

POLITECNICO DI TORINO
Master of Science in Civil Engineering



**Physical hardening of neat and modified
bituminous binders**
**(Indurimento fisico di leganti bituminosi tal
quali e modificati)**

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致我亲爱的父母:
感谢你们一直爱我并支持我!
我全心全意的爱你们!

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ABSTRACT

This thesis focuses on the effects of physical hardening on bituminous binders. Four different 50/70 pen-grade binders were employed, one neat bitumen, one polymer modified binder (PMB) and their combination with an experimental antioxidant (non-commercial). Since thermal cracking and hardening effects become critical in aged conditions, long-term aging was simulated in the laboratory for all materials. The bending beam rheometer (BBR) was used to perform creep tests. Three different storage times (1h, 24h, 72h) were used to analyse the effects of physical hardening. The tests were performed at two different temperatures, selected close to the lower PG limiting temperature of all samples (-6 °C and -12 °C). The creep stiffness $S(t)$ and the relaxation parameter m -value were calculated. Each BBR test has been performed on both sides of the beams, meaning the beam was loaded on one side and then flipped over to perform the next test. Based on the outputs, the hardening index and the ratio between stiffness and relaxation parameter were calculated. Results indicated that physical hardening causes a significant increase in creep stiffness. The effect of antioxidant was found to be strongly dependent on the binder type and temperature. In general, the use of antioxidant causes a reduction in the stiffness for both neat and PMB binder, while its effect on relaxation parameter was not always positive. In addition, results of the hardening index showed that the majority of the increase in creep stiffness happened during the first 24 hours. From the results of both stiffness and relaxation parameters, critical limiting temperatures were calculated. It was highlighted that the relaxation parameter always represented the most stringent criterion for the determination of the critical temperature.

Keywords: Physical hardening; Bituminous binder; Low temperature; Thermal cracking; Pavements.

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CHAPTER 1.

INTRODUCTION

1.1. Introduction

Bitumen is an important component of bituminous material, its properties can significantly affect the performance of bituminous mixture and bitumen pavement, bitumen is a kind of temperature-sensitive materials, hence, the performance and properties of the bituminous mixture are highly dependent on its service temperature.

This thesis focuses on the effects of physical hardening on bitumen. Three different storage times (1h, 24h, 72h) were used to analyze the effects of physical hardening. The tests were performed at two different temperatures, selected close to the lower PG limiting temperature of all samples (-6 °C and -12 °C). The creep stiffness $S(t)$ and the relaxation parameter m -value were calculated.

Currently, several devices and testing methods can be used to measure the mixed bitumen rheological properties, especially for the ageing properties. Among them, Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR) are two of the most commonly used machines. For the conventional DSR, a torque test is applied for the bitumen specimen at low temperature, but when the temperature below about 5°C produced instrument compliance errors in the dynamic responses when the typical thin film binder geometry was used. In the case of the conventional BBR device, the low temperature creep stiffness and relaxation properties are measured by a three-point bending test at low temperature. Due to the drawback of BBR, such as a large amount of material requirement, in this thesis, each BBR test has been performed on both sides of the beams, meaning the beam was loaded on one side and then flipped over to perform the next test, which also removed the deformation caused by previous test on the same beam (the test on the front side). The experimental method based on the BBR device was proposed by this thesis.

1.2. Goals and objectives

The main objective of this study is to investigate the effect of experimental conditions, such as physical hardening on the low temperature rheological properties of bitumen.

1.3. Thesis outlines

This thesis consists of six main chapters. The first chapter is devoted to providing a general overview of research work and motivation. The second chapter do some introduce of the background. The third chapter follows with the literature reviews. The fourth chapter focus on the experimental plan, including the method to homogenize the antioxidant and neat bitumen or polymer modified bitumen (the weight of the AO12 is 0.3% of the total quantity of neat bitumen or polymer modified bitumen), the short-term ageing simulation in RTFOT, the long-term ageing simulation in PAV, and the physical hardening simulation in BBR to get the value of creep stiffness and relaxation parameter in order to do further analysis. The fifth chapter includes the results and some discussions. The sixth chapter contains the conclusions of this dissertation.

CHAPTER 2.

BACKGROUND

In this chapter, a brief introduction to the neat bitumen and polymer modified bitumen. Second, follow with the conventional grading specifications for bitumen. Third to fifth, do some introduce of the physical hardening, thermal cracking and ageing considerations. Sixth, contain the influence factor of bitumen properties and the method to improve the bitumen properties.

2.1. Neat bitumen and Polymer modified bitumen

2.1.1. Neat bitumen

According to the European specification (EN 12597), bitumen is defined as a virtually involatile, adhesive, and waterproofing material derived from crude oil, or present in natural asphalt, which is completely or nearly completely soluble in toluene, and very viscous or nearly solid at ambient temperature [71][72]. It is well-accepted that the original characteristic of bitumen is highly dependent on its production and processing procedure, as well as bitumen crude oil characteristic [73]. Good crude oils and proper distillation processes can enhance bitumen properties. Generally, heavier crude oil gives higher bitumen yields [74]. Therefore, having a complete knowledge on the bitumen characteristics from different aspects is of paramount importance.

From a functional point of view, the bitumen has to be fluid enough at high temperature ($\approx 160^{\circ}\text{C}$) to be pumpable and workable to allow for a homogeneous coating of aggregate upon mixing. Moreover, it has to be stiff enough at high temperatures to resist rutting (according to the local temperature, $\approx 60^{\circ}\text{C}$). Finally, it must remain soft and elastic enough at low temperature to resist thermal cracking [75]. All the mentioned requirements are almost opposite, and most of the available neat bitumen would not provide all the needed characteristics together. Moreover, in some applications, the performance of conventional neat bitumen may not be satisfactory considering the required engineering properties because it is brittle in a cold environment and softens readily in a warm environment. This limited performance temperature range is the main drawback to neat bitumen, limiting its use for both roofing and road paving application.

In addition, as the traffic speed and load has dramatically increased, unplanned overloading has notably shortened the life of asphalt pavements, increasing its costs of maintenance and risks to users. Hence in order to enhance the performance properties of neat bitumen, to date, a variety of additives have been introduced and some have been used successfully for many applications. Modifier and additives have been used to boost bitumen performance include polymers, chemical modifiers, extenders, oxidants and antioxidants, hydrocarbons, and anti-stripping additives. The applicability of using antioxidant additives to retard the ageing of bitumen. The antioxidant additive provide resistance to oxidative hardening of bitumen. Polymer modification improves the temperature susceptibility of bitumen and can improve its resistance to permanent deformation, thermal cracking and fatigue cracking.

2.1.2. Polymer modified bitumen

Polymers are macromolecules synthesized through chemical reaction between smaller

molecules (monomers) to form long chains. The physical properties of the resulting polymer are determined by the chemical structure of monomers and by their sequence inside the polymer. A combination of two different monomers that can be in a random or block arrangement gives a so-called copolymer. Polymers include a board range of modifiers with elastomers and plastomers being the most commonly used types, elastomers are rubber-like at room temperature, whereas plastomers are solid-like at room temperature. Polymer modified bitumen should be used only on wearing course depending upon the requirements of extreme climate variations. The advantages of using modified bitumen are as follows: [70]

- Lower susceptibility to daily and seasonal temperature variations
- Higher resistance to deformation at high pavement temperature
- Better age resistance properties
- Higher fatigue life for mixes
- Better adhesion between aggregates and binder
- Prevention of cracking and reflective cracking

But for the polymer modified bitumen, there are also two types of disadvantages, which are polymer separation and degradation. The polymers are almost always dispersed in the asphalt cement, existing as tiny particles or as an extended network. If they are not well dispersed or if they are chemically incompatible with the base asphalt cement, the particles can re-assemble, resulting in what is commonly referred to as separation. The properties of a polymer-modified binder can also be altered by polymer degradation. The polymer can be altered chemically if the bitumen is heated to temperatures at which the polymer degrades thermally.

2.2. Conventional grading specifications for bitumen

Bituminous materials are temperature-load sensitive material. The performance properties of the asphalt mixture are highly dependent on its service temperature, loading strain/strain level, and loading path. In the case of pure bitumen, at a given loading strain level, its behaviour is strongly dependent on the temperature [76].

Linear viscoelastic behaviour is of highest interest as it represents the domain when the material undergoes small strain and temperatures above the glass transition temperature, T_g , which covers the majority range of its service temperatures in the field; the related characteristic can be expressed with the complex moduli E^* and G^* , when temperature decreases to level below T_g , a linear elastic behaviour can be observed and creep stiffness $S(t)$ and relaxation modulus $E(t)$ are generally used to describe the materials' mechanical response [76].

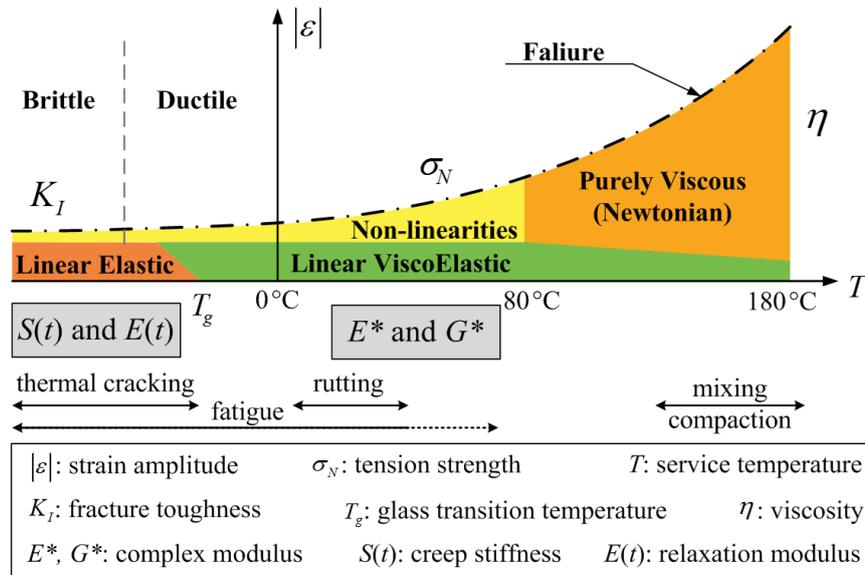


Figure 1 Typical behaviors observed on pure bitumen (Olard et al., 2004).

