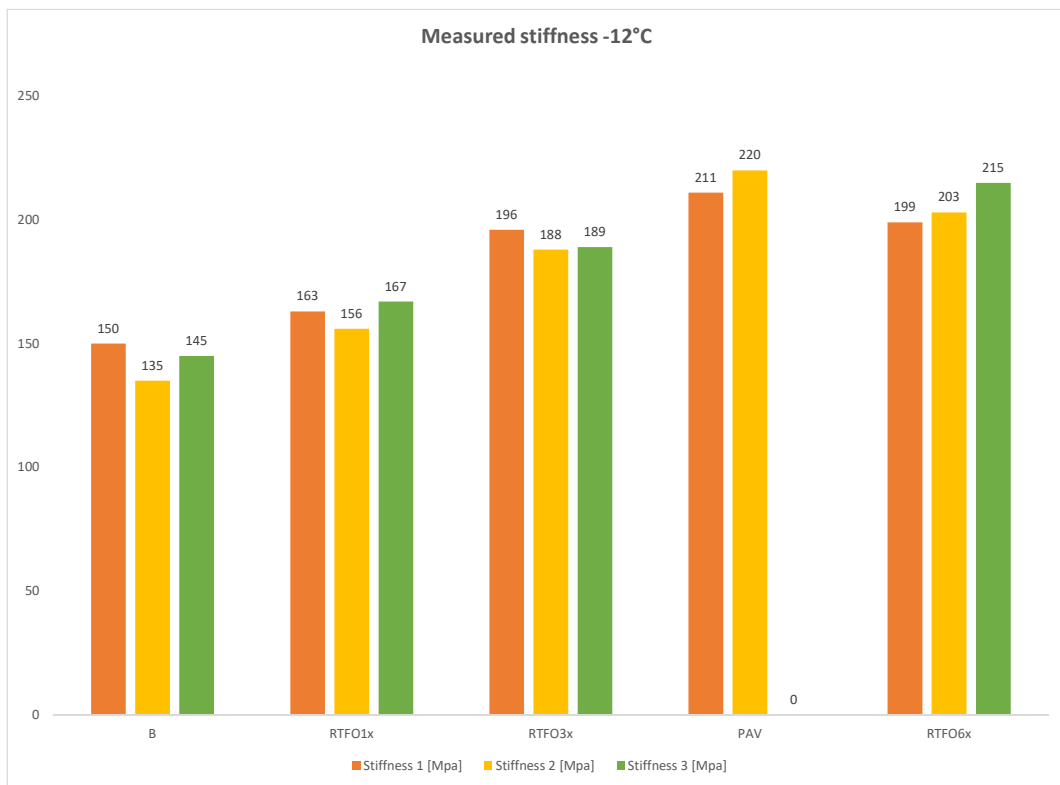
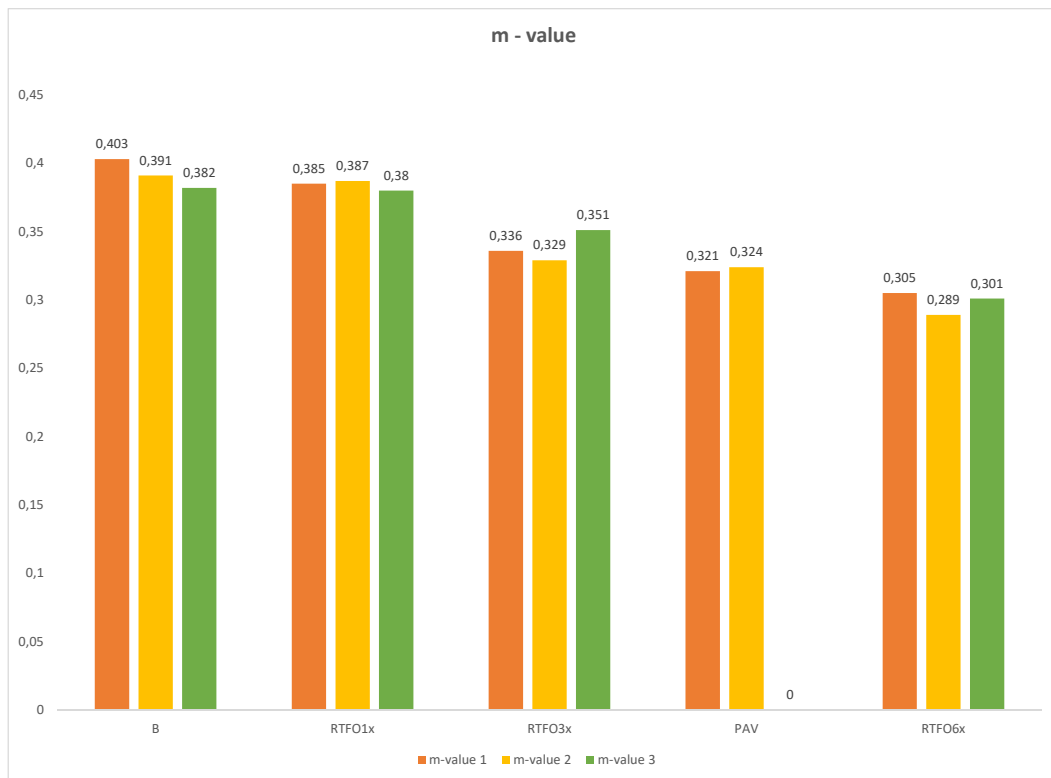


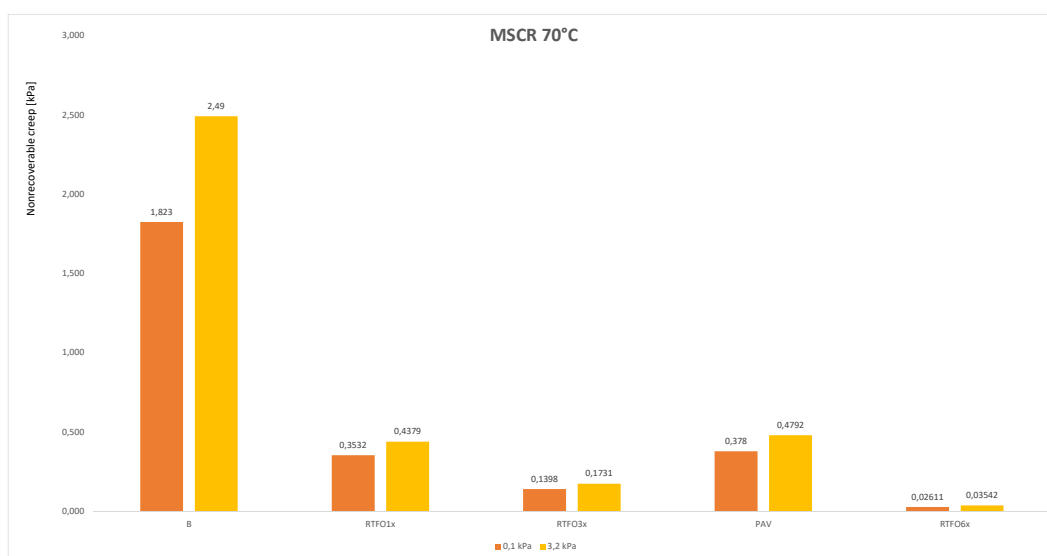
Figure 3.28: Measured stiffness, SBS + Elvaloy™



**Figure 3.29:** m-value at -12°C, SBS + Elvaloy™

cracking and adding SBS to the mixture enhanced this type of performance, but still the best values (the lowest stiffness) shows non modified sample.