To better understand the rheological behavior and mechanical response of bitumen, different standard specifications and testing methods for bitumen have been developed for quality control purposes in different countries and regions. Generally speaking, three main evaluation systems: Viscosity Grading, Penetration Grading, and Performance Grading are used to describe the bitumen's properties currently. [6]

2.2.1. Viscosity Grading

In the early 1960s an improving asphalt grading system was developed that incorporated a rational scientific viscosity test. This scientific test replaced the empirical penetration test as the key bitumen characterization. Viscosity grading quantifies the following bitumen characteristics:

- Viscosity at 60°C
- Viscosity at 135°C
- Penetration depth of 100g needle applied for 5 seconds at 25°C
- Flash point temperature
- Ductility at 25°C
- Solubility in trichloroethylene
- Thin-film oven test (accounts for the effects of short-term ageing):
 - Viscosity at 60°C
 - Ductility at 25°C

Viscosity grading can be done on original (as-supplied) bitumen samples (called AC grading) or aged residue samples (called AR grading). The AR viscosity test is based on the viscosity of aged residue from the rolling thin film oven test. With AC grading, the bitumen is characterized by the properties it possesses before it undergoes the HMA manufacturing process. The AR grading system is an attempt to simulate bitumen properties after it undergoes a typical HMA manufacturing process and thus, it should be more representative of how bitumen behaves in HMA pavements [6].

Table 1 AASHTO M 226 and ASTM D 3381 Viscosity Grades

Standard	Grading based on Original Asphalt (AC)						Grading based on Aged Residue (AR)				
AASHTO M 226	AC-2.5	AC-5	AC-10	AC-20	AC-30	AC-40	AR-10	AR-20	AR-40	AR-80	AR-160
ASTM D 3381	AC-2.5	AC-5	AC-10	AC-20	AC-30	AC-40	AR-1000	AR-2000	AR-4000	AR-8000	AR-16000

2.2.2. Penetration Grading

The penetration grading system was developed in the early 1900s to characterize the consistency of semi-solid asphalts. Penetration grading quantifies the following bitumen:

- Penetration depth of a 100g needle 35°C
- Flash point temperature
- Ductility at 25°C
- Solubility in trichloroethylene
- Thin film oven test (accounts for the effects of short-term ageing that occurs during mixing with hot aggregate)
- Retained penetration
- Ductility at 25°C

Penetration grading basic assumption is that the less viscous the bitumen, the deeper the needle will penetrate. This penetration depth is empirically (albeit only roughly) corrected with bitumen performance. Therefore, bitumen with high penetration numbers (called “soft”) are used for cold climates, while bitumen with low penetration numbers (called “hard”) are used for warm climates.

The penetration grading test is done at 25°C, which is reasonably close to a typical pavement average temperature; also provide a better correlation with low-temperature bitumen properties than the viscosity test, which performed at 60°C; and this test is quick and inexpensive, therefore, it can easily be used in the field. However, its disadvantage is not neglected. First, this test is only an empirical method; no fundamental rheological parameter is measured. The single testing temperature without regard to the asphalt pavement’s service temperature may lead to unreliable results. The test method only considers short term aged binder, even though the long-term aged binder had a significant influence on the fatigue and low temperature cracking. What’s more, bitumen may have significantly different characteristics within the same grading category, and this evaluation system can hardly express the exact performance property of the modified binder [6].

2.2.3. Performance Grading

Bitumen graded by performance. Grading designations are related to the average seven-day maximum pavement design temperature (high PG) and the minimum pavement design temperature (low PG). In total high PG ranges from 46°C to 82°C, while the low PG range from –10°C to –46°C, both of them increase or decrease with a step of 6°C.

To determine the high PG and low PG, three experimental devices and testing methods are recommended by AASHTO M320 (2016). The dynamic shear rheometer (DSR) is suggested to determine the high PG under high and intermediate temperatures, while the bending beam

rheometer (BBR) in combination with the direct tension tester (DTT) are selected to determine the PG at low temperature in the low temperature. Compared to the penetration grading system, the Performance grading (PG) specification presents a series of advantages. First. The measured physical properties are directly related to the field performance with engineering principles. Second, almost the entire range of service temperatures experienced by the asphalt pavement is covered. Third, this grading system is more precise and there is much less overlap between grades. Finally, experimental tests and specifications include both unmodified and modified bitumen.

2.3. Physical hardening

Bitumen is known to undergo significant time-dependent stiffening when stored at low temperatures. This phenomenon, often referred to as physical hardening, has been shown to have significant impact on the laboratory performance of bitumen.

In bitumen as well as many amorphous polymers, physical hardening is a reversible process that occurs at low temperatures. This phenomenon causes time dependent isothermal changes in specific volume and consequently changes in mechanical properties. The effect of physical hardening is completely removed when the material is heated up to room temperatures. Physical hardening can be explained by the free volume theory proposed by Struik and Ferry.[34]

Physical hardening occurs as a consequence of isothermal reduction of free volume at temperature close to the glass transition temperature as indicated in Figure 2. The effect of physical hardening is an increase in stiffness and a reduction of the stress relaxation capacity of the bitumen. [34]

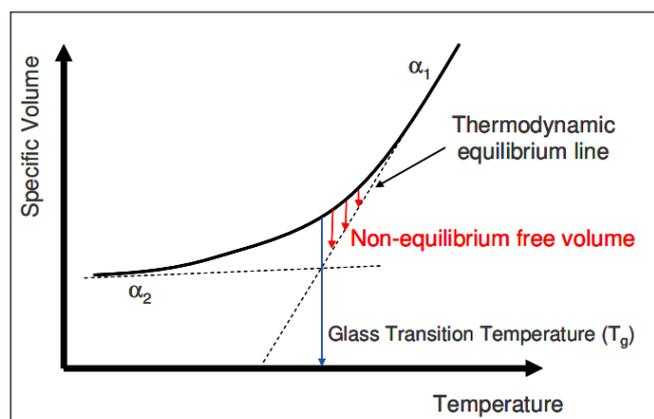


Figure 2 Physical hardening and its relation to free volume

When bitumen is cooled down from high temperatures, volume changes due to molecular adjustments are significantly larger than volume changes due to vibrational motion. Therefore, collapse of free volume follows a linear trend with temperature. However, when reaching the glass transition region, the speed of the molecular adjustment becomes slower, and the reduction free volume cannot be accomplished in the experimental time. Thus, further collapse of free volume is due to the reduction of the vibrational motion of molecules. However, if the

material is kept in isothermal condition for an extended period of time the molecular adjustments can take place. These molecular adjustments at isothermal conditions generate significant changes in the free volume and as a consequence change in the mechanical properties. This phenomenon was called physical hardening. Note that in the glass transition region, the bitumen is in a meta-stable state. And that first order properties, such as entropy, remain continuous but second order properties, such as coefficients of thermal expansion/contraction and heat capacity, are discontinuous. [34]

Based on this hypothesis it is suggested that the occurrence of measurable physical hardening within experimental time frames is limited to the glass transition region. Furthermore, the peak physical hardening rate would happen at the temperature specified by the intersection of the two asymptotic lines of the specific volume-temperature curve. At this point the molecular free volume level has the highest deviation from the two linear “non-transition” states. This temperature is commonly referred to as the “glass transition temperature”. Thus, any accurate prediction model for physical hardening should include the position of the target conditioning temperature relative to the glass transition region of the binder. [41]

2.4. Thermal cracking

Thermal cracking is one of the main distress types affecting asphalt pavements, typically occurring in regions characterized by cold climatic conditions associated with significant daily temperature variations. As proven by the abundant literature on the subject, it is well recognized that the rheological properties of bitumen employed in pavement surface layers play a major role in controlling such distress. In fact, due to their viscoelastic nature, binders have the capacity to relax stresses induced by temperature decreased; however, if these stresses are not dissipated, they can be released by crack formation once the tensile strength of the material has been exceeded.[29]

Limiting thermal cracking can be done one of two ways: decrease the creep modulus of the material or increase the relaxation modulus of the material. Creep modulus and relaxation modulus of the material are key factors that influence thermal cracking. Therefore, theoretically, a limiting value should be able to determine to develop a specification or prediction of performance.[24]

2.5. Ageing considerations

Ageing of bitumen is one of the main factors that can significantly affect the durability of bituminous paving materials. When the bitumen is age hardened, the bitumen mixture will become brittle and its ability to support traffic-induced stress and strains may significantly decrease. Pavements may be deteriorated due to cracking. In addition, excessive hardening can also weaken the adhesion between the bitumen and aggregate, resulting in loss of materials at the surface layer and generate weakening of the asphalt mixture.[70]

The ageing of bitumen is one of the key factors determining the lifetime of a bitumen pavement. The process of ageing involves chemical and/or physical property changes that usually make

bituminous materials hardener and more brittle, thus increasing risk of pavement failure. The ageing-related pavement failure modes include cracking (thermal or traffic induced) and raveling. Cracks on pavement surface may increase ageing of the binder because of increased exposure area to atmospheric oxygen.[70]

In general, bitumen ageing takes place in two stages, namely short-term ageing at high temperature during asphalt mixing, storage and laying, and long-term ageing at ambient temperature during in-service. The mechanisms of ageing include oxidation, evaporation and physical hardening. Physical hardening is a reversible process, which changes the rheological properties of bitumen without changing its chemical composition. At ambient temperatures, physical hardening normally is very slow, but it can speed up at low temperatures.[70]

Therefore, specification properties related to rutting are measured on the original binder and RTFOT residue, The RTFOT residue is intended to simulate the condition of the binder immediately after construction, which is simulated the short-term ageing. Specification properties related to fatigue cracking and thermal cracking are measured on PAV residue, PAV simulate the long-term ageing that occurs in the field.