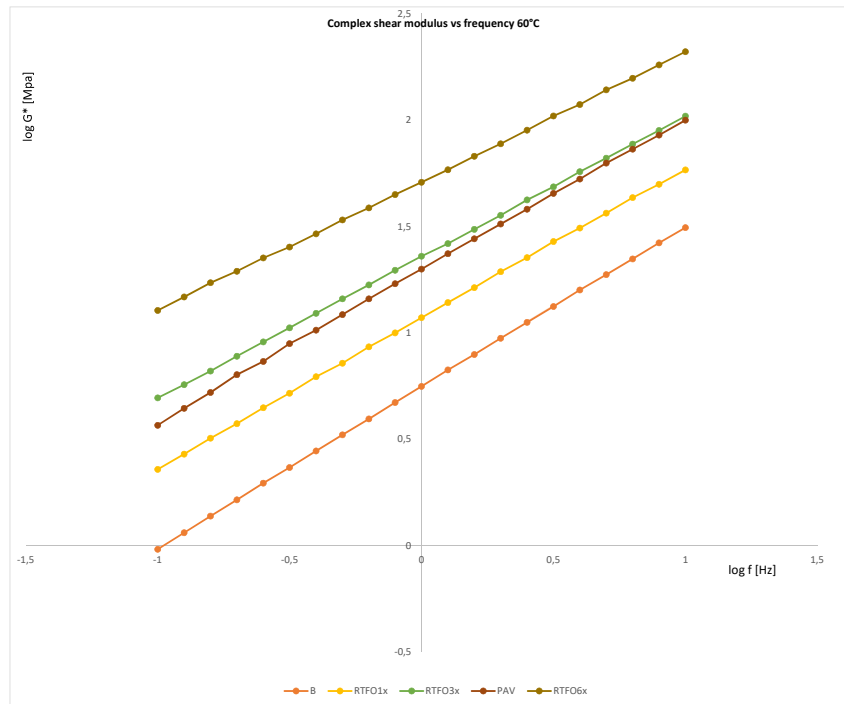
The change of stiffness in time at constant temperature is defined by m-value, in order to prevent the cracking of asphalt concrete the high values are desirable. Again non modified sample shows the best performance, the Elvaloy™PMB shows little bit better performance than the mixture with added SBS, but the difference is really slight, as could be observed when comparing figure 3.29 with figures 3.49 for non modified sample and for Elvaloy™PMB figure 3.17. So the SBS modification improved stiffness but worsen m-value in the same time.



**Figure 3.30:** Jnr values for 0.1 kPa and 3.2 kPa at 70°C, SBS + Elvaloy™

Multiple stress creep recovery performance is getting closer to non modified samples by adding SBS to the mixture, so the binder is more inclined to rut after adding SBS. The numbers are still closer to Elvaloy™PMB but when comparing figures 3.6 for non modified sample, 3.18 for Elvaloy™ and 3.30 for SBS + Elvaloy™, the order of values is more or less the same (contrary to all the other tests performed) but the differences between Jnr values for 0.1 kPa and for 3.2 kPa are small for Elvaloy™PMB (figure 3.18), mostly visible for non aged sample (B) and they get very transparent when adding SBS to the mixture (figure 3.30) when comparing non modified binder (figure 3.6). It is question of further research whether the rutting resistance correlates more with high or low shear loading.

For RTFO6x aged samples it does not really matters whether the sample is non modified, Elvaloy PMB or SBS + Elvaloy<sup>TM</sup>PMB (when comparing the difference between  $J_{nr}$  for 0.1 and 3.2 kPa) but for PAV aged samples there is the same behavior for SBS + Elvaloy<sup>TM</sup> and non modified asphalt (this actually more or less applies for all the states of ageing). So it could be said that adding SBS did not enhanced the elastic recovery behavior of bitumen, as the values for  $J_{nr}$  are higher in compare with Elvaloy<sup>TM</sup> modification.

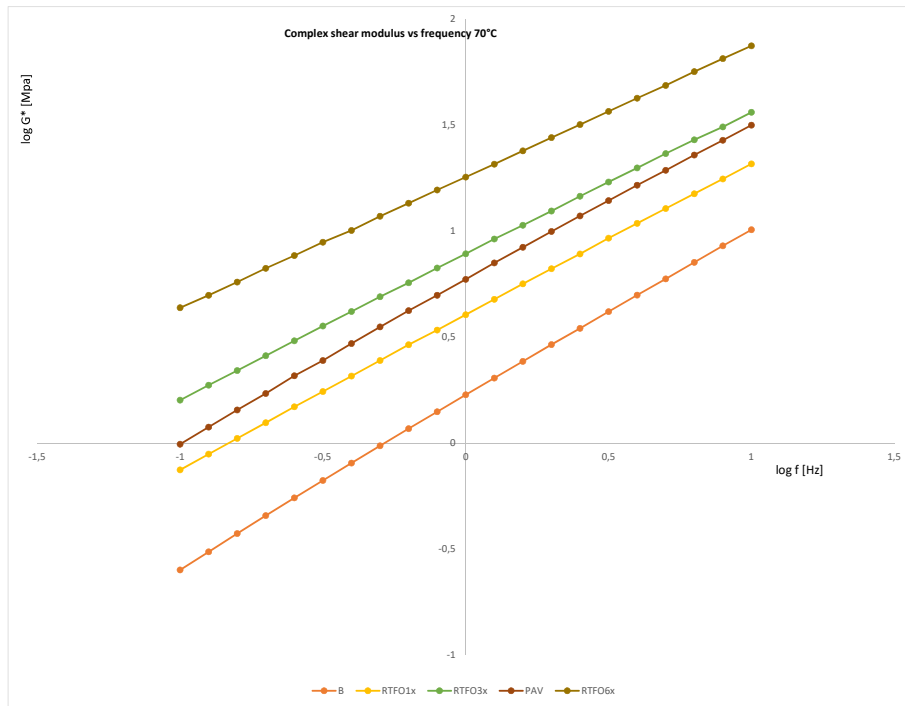


**Figure 3.31:** Isotermic plot at 60°C of Complex shear modulus vs Frequency in logarithmic scale, SBS + Elvaloy<sup>TM</sup>

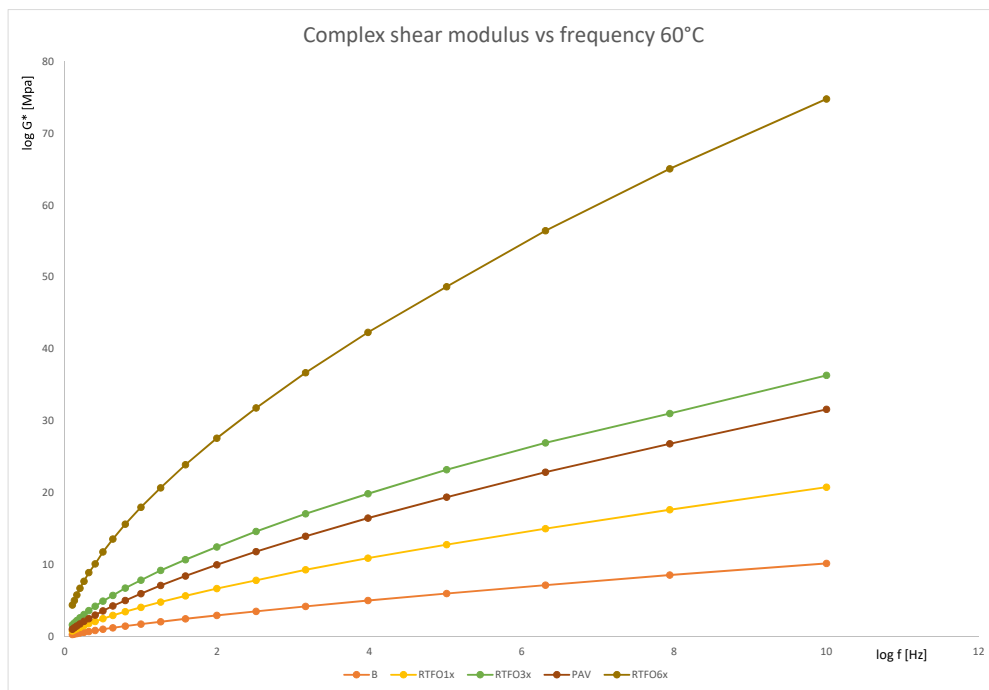
Logarithmic reliances between complex shear modulus  $G^*$  and frequency at temperatures of 60°C and 70°C are shown in figures 3.31 and 3.32. When comparing these two figures the closeness of PAV and RTFO3x ages samples is obvious. The effect of temperature causes that for higher temperature the difference between these two states of ageing is more transparent (although for higher frequencies the effect become less visible).

For Elvaloy<sup>TM</sup> modified binder (figures 3.19 and 3.20) the effect is visio versa - for higher temperature (70°C) the closeness of PAV and RTFO3x samples is more visible than for lower temperature.

For non modified samples (figures 3.8 and 3.46) there is a closeness of these two states of ageing (PAV and RTFO3x) but it is not influenced by the temperature that much as for it is when comparing PMBs.