As a bitumen ages, its viscosity increases, and it becomes stiffer and brittle. Age hardening is a result of a number of factors, the principal ones being:

1) Oxidation

Oxidation occurs when oxygen reacts with the bitumen. This reaction occurs whenever bitumen is exposed to oxygen. Oxidation occurs in the laboratory when samples are heated for processing, during mixing and compaction in the laboratory and field, and during the service in the pavement. The reaction of bituminous molecules with oxygen may be considered a “condensation reaction” during which two or more bituminous molecules combine or “condense” into a single, larger and more polar molecule. The generation of larger more polar molecules stiffens the bitumen.

The rate at which the oxygen reacts with asphalt cement depends on the temperature and the availability of the oxygen to the individual bituminous molecules. The effect of temperature on property change are based on the assumption that oxygen is readily available to individual molecules. If access to oxygen is blocked, as is done with tightly sealed storage containers every 10°C. Because for this to occur, the bitumen must be in very thin films. This illustrates two important considerations-oxidation is highly dependent on temperature and is reduced if access to oxygen is limited. This should make it obvious that the practice of heating a near-empty can, especially on a hot plate or with an open flame, will certainly accelerate ageing.

2) Volatilization

Bitumen contains a wide variety of molecules. When bitumen is heated to elevated temperatures the lighter weight molecules can evaporate. This loss of weight during heating is called volatilization. Volatilization increases with temperature. At room temperature and field service temperatures bitumen exhibit very little volatilization. However, when heated to the

temperature required for processing in the laboratory and to field mixing and compaction temperatures measurable volatilization can occur.

The loss of smaller or lighter weight molecules during volatilization can cause an increase in the stiffness of bitumen. The lighter weight molecules act as a “thinner” and their loss causes the stiffness to increase. For most bitumen volatilization plays a much smaller role during heating than the role played by oxidation.

3) Polymerization

The combining of like molecules to form larger molecules. these larger molecules are thought to cause a progressive hardening.

2.6. Influencing factors on bitumen properties

Before progressing to the definitions and concepts that characterize the mechanical properties of bitumen, the nature of these properties should be appreciated. First of all, the properties of bitumen change significantly as they ageing. Any form of handling which requires heating (testing or mixing in the laboratory and mixing and compaction in the field) or in service exposure affects the mechanical properties. Heating and long-term exposure both cause bitumen to increase in stiffness.

The mechanical properties of bitumen also depend upon the rate or time of loading. Bitumen become stiffer as the test temperature is lowered, the rate of loading is increased, or the loading time is decreased. This interchangeability of the effects of time and temperature is the basis of time-temperature superposition within which increases in test temperature may be equated to increased loading rates or shortened loading times.

This time-temperature superposition concept is used in the BBR test method where the testing temperature is 10°C greater than the specification temperature but the stiffness is measured at 60 seconds as opposed to two hours. Thus, the same values for the stiffness are obtained at $T_{SPEC}+10^{\circ}C$ after 60 s and at T_{SPEC} after 2 hours. In other words, the decrease in stiffness caused by a temperature increases of 10°C is offset by the increase in stiffness caused by increasing the test time from 240 s to 7200 s.

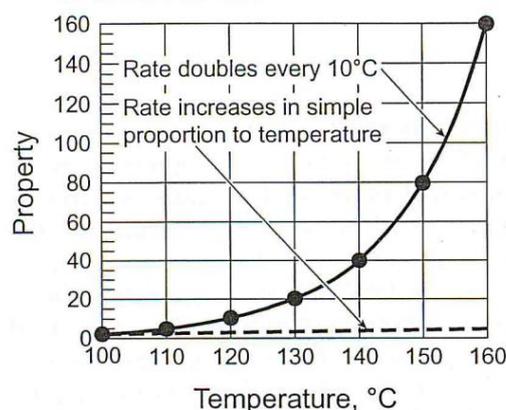


Figure 3 Effect of temperature on property change

It should also be obvious that the effects of heating and the resulting oxidation will increase with time. For this reason, heating time should be held to minimum, only until the binder becomes sufficiently fluid to pour.

In summary, although bitumen must be heated in order to process them for testing, damage can be minimized by:

- Heating the binder to the lowest possible temperature necessary for processing,
- Heating the binder for the shortest possible period of time
- Avoiding hot plates, open flames, or other heating techniques that can cause hotspots
- Avoiding the heating of near-empty cans of bitumen. This comment applies especially to the small tins, e.g., 3 oz tins that are often used during PG testing

2.7. Methods to improve bitumen properties

For the purpose of improving the qualitative properties of bitumen, the modifiers and additives are applied e.g., to increase elasticity, improving the heat stability, improving adhesion to aggregate, to decrease viscosity, increasing the resistance to ageing, to prevent binder drainage from the aggregate surface, etc. the additive can be categorizing by types as:

- modifiers (polymeric)
- adhesion promoters
- Emulsifiers
- Surfactants
- Others (rejuvenators, warm mix additives, fibers, organic materials, and rubber modifiers)

The modifier mainly affects thermos viscous and viscoelastic properties of original binder. The polymer is able to form a three-dimensional network structure within the modified bitumen. Polymer modification improves the temperature susceptibility of bitumen and can improve its resistance to permanent deformation, thermal and fatigue cracking. Modified bitumen is highly elastic. Most commonly used modified is polymer styrene-butadiene-styrene, SBS.

Antioxidant also can be used; antioxidant additive provide resistance to oxidative hardening of bitumen.

CHAPTER 3

LITERATURE

In this chapter, first, it is devoted to experimental tests on bitumen in low temperature, there are two devices can be used, including Bending Beam Rheometer (BBR) and Dynamic Shear Rheometer (DSR). Second, focus on determining the difference of limiting low temperature. Third, contains the energy dissipation, which a ratio between relaxation parameter and creep stiffness. Finally, do some introduce of hardening index and relaxation index, the physical hardening leads to a significant increase in creep stiffness in the first 24 hours.

3.1. Testing devices to evaluate bitumen at low temperature

There are two ways to evaluate bitumen at low temperature, one is Bending Beam Rheometer, another one is Dynamic Shear Rheometer, both of them have pros and cons, which are mentioned as follows:

The 4mm parallel plate geometry in the DSR (Dynamic Shear Rheometer) with new sample installation method is proposed to evaluate low temperature rheological properties of bitumen. [62]

Low temperature properties of bitumen are traditionally specified by conventional testing methods such as bending beam rheometer (BBR). BBR testing requires a huge amount of material (appr. 150g) and may lead to misinterpretation because of the significant influence of specimen preparation. Hence, these testing methods have considerable limitations and are not expedient for low temperature testing on a board range.[62]

During the Strategic Highway Research Program (SHRP), the performance grade was established to determine bitumen properties in terms of BBR and DSR. The DSR is a fundamental test device with a wide variability of test parameters (load type, load level, temperature. Frequency, etc.). For replacing BBR by DSR measurements, many correlations have been identified by various authors between both test methods [62][63][64][65]. In general, the DSR allows to test rheological bitumen properties over the whole range of service and processing temperatures, approximate -40°C to $+200^{\circ}\text{C}$, and only requires a very small number of materials. However, DSR bitumen testing at low temperature is not common practice in many counties.[62]

Low temperature measurements may also be carried out using a Dynamic Shear Rheometer (DSR) with 8mm parallel plates. But the 8-mm geometry cannot measure accurately at high stiffness levels or very low temperatures because of instrument compliance. To solve the problems, a new test protocol using parallel plates of 4 mm in diameter (or called 4-mm DSR) has been proposed by Western Research Institute (WRI) in the US. A AASHTO standard method for this test is also available. [66]

DSR with parallel plate geometry was considered for the low temperature PG system, but it was not selected because it was recognized that DSR measurements at low temperatures below about 5°C produced instrument compliance errors in the dynamic responses when the typical thin film binder geometry was used. Thus, SHRP developed the BBR to measure the low temperature rheological properties of bitumen (AASHTO T313). [67]

3.2. Limiting temperatures determination

For BBR (Bending Beam Rheometer) test, specimens are conditioned at one temperature above the pavement design temperature, $T_{\text{design}}+10$. The continuous limiting temperature where creep stiffness, $S(60s)$, reaches 300 MPa and $m(60s)$ reaches 0.300 are determined by pass/fail testing after 1h, 24h and 72h of conditioning. The warmest temperature determined in the paper sets the grade for the physically aged bitumen. [68]

Impact of low temperature ageing-related cracking potential of the natural bituminous modified binders is determined on the basis of test results obtained using BBR. Values of the stiffness modulus $S(60s)$ and the relaxation parameter $m(60s)$ are used to determine the critical low temperature of a bitumen. Critical low temperature means temperature 10°C lower from the one at which at bitumen reaches the maximum value of stiffness $S(60s)$ equal to 300 MPa or the minimum relaxation parameter m -value equal to 0.300. The bitumen that shows greater difference between the critical low temperatures of $S(60s)=300$ MPa and $m(60s)=0.300$ are considered to be more prone to thermal cracking. The loss of relaxation capacity of a bitumen as a result of ageing process leads to reduce of durability and to potential increase of the risk of on-load associated cracking. Based on this idea Anderson et al. (2011) [69] introduce the ΔT_C , which is defined as the difference between limit low temperature $T_{c,S}$ and $T_{c,m}$. [30]

The ΔT_C parameter, which is defined as the difference between two low temperature $T_{c,S}$ and $T_{c,m}$. the critical low temperature was calculated using Equation 1 in the case of value of stiffness modulus and Equation 2 in the case of m -values. Values of the ΔT_C parameter were calculated using Equation 3.