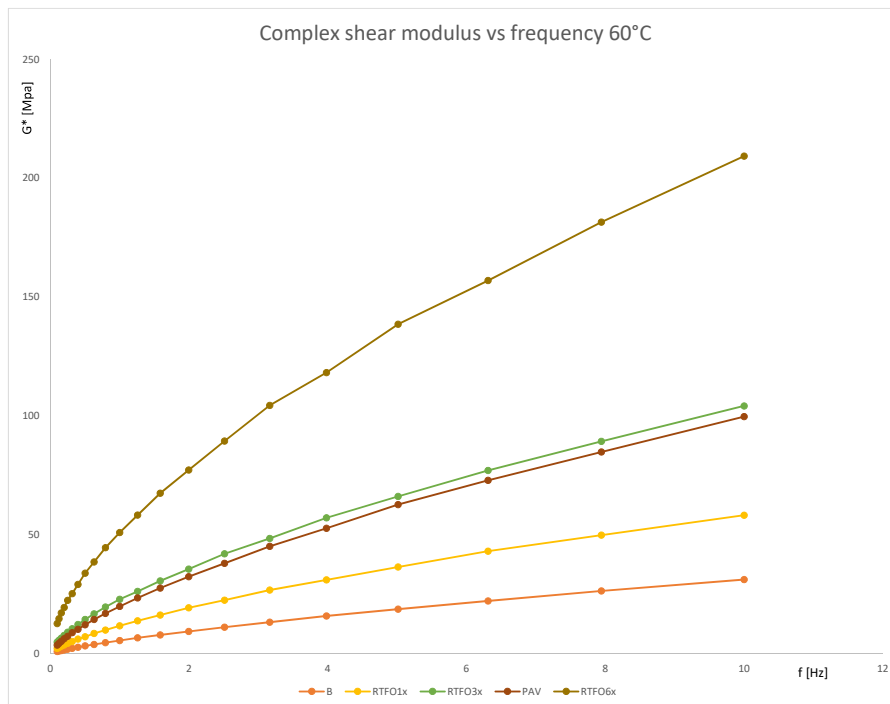


**Figure 3.32:** Isothermic plot at 60°C of Complex shear modulus vs Frequency in logarithmic scale, SBS + Elvaloy™



**Figure 3.33:** Isothermic plot at 70°C of Complex shear modulus vs Frequency, SBS + Elvaloy™





**Figure 3.34:** Isothermic plot at 60°C of Complex shear modulus vs Frequency, SBS + Elvaloy™

Again for better understanding the difference between asphalt ageing and its change in high frequencies in figures 3.34 and 3.33. The gap between values for non aged sample (B) and RTFO6x aged one is pretty much the same for both PMBs, which means for lower temperature there is a big difference in values for the highest frequency (10 Hz) when for ten degrees higher temperature the difference in values is less transparent.

When comparing the both PMBs, figures 3.36 and 3.35 for SBS + Elvaloy™ modification and figures 3.24 and 3.23 for only Elvaloy™ modified binder, the behavior of binder (an order of values, mainly PAV and RTFO3x) at temperature of 60°C is very similar, same can be said about higher temperature.

### 3.3.1 Summary of SBS + Elvaloy™ modified binder

By modifying the binder by SBS + Elvaloy™ the asphalt became softer and more elastic. When comparing the effect of ageing on asphalt modified by SBS + Elvaloy™ with binder modified just by Elvaloy™, it could be said that the effect of ageing was lesser - the hardening of binder is less transparent (this effect can be seen p.e. at MSCR results), although when comparing the results for RTFO6x or for higher temperatures, the difference between these two kind of modifications become lesser. Results for this type of modification are closer to non modified binder when talking about soft/hard properties of binder. Though, it can not be said that by adding SBS to the mixture the

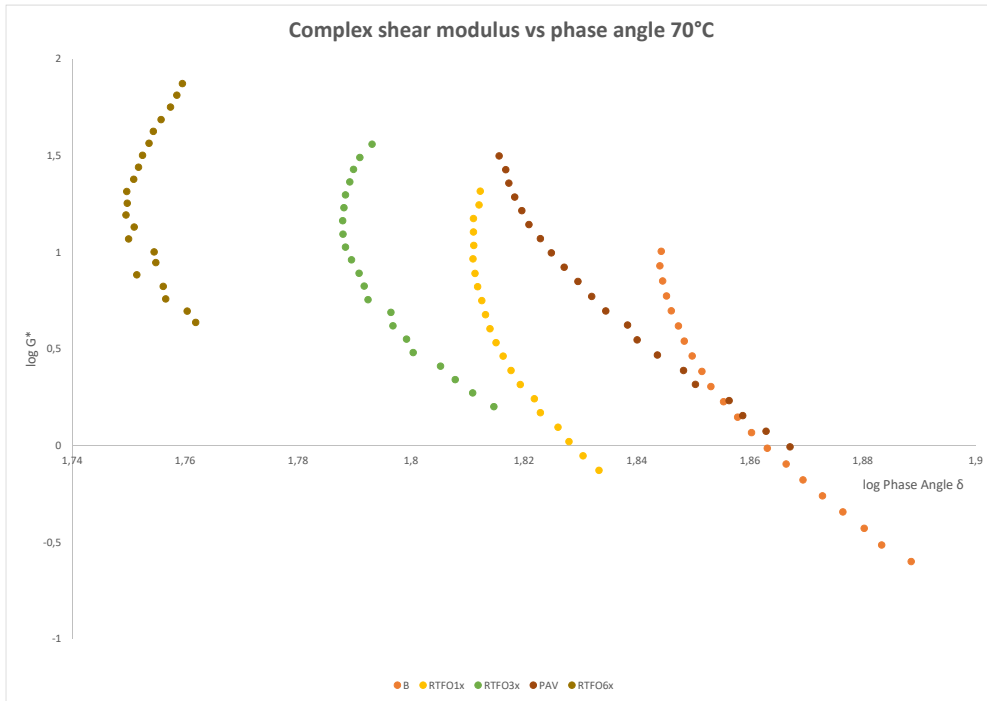


Figure 3.35: Log G\* vs log Delta at 70°C, SBS + Elvaloy™

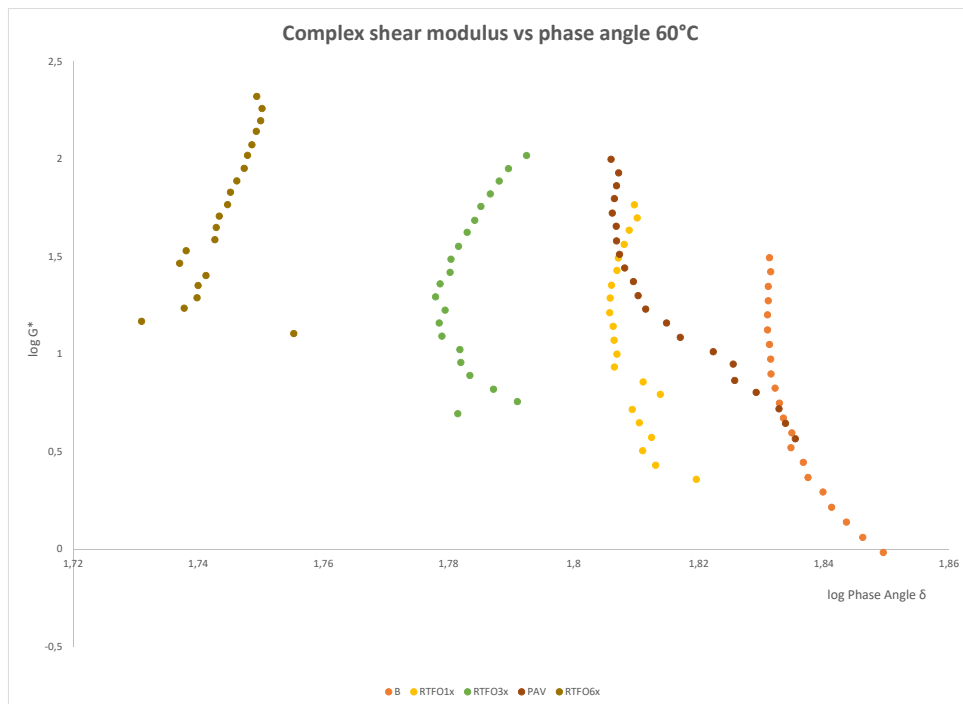


Figure 3.36: Log G\* vs log Delta at 60°C, SBS + Elvaloy™

asphalt becomes better over all (p.e. by enhancing m-value when lowering stiffness in the same time).

Talking about the possibility to replace PAV ageing by RTFO done three times in a row (RTFO3x), the case is the same as for Elvaloy™ modification - for some tests (DSR testing at lower temperatures or more or less penetration, softening point or elastic recovery test) this could apply but overall results suggest that it is not possible to replace these two kinds of ageing, which is similar case to Elvaloy™ modification.