Equation 1 The limiting temperature for creep stiffness

$$T_{c,S} = T_1 + \left\{ \left(\frac{\log(300) - \log(S_1)}{\log(S_1) - \log(S_2)} \right) \cdot (T_1 - T_2) \right\} - 10$$

where:

$T_{c,S}$: stiffness critical temperature °C,

T_1, T_2 : test temperature

S_1, S_2 : stiffness modulus determined at temperature T_1 or T_2 , respectively, MPa

Equation 2 The limiting temperature for m-value

$$T_{c,m} = T_1 + \left\{ \left(\frac{0.300 - m_1}{m_1 - m_2} \right) \cdot (T_1 - T_2) \right\} - 10$$

where:

$T_{c,m}$: relaxation critical temperature °C,

T_1, T_2 : test temperature, °C

m_1, m_2 : m -values at temperature T_1 or T_2 , respectively.

Equation 3 The difference of temperature of limiting low temperature

$$\Delta T_C = T_{c,S} - T_{c,m}$$

where:

ΔT_C : difference of temperature of limiting low temperature, °C

The value of $T_{S(300MPa)}$ and $T_{m(0.300)}$ were calculated on the base of the results of BBR test obtained at two temperatures -6°C and -12°C , depending on the range in which the value of stiffness modulus 300 MPa or m-value 0.300 is located. [30]

3.3. Dissipated energy

Liu et al. (2010) deduced mathematical relations between low temperature rheological properties obtained from BBR tests fitting creep data using a Burger's model (Figure 4). That model is obtained by the association of two springs and two dashpots. One of the dashpots is in parallel with one of the springs and this association is in series with the other spring and the other dashpot. Those authors found that there is a highly significant linear relation between m/S (taken at 12°C) and the dissipated energy during the test. That relation depends on the material and on the model fitting to BBR data. The ratio m/S can even be approximated by a constant, which depends on binder's linear viscoelastic properties. The larger m/S is, the higher is the dissipated energy. So, m/S could be used as an indicator of material's ability to relax stresses.[58]

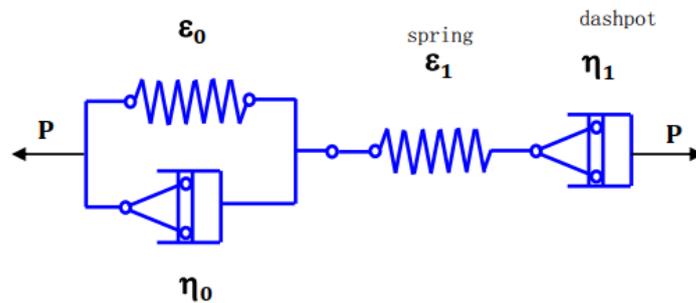


Figure 4 Burger model

m/S, which depends on binder's linear viscoelastic properties, the larger m/S is, the higher is the dissipated energy, high creep rate are related to high energy dissipated rate in viscoelastic flow, less energy being dissipated, in the propagation of crack. In the conditioning time 1h, there is the largest m/S, which means the ability to dissipated energy is the biggest, as the conditioning time increase, the ability to dissipated energy will decrease.

The following formula can be used to calculate the ratio of relaxation parameter and creep stiffness, m/S:

Equation 4 Dissipated energy

$$\frac{m}{S} = \frac{m (-)}{S (MPa)} \times 1000 [\%]$$

where:

m is relaxation parameter

S is creep stiffness, MPa

3.4. Hardening and relaxation index

Lu and Isacson [59] investigated the rate of physical hardening for five unmodified and 35 polymer modified binders. They noticed that the hardening index did not always increase with decreasing storage temperature. They also concluded that the kinetics of physical hardening in modified binders seems to be largely dependent on the base binders.

A hardening index, S_i/S_0 , defined as the ratio of the creep stiffness, $S(60s)$, after time t_i of isothermal storage to the initial stiffness measurement after time t_0 of isothermal storage (t_0 is one hour of this research), is generally used to show the rate at which physical hardening occurs at different isothermal conditions. The relaxation index, m_i/m_0 , is introduced to describe the relaxation properties of this material, a similar definition is used to describe this index. In this research, it is assumed that physical hardening phenomena inducing an increase in stiffness is completed when the conditioning time extended up to 72h; the corresponding stiffness value at a selected time can be used to calculate the relative degree of physical hardening (relative stiffening effect) at that specific time. [33][59][40][61]

CHAPETR 4.

EXPERIMENTAL PLAN

4.1. Materials

4.1.1 Bitumen

Two different 50/70 pen-grade binders were studied, one neat bitumen, one polymer modified binder (PMB), which is coded N2 and P1.

4.1.2 Additive

Talk about the additive, the experimental antioxidant has been used, which is coded AO12, the weight of the AO12 is 0.3% of the total quantity of neat bitumen or polymer modified bitumen.

4.1.3 Preparation of bitumen samples

The preparation of the modified binders includes a series of operations necessary to provide a representative specimen of the material under examination. The correct execution of specimen is necessary condition to obtain reliable results from laboratory tests to which the specimen will be subjected. In order to homogenize the additive with the neat bitumen and the additive with the modified polymer bitumen, the samples were mixed with a HEIDOLPH stirrers RZR 2041 (Figure 5), particular, for the heating system, the use of oil heater to homogenous temperature, because the can is surrounded by the oil, the temperature will be setting as 160 °C for neat bitumen (170 °C for the polymer modified bitumen).



Figure 5 RZR 2041 in the laboratory

4.2. Short-term ageing simulation

4.2.1. Theory behind the RTFO

RTFO (Rolling Thin Film Oven) test provides a means for conditioning bitumen to simulate the short-term ageing that occurs during the mixing and compaction of hot-mix asphalt concrete (HMAC).

The test method also provides a measurement (optional) of the mass change that occurs during the test. Residue from the RTFOT is further aged in the PAV test method. The mass change and properties measured on the residue from the RTFOT and the PAV are used to grade binders in accordance with AASHTO M 320 and AASHTO R 29.

Ageing is enhanced during the test procedure by rotating the containers, so that the film of asphalt coating the inside of the containers is continuously “rolled over”. Hence the name “rolling” thin film oven test. Continuous renewal of the surface enhances the opportunity for volatilization and for bitumen to react with oxygen [17].

4.2.2. RTFO test apparatus

The test apparatus consists of loading frame, controlled temperature bath, computer-based data acquisition and test control system, calibration or verification items, moulds for forming test specimen.



Figure 6 RTFO test oven in the laboratory



Figure 7 Container filled with bitumen

4.2.3. Test procedure

1) The steps for the RTFO test:

- Heating the bitumen in one hour, for the neat bitumen, the heating temperature is 160°C, for the polymer modified bitumen, the heating temperature is 170°C.
- Turn on the RTFO machine, and the temperature have already been set (160°C), turn on the machine and put the glass container inside the machine, and the heating time is one hour, turn on the evaporation machine, the temperature is 500-550 °C.

- Turn on the mixing machine, for the neat bitumen, the mixing machine will be setting as 160°C, for the polymer modified bitumen, the mixing machine will be setting as 170°C.

2) One hour later, if the bitumen is fluid:

- Mixing the additive inside the container and mix the bitumen with the mixing machine in five minutes, take care, the rotate bar does not touch the side of the container and also do not touch the bottom side of the container.
- Prepare one aluminium box for containing the bitumen, in order to be more precise to fill the bitumen inside the glass container.
- Prepare one shelf for cooling the glass containers with the bitumen.
- Take outside one glass container, read the value in the balance, fill bitumen inside the glass container, when the weight reaches the 35 grams, then stop, the difference is +0.5 and -0.5 grams, read the value of the weight for the first glass container.
- Put the glass container on the shelf for cooling.
- Take outside the second glass container, read the value in the balance (which is the weight of the empty glass container), fill bitumen inside the glass container, when the weight reaches the 35 grams, then stop, the difference is ± 0.5 grams, read the value of the weight for the second glass container
- Repeat the steps till fill all the eight glass containers, recording the time, the cooling time for the bitumen is one hour.

3) One hour later:

- Put the glass container inside the RTFO machine, the opening side should be face to the door, and the glass container should be put in the suitable place, otherwise, when the rotate switch has been turned on, it will be not rotate.
- If the RTFO keep rotating, recording the time in 85 minutes.