### 3.4 Data evaluation

For evaluating the data, the values of non modified binder and PMBs were put together for each test. Then the results were standardized by percent scale, non aged sample (Base binder) considered as 100 percent of value, so the change in binder's performance caused by its ageing for non modified samples and for PMBs is more transparent.

Also in order to get more into the actually rheological properties of the binder, this chapter is divided not by the tests performed but by the actual properties of asphalt; they are softening, hardening, elasticity and the bitumen's shear properties.

#### 3.4.1 The Effect of Ageing on Softening and Hardening

The hardening of asphalt and its change due to the modification and ageing is shown in figure 3.37. The upper chart shows the actual measured values and the lower one shows the change in percent over non aged sample (base asphalt). So the values for each bar in the lower chart is calculated simple by formula:

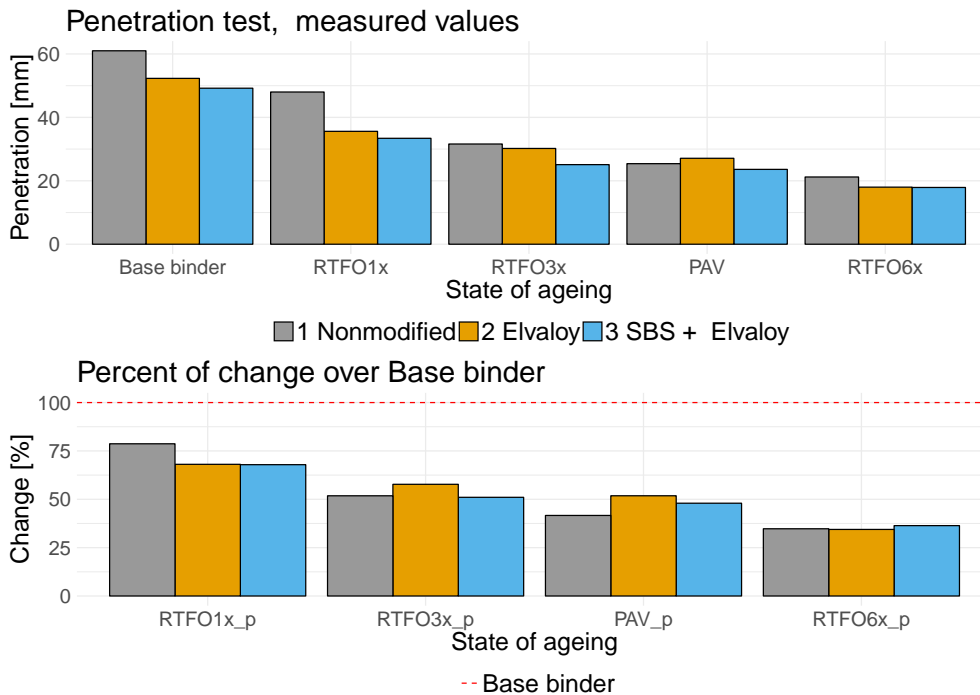
$$RTFO1x_p = \frac{RTFO1x}{Basebinder} \times 100$$

And so on for each state of ageing (RTFO1x, RTFO3x, PAV and RTFO6x). This simple formula (and charts) helps to clarify the change that was made by ageing for each type of modification.

It is obvious that with ageing the binder gets harder (the penetration gets lower). The non modified sample hardens the most after one cycle of RTFO (RTFO1x), RET modified PMB (yellow bar) is most inclined to hardening after three cycles of RTFO (RTFO3x) and PAV (as can be observed in the lower chart). After six cycles of RTFO it is obvious (lower chart in figure 3.37) that the effect of ageing is not being reduced by either type of modification (and it is about 30%). According to penetration test results in case of binder modified with SBS + RET (blue bar), the correlation between PAV and RTFO3x is obvious - it could be possible to replace one cycle of PAV ageing by three cycles of RTFO, but almost only for penetration test, same trend could be observed in figures p.e. 3.40 - viscosity at higher temperature or for SBS + RET sample.

Figure 3.38 shows ring and ball softening point measured in water or glycerin, according to the actual measured value.

When observing the change after one cycle of RTFO, it is obvious that modification did not influenced the change caused by ageing that much (the change of all three binders is more or less the same - about 110%, but of course the values differentiate).



**Figure 3.37:** Penetration test, values and change over Base binder

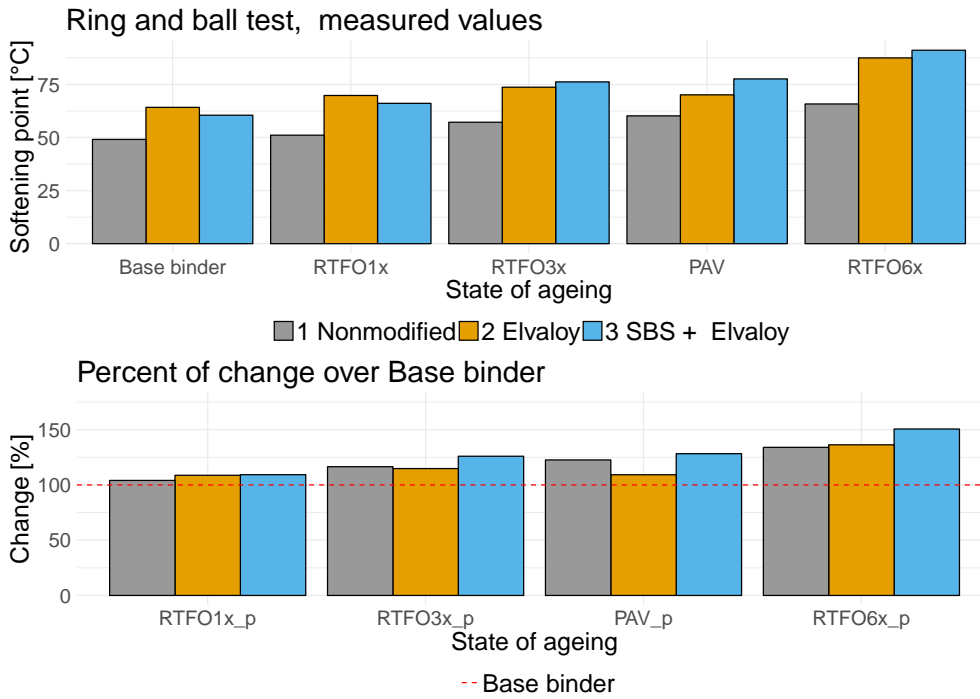
When comparing RTFO3x and PAV, for SBS + RET, again, there could be a switch between those two types of ageing. For other two samples (non modified and RET) the situation is different. *RET polymer modification behaves almost the same (changes the values almost the same) as non modified sample after six cycles of RTFO, the SBS + RET still becomes even softer.*

Comparing six cycles of RTFO for penetration and softening point (figures 3.37 and 3.38) - both tests somehow show hardening of bitumen - the penetration was changed in the same way, either in case of original or modified binder. Softening point though was changed way more for SBS + RET modified asphalt (blue bar).

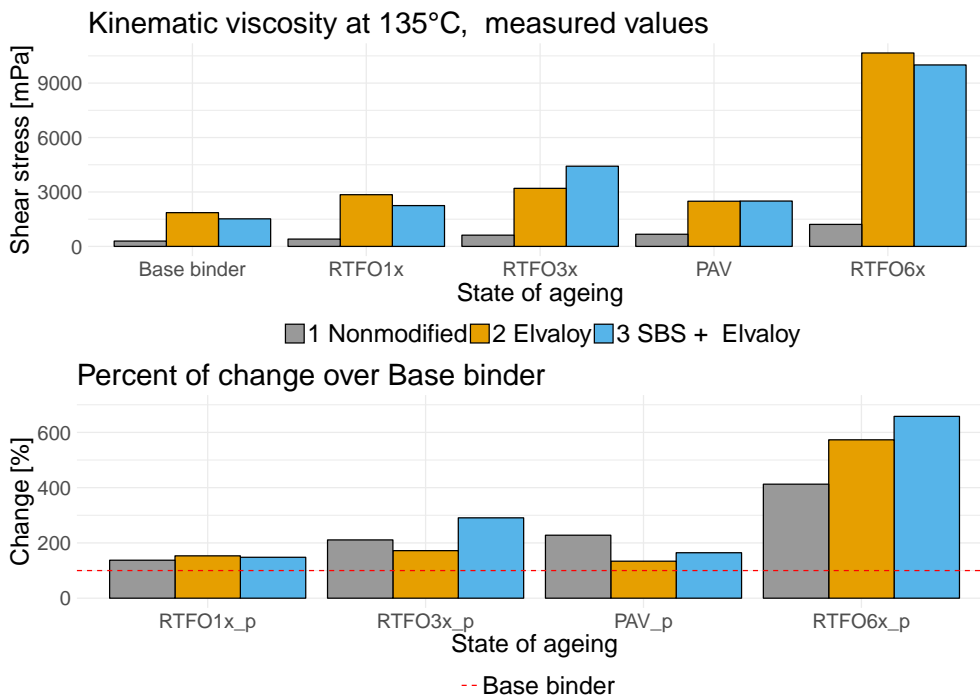
### 3.4.2 The Effect of Ageing on Visco - Elastic Behavior

Figure 3.39 shows viscosity measured at temperature of 135°C. For RTFO cycle done one time (RTFO1x) a similar case as for Ring and Ball test (figure 3.38) can be observed, the change in values was almost the same no matter the modification of the binder.

Comparing RTFO3x and PAV aged samples it could be observed that the situation is different, not even SBS + RET modified sample shows the same change in values like it did for softening point or for penetration (figures 3.38 and 3.37). The same case (with an exception of RTFO6x) can be observed for temperature of 165°C in figure 3.40. The values - or the percent of change - for higher temperature are much lesser though than for temperature of 135°C. Also at higher temperature the effect of ageing

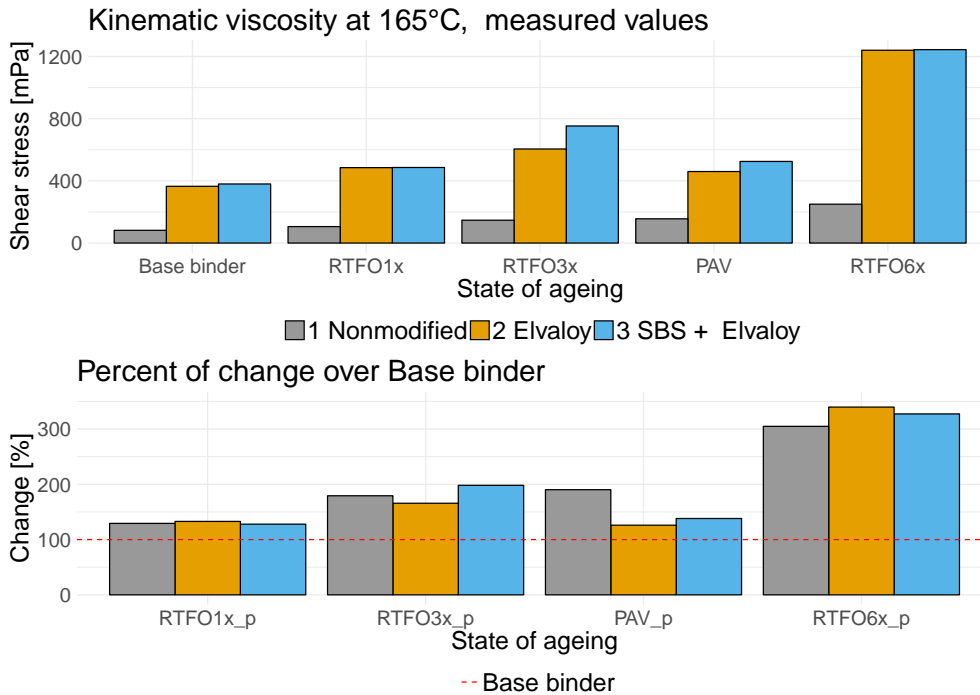


**Figure 3.38:** Ring and Ball test, values and change over Base binder



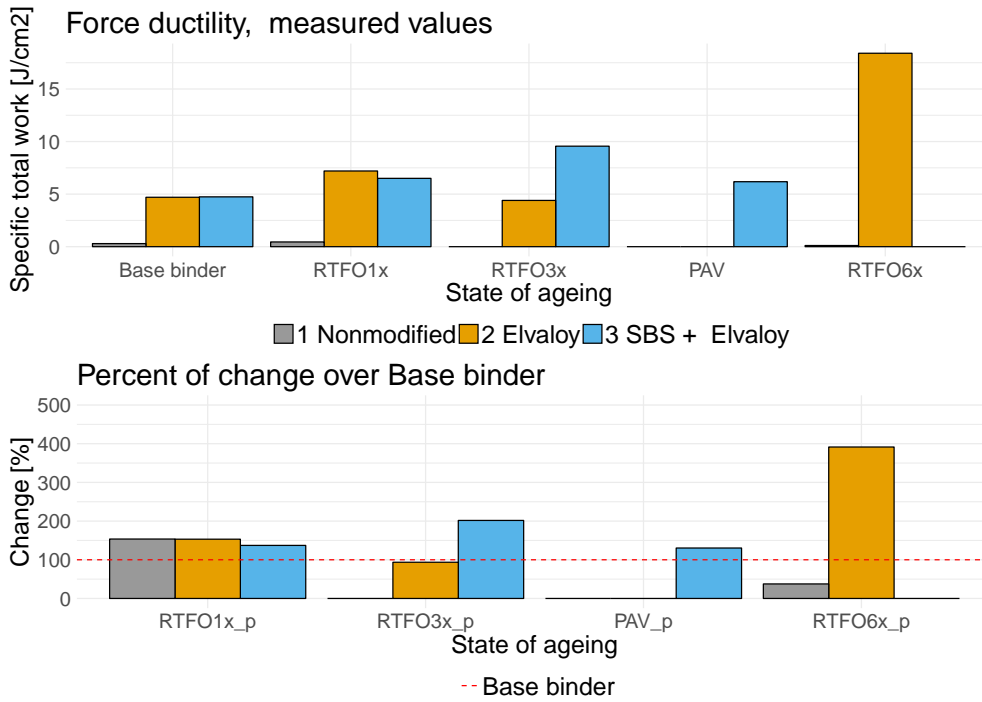
**Figure 3.39:** Viscosity at 135°C, values and change over Base binder

is the same for all the modifications at RTFO6x, which was not the case for the lower temperature (compare RTFO6x in figures 3.39 and 3.40). At temperature of 165°C, the modification (it's change in %) is almost insignificant. *The values change, according to the modification, but the effect of ageing is the same (sample modified or not).*

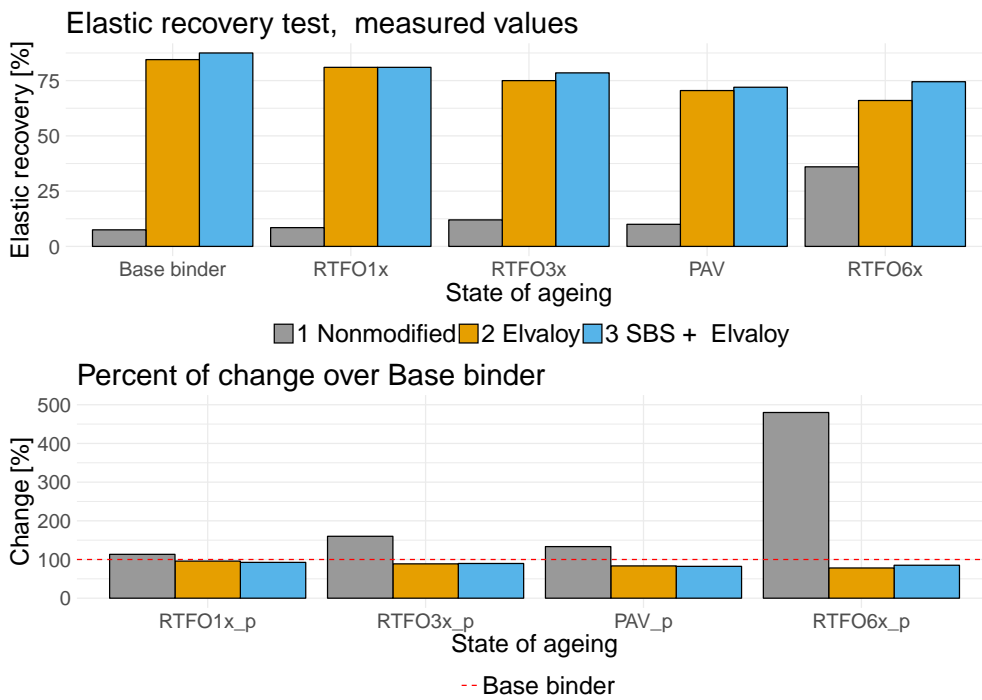


**Figure 3.40:** Viscosity at 165°C, values and change over Base binder

Figure 3.41 shows the ductility of binder measured at 10°C. Some samples could not be measured due to high brittleness - mostly non modified binder but after PAV ageing the only sample that did not crack was SBS + RET modified one. When the samples were not aged (base asphalt samples) for both PMBs the actual measured value was almost the same, this changed a lot with ageing and for PAV the only sample that withstood the strain was SBS + RET sample. The situation for RTFO done six times in a row is different though and only RET PMB passed the test and did not crack, so the value could be measured. Again it is not possible to replace RTFO3x and PAV ageing for neither PMBs or for non modified asphalt. *An interesting fact is that values measured (and change in %) for PAV gets actually closer to RTFO1x than to RTFO3x, which is trend that could be observed in kinematic viscosity tests as well (figures 3.39 or 3.40).* Binder's elastic behavior was measured by Elastic Recovery test at temperature of 25°C. The results of this test show that the modification did not influence the change made by ageing (figure 3.42). Non modified sample shows big differences in values (and in percent of change) but the two PMBs show very similar values so it could be assumed that the modification did not influenced binder's elastic response to strain that much and that the effect of ageing is also minor for this type of elastic behavior. Another