4) After 85 minutes later:

- Prepare the trays, the special scarper, the flat scarper, and the balance.
- Put the tray on the balance, set the balance to zero, take out one glass contain, read the value of the glass container, pour the bitumen into the first tray, if glass container remains some bitumen inside, use the special scarper to scarp
- Take out the second glass container, first read the value of weight with tray with the pour bitumen, put the glass container on the balance, read the value of the weight, pour the bitumen to the first tray, when the weight inside the tray reached 50 grams, change the second tray on the balance, set the balance to zero, pour second glass container's bitumen to the second tray.
- Repeated the steps until finished the eight glass containers.
- Put the tray into the PAV machine, when do not need to the PAV test, do not running the machine, just close the cover. To make inside as vacuum.
- Put the dirty glass containers into the evaporation machine, turn on the burn switch, waiting for more or less twenty minutes, the procedure will be finished, if the bell is ringing, Also can directly turn off the machine, due to the temperature inside the machine is very high, the glass container cannot be deal with immediately, just remain the glass container inside the evaporation machine, in the next day morning, clean the glass container.
- For cleaning the dirty glass containers, clean the glass container with the paper and the

scarper will be help, and then use the high-pressure air the clean the remain dash.

When the containers are inserted into the oven, the oven must be at the test temperature with the air flow turned on. Any empty positions in the carriage must be filled with empty containers. Open the door of the oven and place all eight containers in the carriage. Immediately after placing all eight containers in the oven close the door, turn on the fan (if turned off) and start the carriage rotation. Once the door is closed it must remain closed for 85 minutes. The oven must recover to the test temperature within 10 minutes after closing the door or the test must be declared invalid. The temperature must be measured using the test thermometer and not the temperature indicated by the digital display of the temperature controller [17].

At least 90 percent of the residue be removed from the container. All of the containers must be removed from the oven and scarped within five minutes of removing the first container. Immediately after removing each container, close the oven door. The airflow should remain on continuously as the containers are removed and the carriage should be running whenever the door is closed.

4.2.4. Reporting requirements

There are no reporting requirements for this test method, unless the mass change is determined. The test method no longer refers to mass loss, but instead to mass change. With this terminology a negative value indicates a loss of mass during the test and a positive value indicated a mass gain.

The mass change is usually negative indicating that the binder has lost mass during ageing process. Occasionally a binder will exhibit a positive mass change. When this occurs the uptake of oxygen is greater than the loss of volatiles.

Equation 5 The mass change

$$\% \text{ change} = \frac{(M_i - M_e) - (M_f - M_e)}{(M_i - M_i)} \times 100$$

where:

M_e : mass of empty container

M_i : initial mass of sample and container

M_f : final mass of sample and container

4.3. Long-term ageing simulation

4.3.1. Theory behind the PAV

During long-term exposure in the field, bitumen hardens as a result of oxidation. PAV (Pressure ageing vessel) test provides a means for accelerating the long-term, in-service oxidative ageing of bitumen. The ageing is accelerated in the laboratory as a result of the application of elevated

pressure and temperature. Elevated pressure forces air into the bitumen which increase the amount of oxygen that is available for reacting with the bitumen molecules [17].

The basic PAV procedure takes RTFO aged bitumen samples, place them in stainless steel pans. The combined effect of elevated temperature and pressure produces a highly accelerated rate of ageing. Five to 10 years of long-term field ageing can be simulated in 20 hours in the PAV. The stiffness of materials aged in the PAV increase approximately eight-fold although the actual increase will vary for asphalts from different sources [17].

4.3.2. PAV test apparatus

The main components of the PAV include the pressure vessel and its environmental chamber, electronics to control and measure temperature, electronics to control and measure test pressure and a vacuum oven for degassing the PAV residue.



Figure 8 PAV in the labpratory



Figure 9 Trays with bitumen

4.3.3. Test procedure

1) The PAV need to be heated in 100°C

- When the short-term bitumen has been already put inside the trays, tighten the screws in the diagonal.
- Open the air pressure, recording the time as 20 hours.

2) When finished the long-term aging in 20 hours

- Close the air pressure waiting for 10 minutes, pay attention, must wait for all the air pressure release from the PAV machine, otherwise it will be very danger which the cover will be pup up due to the high air pressure, the west screw should not be removed at the whole time, it should be always stay there with the cover.
- The steps to remove the cover, always remember that remove the screw in the diagonal

- Take out the trays, use scarper to remove the bitumen as soon as possible, due to the temperature become to the room temperature, the temperature is decreasing, and the bitumen will become stick and very difficult to remove from the tray, which means some bitumen will be loosened, the more time spent the more bitumen will be loose.
- Use aluminium box to carry the bitumen which comes from the trays. Each aluminium should be written the name of the bitumen, the additive's name, the portion of the bitumen, in which test you are done.
- When most of the bitumen has been removed from the trays, use bio-oil to clean the remain bitumen, use brush scribble the surface of the trays, waiting for one or two hours, use paper and scarper to clean the remain bitumen and the bio-oil. Be sure that use the paper to clean all the bio-oil from the trays surface, otherwise it will influence the result of next test.
- Using the bio-oil to clean the table.

Bitumen placed in the pans must be weighted to $50 \text{ g} \pm 0.5 \text{ g}$, giving a layer of bitumen that is approximately 3.2 mm thick. If the residue from the RTFOT is allowed to cool it should be reheated until it is sufficiently fluid to pour.

4.3.4. Data collection

The mass change is not measured as part of this procedure. Mass change is not meaningful because the bitumen absorbs air as a result of pressurization. Any gain in mass as a result of oxidation is masked by air absorbed by the bitumen as a result of the pressurization.

4.4. Physical hardening simulation

4.4.1 Theory behind the BBR

Bending Beam Rheometer provides a means for measuring the flexural creep stiffness of bitumen. The design of the system limits its measurement range from 20 MPa to 1 GPa. Test results for beams that deflect less than 0.08 mm or more than 4 mm are not considered valid [17].

The BBR is used to determine the creep stiffness and relaxation parameter (m-value) of bitumen at low temperatures. A constant load 100 g is applied for 240 s to midpoint of a simply supported beam of binder. The midpoint deflection of the beam versus time is measured.

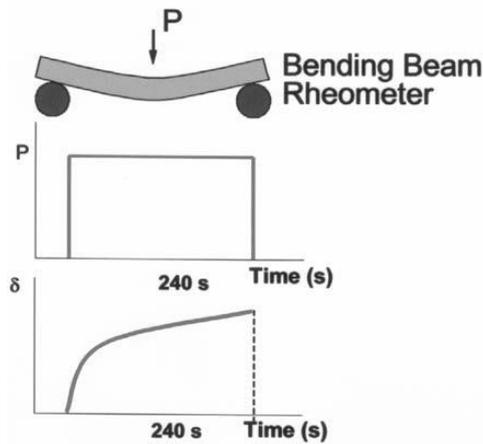


Figure 10 Principle of the BBR-test

4.4.1. BBR test apparatus

The test apparatus consists of loading frame, controlled temperature bath, computer-based data acquisition and test control system, calibration items, moulds for forming test specimen.



Figure 11 BBR in laboratory

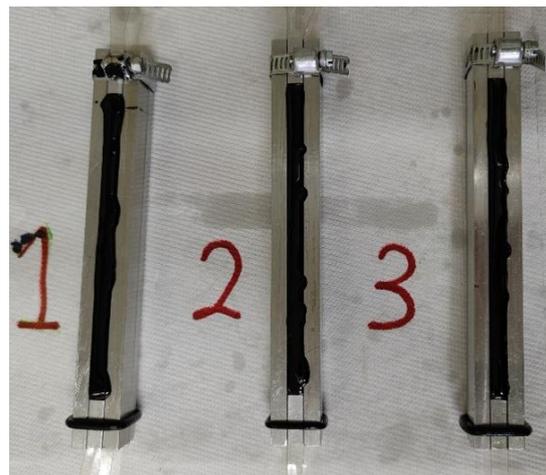


Figure 12 Specimen in the mould

4.4.2. Test summary and fundamentals

The test procedure is based upon the measurement of the deflection of the midpoint of the test specimen during application of a constant load. The load and deflection are used to calculate the maximum stress and strain in the beam, and the stiffness is calculated by divided the maximum stress by the maximum strain.

4.4.3. Standardization

The calibration of certain components within the BBR must be verified each day before conducting a test. The verification may be done manually or with the standardization routine is included in the BBR software.

4.4.4. Test procedure

The test specimens must be conditioned at the test temperature for 60 ± 5 minutes before the testing can be started. This strict requirement with respect to testing time is necessary to control the effects of physical hardening. Even though physical hardening may be present after 60 ± 5 minutes, by controlling the conditioning time, the effect will be minimized between and within laboratories.

1) Verification of temperature

On each day, before conducting tests, and whenever the test temperature is changed, verify calibration of the temperature detector by using a calibrated thermometer. With the loading frame placed in the liquid bath. If the temperature by the data acquisition system does not agree with the thermometer within ($\pm 0.1^\circ\text{C}$), calibration is required.

2) Preparation of moulds

Inspect the mould and press the plastic film against the aluminium to force out any air bubbles. If air bubbles remain, disassemble the mould and recoat the aluminium face with grease. cover the inside faces of the two end pieces with a thin film of glycerol and talc to prevent the bitumen from sticking to the aluminium end pieces. After assembly, keep the mould at room temperature until pouring the bitumen.