**Figure 3.41:** Force Ductility at 10°C, values and change over Base binder



**Figure 3.42:** Elastic Recovery Test, values and change over Base binder

test that shows elastic response to stress is MSCR - applied shear stress results in shear strain measured with dynamic shear rheometer (DSR). MSCR test was measured at 70°C and both values for Jnr (0.1 and 3.2 kPa) were evaluated, the difference is so marginal that only Jnr values for 3.2 kPa will be listed in this paper.

Binder’s elastic response to shear strain at 70°C is shown in figure 3.43. For base binder samples, the difference between modified binders and non modified asphalt is the most transparent one, for RTFO1x the values of modified binders gets closer, at PAV state of ageing it does not matter any more whether the binder is modified or not. Replacing PAV with RTFO3x is not possible for this test neither. *The biggest influence by ageing was for RET modified binder aged by PAV method.*

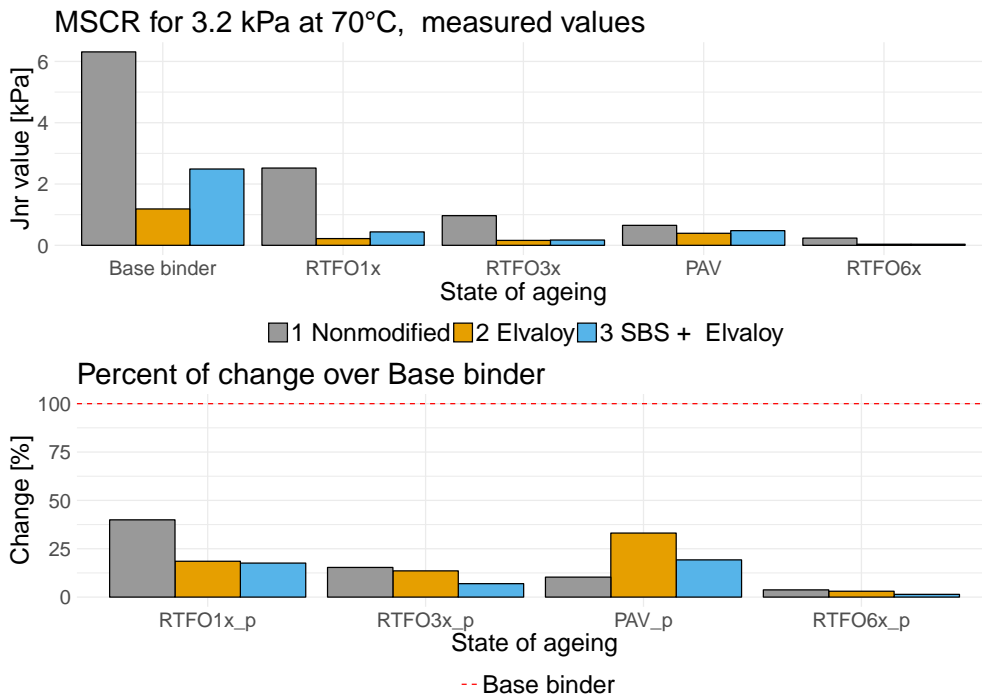


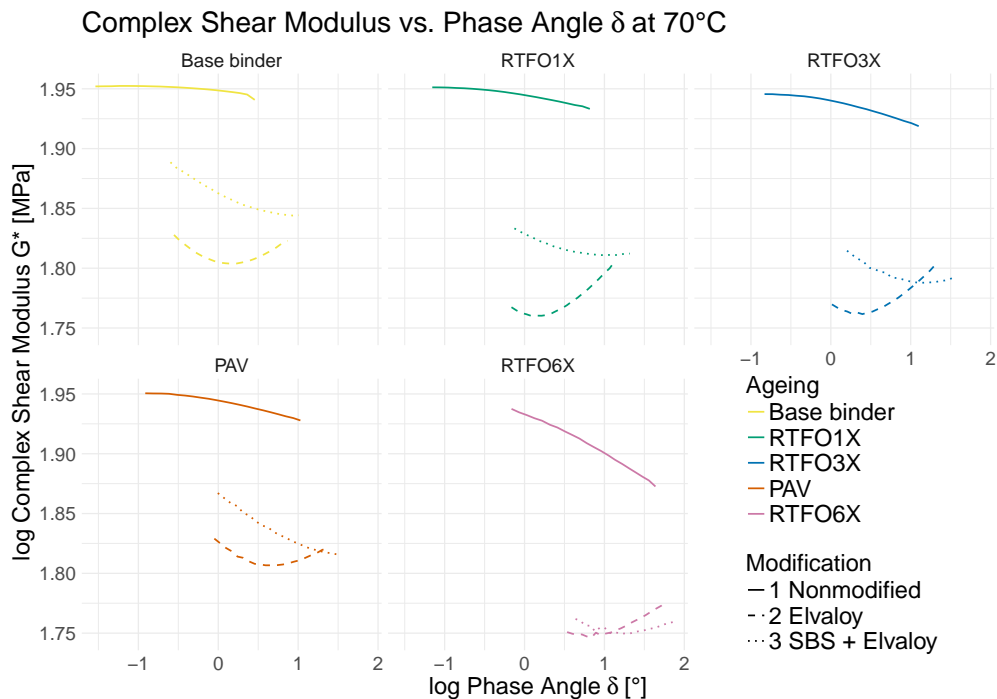
Figure 3.43: MSCR test at 70°C, values and change over Base binder

### 3.4.3 The Effect of Ageing on Shear Properties

Black’s diagrams for temperatures 70°C and 60°C are shown in figures 3.44 and 3.45. For both temperatures there is a clear effect of modification - for non modified samples (both temperatures no matter the ageing) the reliance is displayed by linear (maybe concave) downward slopping curve, for both PMBs, the reliance is neither downward slopping nor linear. The closely the reliance gets to being linear is for sample aged RTFO6x at lower temperature but it is still far from downward slopping curve.

The effect of ageing for this reliance is neither that high when compared with other tests (p.e. viscosity at figure 3.39 or elastic recovery at figure 3.42). The samples aged