3) Heat the bitumen

In an oven set at the minimum temperature and for the minimum time necessary (60 minutes) for it be sufficiently fluid to pour. The heating temperature is 160°C , readily pours but not overly fluid, heating time should be minimized, heating one hour is enough, during the heating process, the sample should be covered and stirred occasionally to ensure homogeneity.

4) Moulding

Pour the binder from the one end of the mould and move toward the other end, slightly overfilling the mould. When pouring, hold the sample container 20 to 100 mm from the top of the mould and pour continuously toward the other end in a single pass. Allow the mould to cool 60 minutes to room temperature after pouring, and trim to the exposed face of the cooled specimens flush with the top of the mould using a heated spatula. time-dependent increase in stiffness can occur when bitumen is stored at room temperature for even short periods of time.

5) Cooling the aluminium mould

Prior to the testing, cooling the aluminium mould containing the test specimen in a freezer at -5°C ($\pm 7^\circ\text{C}$) for 10 minutes, only long enough to stiffen the bitumen beam can be readily demoulded without distortion. Excessive cooling may cause unwanted hardening of the beam, thereby causing increased variability in the test data.

6) Conditioning the specimens

When testing a specimen for compliance with M 320, select the appropriate test temperature (-6 °C, -12 °C), after demoulding, immediately place the test specimen in the testing bath and condition it at the test temperature for 60 minutes (± 5 minutes).

7) Checking the contact load and the test load

Place the thick steel beam in position on the beam supports, using the test load regulator valve, gently increase the force on the beam to 980 mN (± 50 mN), switch from the test load to the contact load, and adjust the force on the beam to 35 mN (± 10 mN), switch between the test load and contact load four times.

8) Enter the specimen identification information

Includes the test load, test temperature, time the specimen is placed in the bath at the test temperature, and other information as appropriate into the computer which controls the test system.

9) Place the test beam on the test supports

After conditioning, place the test beam on the test supports, and initiate the loading sequence of the test. Maintain the bath at the test temperature (± 0.1 °C) during testing, otherwise, the test shall be rejected. Manually apply a 35 mN (± 10 mN) contact load to the beam to ensure contact between the beam and the loading head for no more than 10 s.

10) Remove the test load and terminate the test

At the end of the initial seating load, and the end of the test, monitor the computer screen to verify that the load on the beam returns to 35 mN (± 10 mN) in each case, if the beam does not return to 35 mN (± 10 mN), the test is invalid, and the rheometer should be calibrated. Remove the specimen from the supports and proceed to the next test.

4.4.5. Data collection

The beam deflection applied load and loading time is acquired by the data acquisition unit and sent to the personal computer during the test. Immediately following the test, the computer software automatically reduces the test data and computes the creep stiffness and relaxation parameter. The creep stiffness and relaxation parameter are reported at six loading times: 8, 15, 30, 60, 120, 240 s. For each test temperature, the average m-values and average creep stiffness using the recorded m-value and creep stiffness at 60 s. Values of the stiffness modulus $S(60s)$ and the slope of stiffness modulus curve $m(60s)$ are used to determine the critical low temperature of bitumen. Critical low temperature means temperature 10°C lower from the one at which the bitumen reaches the maximum value of stiffness $S(60s)$ equal to 300 MPa or minimum m-value equal to 0.300.

Based on the measurement results, the materials' low temperature creep stiffness, $S(t)$, can be calculated by use of Equation 6.

Equation 6 Creep stiffness, $S(t)$

$$S(t) = \frac{P \cdot l^3}{4 \cdot b \cdot h^3 \cdot \delta(t)}$$

where:

$S(t)$: is the stiffness at time t [Pa]

P : is the applied constant load equals to 980 mN

l : is the distance between the beam support (102 mm)

b : is the specimen width (12.5 mm)

h : is the specimen thickness (6.25 mm)

$\delta(t)$: is the measured deflection at time t [mm]

m -value which stands for the gradient of the creep stiffness function, can be determined by the following procedure. First, the calculated creep stiffness values $S(t)$ can be fitted by adaption to a quadratic polynomial equation as follows:

Equation 7 Creep stiffness $S(t)$

$$\text{Log}S(t) = A + B \times \log(t) + C \times [\log(t)]^2$$

where:

$S(t)$: is the value of creep stiffness at time t [Pa]

t : is the loading time with the unit of second

A , B and C : are the regression coefficient

Then, m -value can be expressed with the same regression coefficient B and C :

Equation 8 Relaxation parameter, m -value

$$m(t = 60s) = \frac{d\text{Log}S(t = 60s)}{d\text{Log}(t = 60s)} = |B + 2C \times [\log(t)]|$$

Based on the previously calculated results, BBR method relies on two threshold limits for stiffness (300 MPa) and relaxation properties (0.3 for m -value) to determine the critical temperature of bitumen. Higher creep stiffness indicates a higher susceptibility for low temperature cracking. However, larger m -values are associated with good capabilities of resistance against thermal cracking.

4.4.6. Major factors affecting precision and accuracy

A number of factors are likely to affect the precision and accuracy of the test results and, in particular, should receive the close attention of the operator:

1) Specimen dimensions

The thickness of the test specimen is the most critical specimen dimension. Without dwelling on the details or derivation of the equation simply not that the calculated stiffness depends on the thickness, h raised to the third power. Specimen thickness is controlled by the condition of the inserts and the presence of any separation of the plastic strips from the sides of the mould, the effective thickness of the inserts and resulting thickness of the specimens may be increased

by the presence of dings or burrs.

2) Integrity of the test specimens

The test results will be affected if the test specimens become distorted as a result of demoulding and handling. If the test specimens become warped, they will not fit firmly on the specimen supports.

3) Adjustment of contact load after test specimen is mounted

Adjusting the contact load after the test specimen has been placed on the supports can lead to serious errors, especially in the m-value. The contact load must be adjusted to 35 ± 10 mN using the steel beam before the specimen is mounted. The procedure described in the manual should be followed carefully.

4.4.7. Advantages of using BBR test

This research investigates the idea of performing creep tests on bitumen beam specimens with the Bending Beam Rheometer (BBR). The BBR testing procedure has a number of important advantages:

- The instrument has a reasonable price, and many laboratories have this instrument.
- The BBR has a well-documented history of good performance.
- The BBR has a user-friendly calibration verification.
- The test procedure is very simple, and the repeatability of the test results is very high.

4.5. Methodology

4.5.1. Overview of the test

The BBR test for four different types of bitumen, which is N2, N2+AO12, P1, P1+AO12, the weight of the AO12 is 0.3% of the total quantity of neat bitumen or polymer modified bitumen. Each BBR test has been performed on both sides of the beams, meaning the beam was loaded on one side and then flipped over to perform the next test, so there are eight different type tests performed. And the test has been done in two different temperatures (-6 °C and -12 °C). In three conditioning time (1h, 24h, and 72h). is showing in Table 2.

Table 2 Different conditioning temperature and conditioning time

Storage temperature (°C)	Storage time (h)
-6	1
	24
	72
-12	1
	24
	72

4.5.2. Statistic requirements for coefficient of variation (COV)

For the single-operator precision: Two results obtained in the same laboratory, by the same operator using the same equipment, the statistic requirements for coefficient of variation (COV) are showing in Table 3.

Table 3 Coefficient of variation (COV)

Precision and bias (two results)-Single Operator	
Stiffness	2.5
m-value	1

when there are more than two results, the maximum acceptable range is showing in Table 4.

Table 4 Maximum Acceptable Range

Maximum Acceptable Range	
Number of Test Results	Multiplier of (1s) or (1s%) for Maximum Acceptable Range
2	2.8
3	3.3
4	3.6
5	3.9
6	4.0
7	4.2
8	4.3
9	4.4
10	4.5

In the thesis, there are 6 repetitions for each case, the range (difference between highest and lowest) of the group of the test results must be compared to a maximum acceptable range for the applicable system of causes and number of test results. The range for different number of tests results is obtained by multiplying the appropriate deviation by the appropriate factor is showing in Table 5.

Table 5 Maximum acceptable range of more than two results

Maximum acceptable range of more than two results			
Number of test results	Multiplier for maximum acceptable range	Creep stiffness	Relaxation parameter (m-value)
(-)	(-)	(%)	(%)
2	2.8	7.0	2.8
3	3.3	8.3	3.3
4	3.6	9.0	3.6
5	3.9	9.8	3.9
6	4.0	10.0	4.0

4.5.3. Select reliable specimen

There are six repetitions, in order to select reliable specimen, the specimen has been selected according to the statistic requirement, when one specimen run a test in BBR, the value of stiffness and m-value given by the software at the same time. Supposing there are four different situations, only both stiffness and m-value satisfied at the same time, the results of this specimen are reliable, otherwise it will be excluded. Suitable both for the front side and back side. As the Table 6 showing the optimize procedure below:

Table 6 Select reliable specimen

	Stiffness		m-value	
	Specimen condition	Included or Excluded	Specimen condition	Included or Excluded
Before selection	1	Included	1	Included
	2	Excluded	2	Included
	3	Included	3	Excluded
	4	Excluded	4	Excluded
After selection	1	Included	1	Included
	2	Excluded	2	Excluded
	3	Excluded	3	Excluded
	4	Excluded	4	Excluded

According to the previously mentioned rules, The selected results can be got, the following Table 7 shows one example, N2 specimen in -6 °C in 1 hour conditioning time:

Table 7 Example N2 specimen in -6 °C in 1 hour conditioning time

	N2-(-6 °C) -1h			
	Number of specimen (front side)	Included or Excluded	Number of specimen (back side)	Included or Excluded
Stiffness	1	Included	1	Included
	2	Included	2	Included
	3	Excluded	3	Included
	4	Included	4	Included
	5	Excluded	5	Included
	6	-	6	-
m-value	1	Included	1	Included
	2	Included	2	Included
	3	Excluded	3	Included
	4	Included	4	Included
	5	Excluded	5	Included
	6	-	6	-

In this case, for specimen 3 and specimen 5 are not satisfied in stiffness, and they are satisfied

in m-value, due to previous rule, the specimen 3 and the specimen 5 have been excluded.