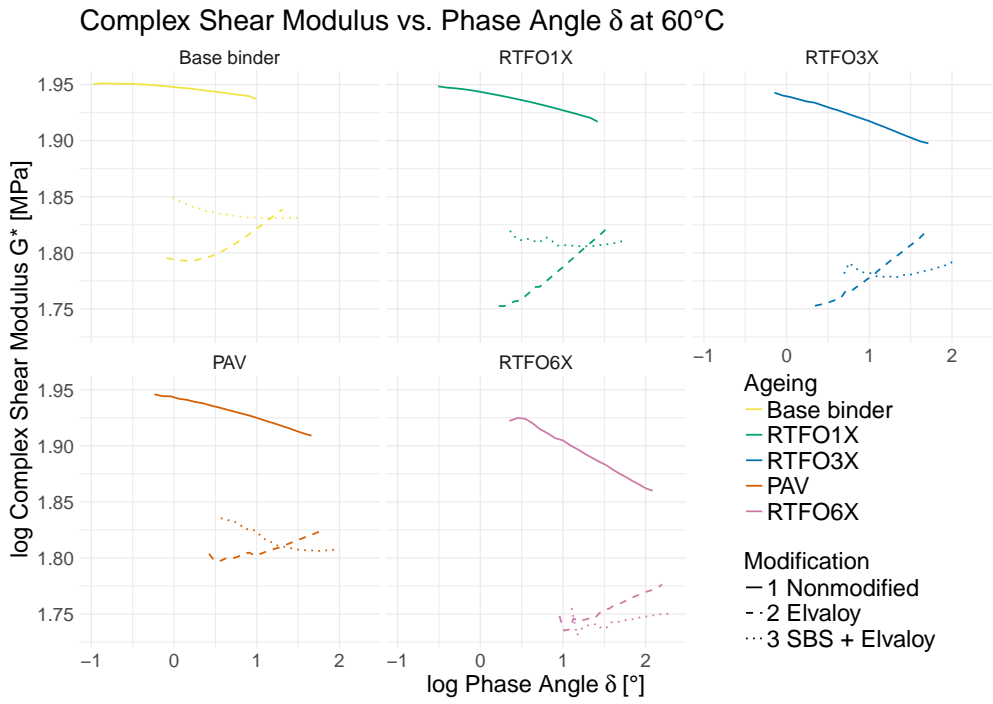


**Figure 3.44:** Complex shear modulus vs phase angle  $\delta$  at 70°C

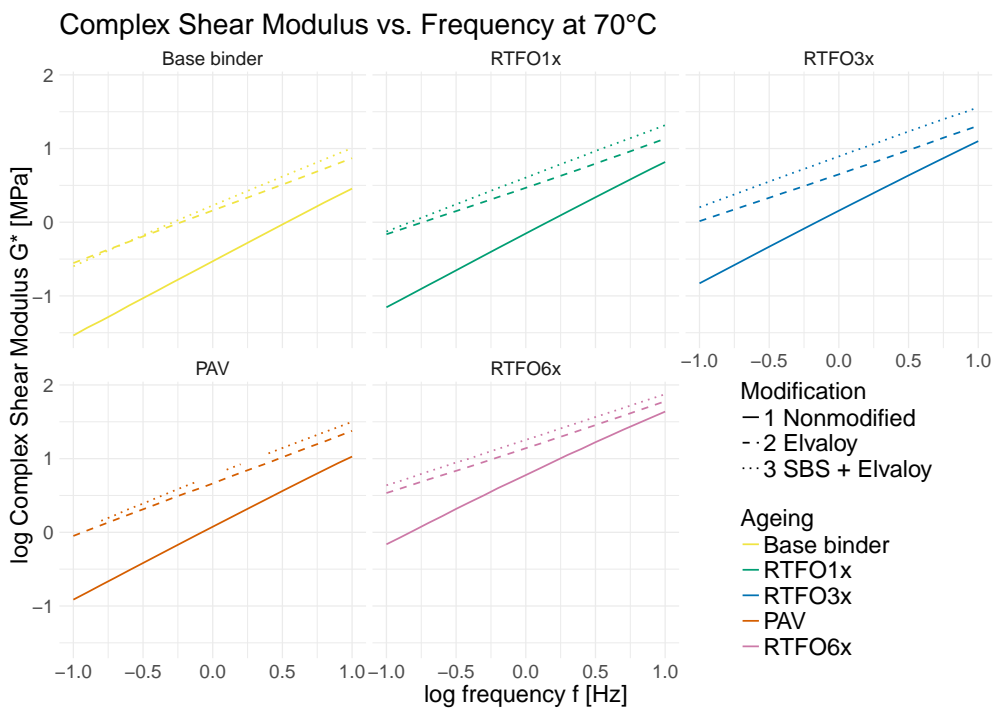
RTFO6x is out of order or reliance when compared to other states of ageing (both temperatures) but *the other states of ageing display more or less same reliance, especially when comparing RTFO1x and PAV - those two states of ageing are again closer in values than RTFO3x and PAV (same as in figures 3.39 or 3.40)*. For temperature of 60°C the values for SBS + RET modified binder are higher than those for RET modified samples for all ageing, this rule does not apply for higher temperature though. In figure 3.44 values at lower frequencies for all the states of ageing are lower for RET, when adding SBS to the mixture, the values actually switch the order and *from mid frequencies to the highest ones the asphalt modified with SBS shows higher values than the one modified only with RET (this applies for temperature of 70°C only)*.

Comparing the reliance between complex shear modulus  $G^*$  and frequency, for lower temperature the PMBs values get closer together especially at lower frequencies (figure 3.46). On the other hand *at higher frequencies the values of non modified samples get closer to both PMBs - this rule applies for both temperatures (figures 3.46 and 3.46)*.

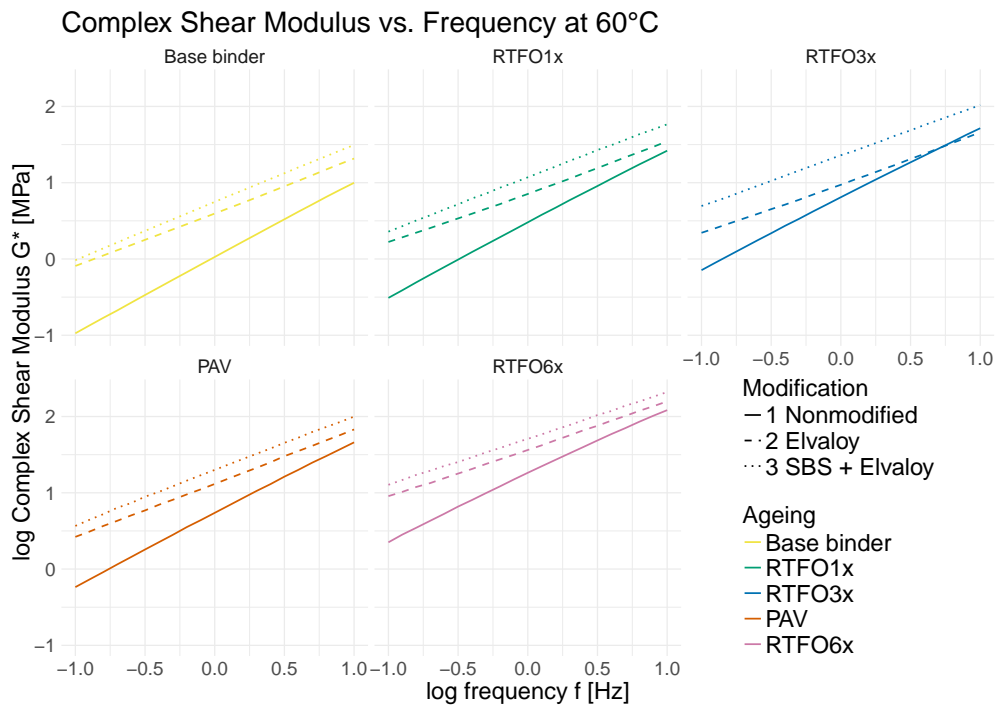
In figure 3.46 at higher frequencies not only the values of non modified sample get closer PMBs values but in the same time the gap between values of RET and SBS + RET for higher frequencies gets more and more transparent. In other words: for higher temperature non modified binder gets closer to RET modified sample at higher frequencies and SBS + RET modified sample's values become more different at these (higher) frequencies when the reliance at lower frequencies is vice versa - this behavior can be observed at lower temperature as well (figure 3.47) but not that transparent.



**Figure 3.45:** Complex shear modulus vs phase angle  $\delta$  at 60°C



**Figure 3.46:** Complex shear modulus vs frequency  $\delta$  at 70°C

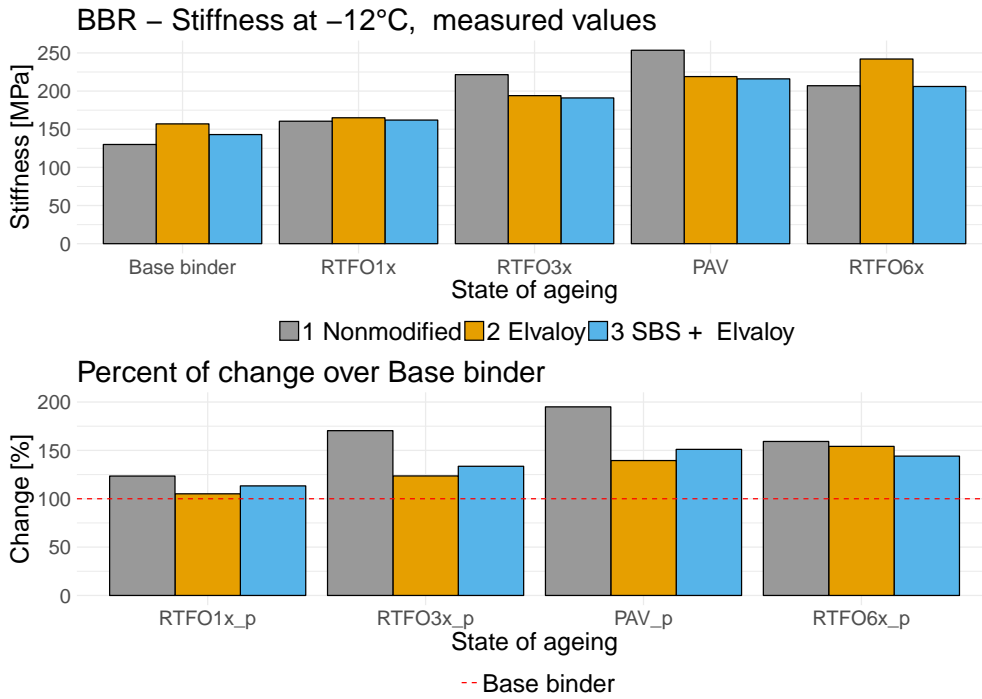


### 3.4.4 The Effect of Ageing on Stiffness

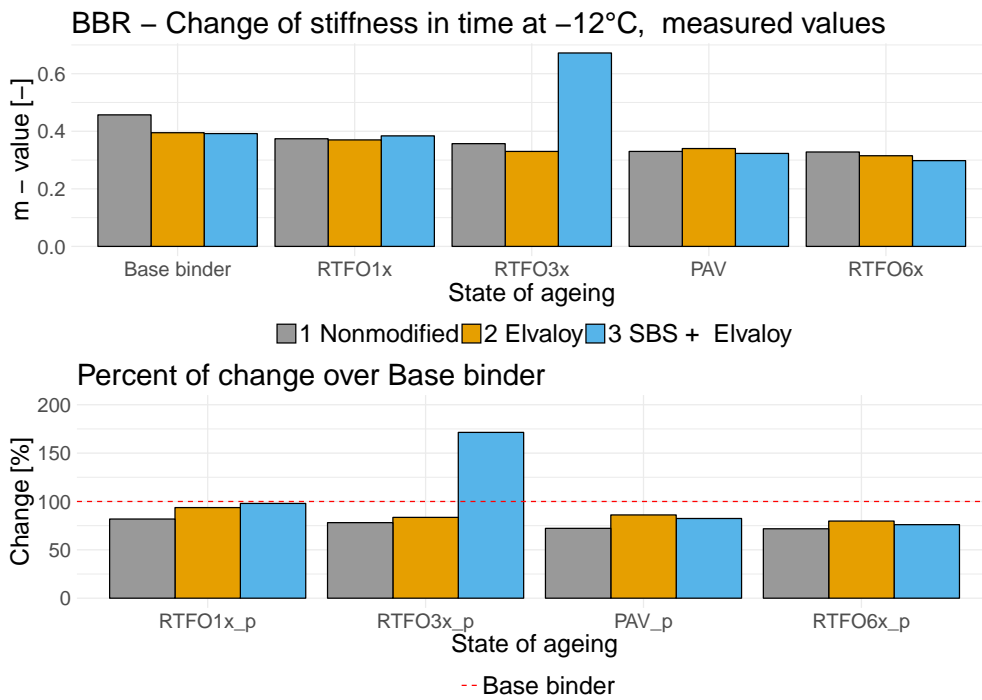
For BBR testing there were always three beams were measured and then, if the difference between the values was no higher than 5%, an average was calculated as a result of stiffness and m-value. Discussing the stiffness at temperature of -12°C (in figure 3.48) it is obvious that the effect of modification was marginal, when comparing PMBs reply to different states of ageing (the lower chart in figure 3.48). Not according to the expectations, adding SBS to the mixture did not enhance it's low temperature behavior, as the better results show only RET modification for all the state of ageing. Replacing RTFO3x with PAV ageing is not possible for BBR testing neither as could be observed in the upper chart in figure 3.48.

Modification enhanced the change of stiffness with increasing ageing, as could be seen when comparing the grey bars (non modified samples) with the other two datasets. *Contrary to the measured stiffness in figure 3.48 the binder's change to stress in time was enhanced the most by adding SBS to bitumen* (the big blue bar in the lower chart in figure 3.49). From measured values it is obvious though that neither modification neither ageing did not influence binder's m - value in a big scale.

All in all asphalt's low temperature behavior (BBR testing) was not influenced that much by the modification as it was by ageing (with difference of SBS + RET after three cycles of RTFO in figure 3.49).



**Figure 3.48:** Stiffness at -12°C, values and change over Base binder



**Figure 3.49:** M - value at -12°C, values and change over Base binder

## Conclusion

Hardening of binder from ageing was reduced by modification especially for base binder and RTFO (one and three times) aged samples - both modification displays lesser values (better resistance to ageing) than neat asphalt. After PAV it does not matter if modified or not, although the RET PMB shows the best results but only very slightly, the effect is almost the same for both PMBs. After RTFO six times is actually non modified sample the one with the higher penetration value (the softest one).

For point from which the binder behaves like a liquid and not like a solid (softening point) applies the same - not that big a difference between RET polymer modification and SBS + RET.

For the viscosity behavior of bitumen, at both temperatures, adding SBS to the RET mixture did not influence the values in a big scale neither. For both temperatures also applies that PAV values are closer to RTFO1x than to three cycles of RTFO - this trend can be also observed for other tests like viscosity (both temperatures) or when evaluating the reliance between  $G^*$  and phase angle.

After one cycle of RTFO the binder with RET is less inclined to brittle (force ductility value is higher) than the one with SBS added but after PAV the situation is completely opposite. RET sample is the one that is the most effected by ageing when it comes to force ductility but only after RTFO6x. Very high brittleness for non modified samples were measured at each state of ageing.

For elastic recovery a big difference between non modified and PMBs, although for RET and SBS + RET almost the same values were measured, only after six cycles of RTFO the difference between RET modified asphalt and non modified sample gets lesser whereas the SBS still has high values.

SBS + RET also influenced better the creep and recovery behavior of the binder and the neat binder still shows the worst behavior, after PAV ageing the values of all binder gets so close together that the effect of modification remains marginal. So it could be said SBS influenced the elastic (recovery) behavior better than only RET after PAV ageing the difference is not that transparent anymore.

For logarithmic reliance between complex shear modulus  $G^*$  and phase angle  $\delta$  an interesting shift in values occurred. For neat binder this reliance is characterized by a downward slopping curve by both measured temperatures (60 and 70°C). By both modified binders this reliance was always characterized by a convex curve, also at lower temperature the PMBs switch order of values usually in mid frequencies. This trend in

switching values occurred for higher temperature as well but only for far ended states of ageing.

At lower frequencies SBS + RET modified sample shows better behavior in this reliance but from mid to high frequencies RET modified asphalt is the one that gets higher values.

Comparing logarithmic reliance between complex shear modulus  $G^*$  and frequency, different behavior according to the temperature also occurs. For higher temperature (70°C) PMBs values almost cover each other at lower frequencies and they tend to go apart at higher frequencies, only after RTFO ageing done six time in a row this trend weakens. In the same time, in lower frequencies neat binder's values tend to be lower when from mid to high frequencies they get closer to both modified asphalts. At lower temperatures (60°C) this trend is weaker for modified asphalts when for neat binder the trend is stronger, for RTFO samples the modified binder even tend to get farer apart each other.

Low temperature behavior was evaluated by BBR testing at -12°C. Neither here it is not easy to decide whether adding SBS to RET modified asphalt enhanced the mixture or not. When measuring the stiffness of binder RET PMB gets slightly better values that the one with SBS added especially when comparing base binder values or RTFO6x, but both PMBs values were very close. For m-value the results were similar to stiffness ones (adding SBS did not make a big difference) with the only exception of RTFO3x ageing where the time change of stiffness at constant temperature is enhanced in a big scale. As both, stiffness and m-value, are calculated as averages for this paper, this is not a single value mistake but it could be said that the binder behaves like that after this ageing.

Neither of the tests performed showed that it could be possible to completely replace PAV ageing by RTFO done three times in a row. For some tests (penetration, ring and ball test or force ductility) it could be said that for modification SBS + RET it is possible to replace these two kinds of ageing simulations, for others it depends a lot on selected temperatures of on frequency of test cycles (DSR testing) but overall, according to the performed tests, it does not appear that it could be possible to replace PAV by RTFO3x.

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