Pay attention, if the front specimen has been excluded, there are no influence in the result of the back side specimen.

4.5.4. Methods to determine the limiting grade T_L

A durable bitumen should have physical properties necessary for desired initial product performance and should be characterized by resistance to physical properties change during long term ageing in environmental conditions, in order to assess the resistance of a bitumen (in consequence also a bitumen mixture) to low temperature cracking at present the following parameters are used: the limiting grade T_L ($^{\circ}\text{C}$). according to section 3.2. to determine the limiting temperature $T_{c,s}$ and $T_{c,m}$, the warmer limiting low temperature has been chosen as the limiting grade.

CHAPTER 5.

RESULTS and DISCUSSION

The results of the tests performed in this study are presented in this chapter. According to the analysis method explained in section 4.5.3., the reliable results have been selected and the average values are presented here.

As all the samples were tested on both sides, the results are also presented for these two different sides. The initial goal of this thesis is studied based on the results of ‘front side’ and ‘back side’, the back side means the beam had been flipped over to be tested on the backside which also removed the deformation caused by previous test on the same beam (the test on the front side)

5.1. Analysis of average stiffness

Since all the sample were tested on both sides, in order to have a good comparison, we can make a difference of stiffness, showing in Equation 9.

Equation 9 Difference of stiffness between act on Front & Back side

$$\begin{aligned}\Delta S_{N2 \& N2\text{-opposite}} &= \frac{S_{N2} - S_{N2\text{-opposite}}}{S_{N2}} \times 100 \\ \Delta S_{N2\text{-A012} \& N2\text{-A012}\text{-opposite}} &= \frac{S_{N2\text{-A012}} - S_{N2\text{-A012}\text{-opposite}}}{S_{N2\text{-A012}}} \times 100 \\ \Delta S_{P1 \& P1\text{-opposite}} &= \frac{S_{P1} - S_{P1\text{-opposite}}}{S_{P1}} \times 100 \\ \Delta S_{P1\text{-A012} \& P1\text{-A012}\text{-opposite}} &= \frac{S_{P1\text{-A012}} - S_{P1\text{-A012}\text{-opposite}}}{S_{P1\text{-A012}}} \times 100\end{aligned}$$

The temperature changes from -6 °C to -12 °C, a comparison can be done, creep stiffness and conditioning time are in logarithm scale, same for test act on front side and back side, showing in Equation 10.

Equation 10 Difference stiffness between -6 °C and -12 °C

$$\begin{aligned}\Delta S_{N2(-6^\circ\text{C} \& -12^\circ\text{C})} &= \frac{S_{N2(-6^\circ\text{C})} - S_{N2(-12^\circ\text{C})}}{S_{N2(-6^\circ\text{C})}} \times 100 \\ \Delta S_{N2\text{-A012}(-6^\circ\text{C} \& -12^\circ\text{C})} &= \frac{S_{N2\text{-A012}(-6^\circ\text{C})} - S_{N2\text{-A012}(-12^\circ\text{C})}}{S_{N2\text{-A012}(-6^\circ\text{C})}} \times 100 \\ \Delta S_{P1(-6^\circ\text{C} \& -12^\circ\text{C})} &= \frac{S_{P1(-6^\circ\text{C})} - S_{P1(-12^\circ\text{C})}}{S_{P1(-6^\circ\text{C})}} \times 100 \\ \Delta S_{P1\text{-A012}(-6^\circ\text{C} \& -12^\circ\text{C})} &= \frac{S_{P1\text{-A012}(-6^\circ\text{C})} - S_{P1\text{-A012}(-12^\circ\text{C})}}{S_{P1\text{-A012}(-6^\circ\text{C})}} \times 100\end{aligned}$$

5.1.1 Results of the test at -6 °C

1) The front side

For the average stiffness in the -6 °C, the conditioning time is 1h, 24h, 72h, the stiffness and the time in logarithm scale, as Table 8 shows:

Table 8 Front side-Average stiffness (MPa) in -6 °C

Average stiffness (MPa – log scale) in -6 °C			
Bitumen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2	2.15	2.20	2.22
N2-AO12	2.08	2.19	2.20
P1	1.97	2.03	2.04
P1-AO12	1.87	1.92	1.94

According to upper data, Figure 13 is illustrating the diagrams of stiffness and time in logarithmic scale for each of the samples.

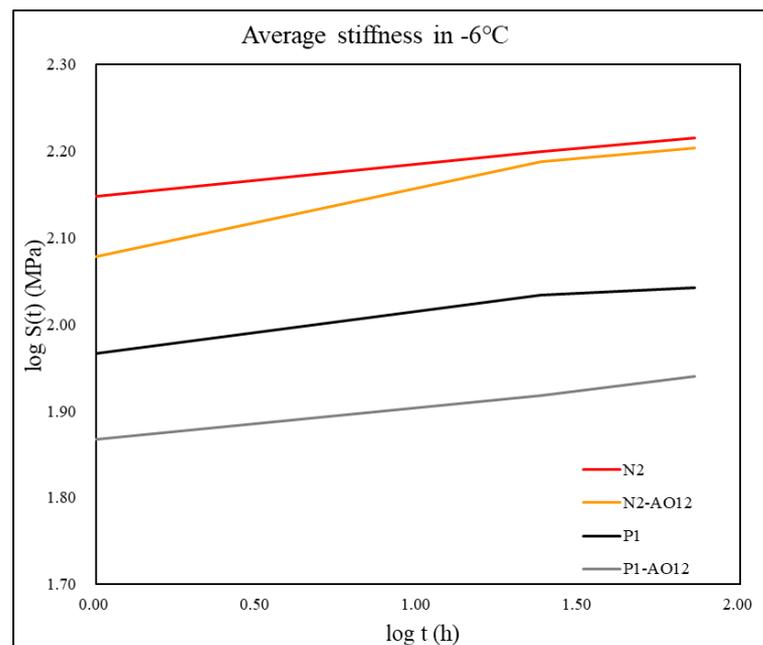


Figure 13 Front side-Average stiffness in -6 °C

In the -6 °C, the specimens have been storage in the isothermal ethanal, as the conditioning time increase, the stiffness will increase, as respectively.

2) The back side

For average stiffness for the opposite side at the -6 °C (with the same conditioning times), the stiffness and the time in logarithm scale, as Table 9 shows below:

Table 9 Back side-Average stiffness (MPa) in -6 °C

Average stiffness (MPa – log scale) in -6 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2-opposite	2.03	2.16	2.19
N2-AO12-opposite	2.06	2.15	2.17
P1-opposite	1.86	1.95	2.02
P1-AO12-opposite	1.81	1.88	1.90

According to upper data, Figure 14 is illustrating the diagrams of stiffness and time in logarithmic scale for each of the samples.

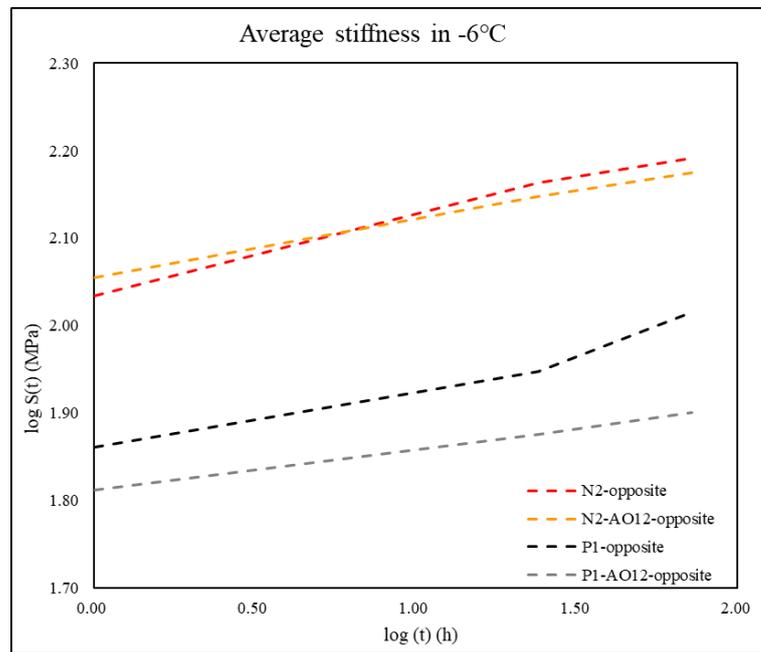


Figure 14 Back side-Average stiffness in -6 °C

In the -6 °C, when the specimens have been storage in the isothermal ethanal, as the conditioning time increase, the stiffness will increase, as respectively.

3) The comparison between the front side and the back side

For the average stiffness in the -6 °C, the conditioning time is 1h, 24h, 72h, the stiffness and the time in logarithm scale, in order to do the comparison, the results from the front side and back side have been put in the same table, as Table 10 shows below:

Table 10 Front side & Back side-Average stiffness (MPa) in -6 °C

Average stiffness (MPa – log scale) in -6 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2	2.15	2.20	2.22
N2-opposite	2.03	2.16	2.19
N2-AO12	2.08	2.19	2.20
N2-AO12-opposite	2.06	2.15	2.17
P1	1.97	2.03	2.04
P1-opposite	1.86	1.95	2.02
P1-AO12	1.87	1.92	1.94
P1-AO12-opposite	1.81	1.88	1.90

According to upper data, Figure 15 is illustrating the diagrams of stiffness and time in logarithmic scale for each of the samples.

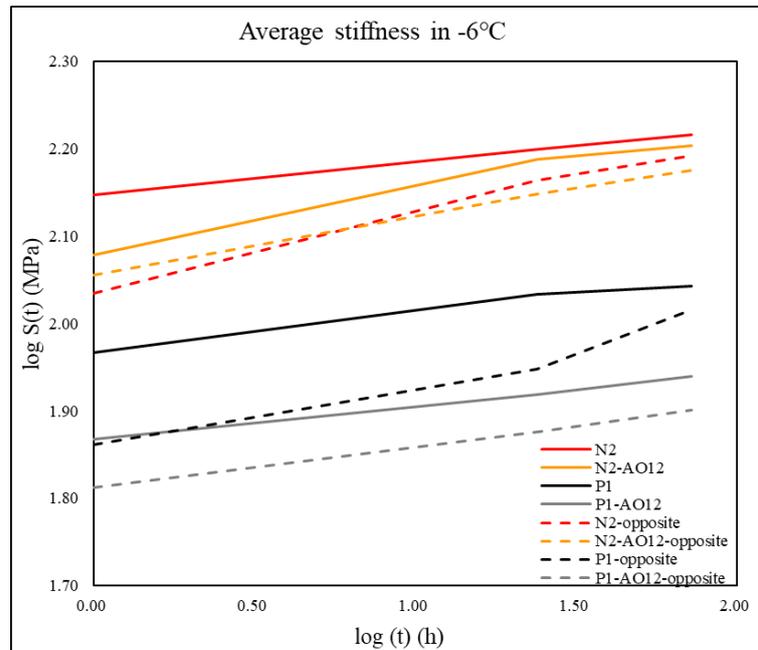


Figure 15 Front side & Back side-Average stiffness in -6 °C

According to Equation 9, the results have been shown in the Table 11.

Table 11 Front side & Back side-Difference average stiffness (%) in -6 °C

Difference average stiffness (%) in -6 °C			
Specimen type	Conditioning time (h)		
	1	24	72
N2 & N2-opposite	23.0	7.9	5.4
N2-AO12 & N2-AO12-opposite	5.1	8.9	6.4
P1 & P1-opposite	21.6	17.8	6.0
P1-AO12 & P1-AO12-opposite	11.9	9.2	8.6

The difference average stiffness between front side and back side can be plotted in Figure 16.

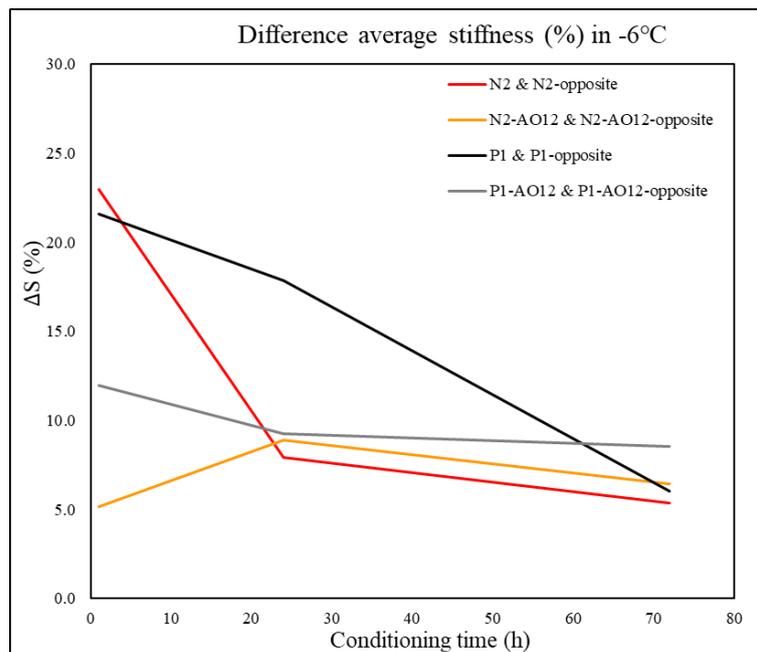


Figure 16 Front side & Back side difference average stiffness (%) in -6 °C

In Table 11, all the data are positive, which means the physical hardening load in front side of the specimen are more serious than load in the back side of the specimen; in the same conditioning temperature, as the conditioning time increase, the difference of the creep stiffness between front side and back side become smaller, except the bitumen type N2-AO12, the difference is waving.

5.1.2 Results of the test at -12 °C

1) The front side

For the average stiffness in the -12 °C, the conditioning time is 1h, 24h, 72h, the stiffness and the time in logarithm scale, as the Table 12 shows below:

Table 12 Average stiffness (MPa) in -12 °C

Average stiffness (MPa – log scale) in -12 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2	2.41	2.53	2.55
N2-AO12	2.41	2.51	2.54
P1	2.19	2.28	2.30
P1-AO12	2.20	2.26	2.29

According to upper data, Figure 17 is illustrating the diagrams of stiffness and time in logarithmic scale for each of the samples.

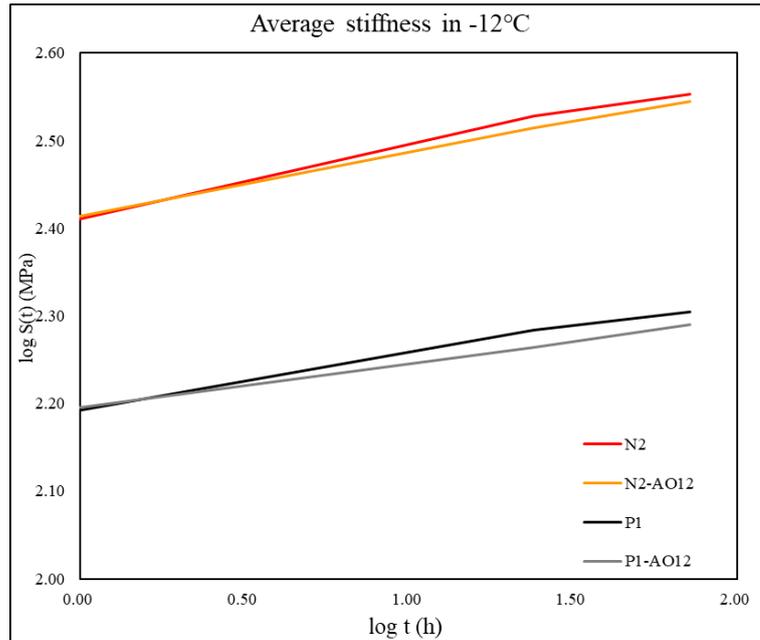


Figure 17 Average stiffness in -12 °C

In the -12 °C, in the isothermal conditioning, when the specimens have been storage in the isothermal ethanal, as the conditioning time increase, the stiffness will increase, as respectively.

2) The back side

For average stiffness for the opposite side at the -12 °C (with the same conditioning times), the stiffness and the time in logarithm scale, as Table 13 shows below:

Table 13 Back side-Average stiffness (MPa) in -12 °C

Average stiffness (MPa – log scale) in -12 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2-opposite	2.38	2.50	2.52
N2-AO12-opposite	2.38	2.48	2.50
P1-opposite	2.15	2.26	2.28
P1-AO12-opposite	2.15	2.24	2.25

According to upper data, Figure 18 is illustrating the diagrams of stiffness and time in logarithmic scale for each of the samples.

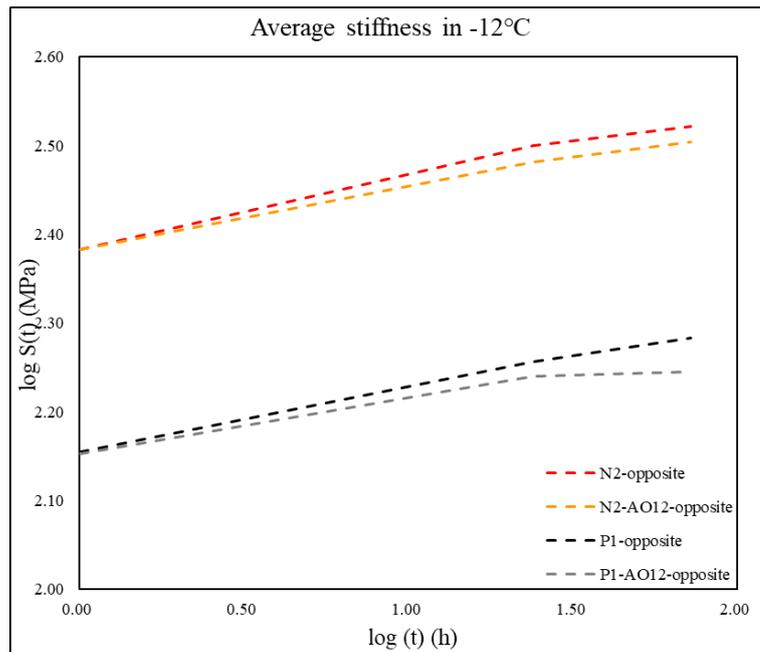


Figure 18 Back side-Average stiffness in -12 °C

In the -12 °C, in the isothermal conditioning, when the specimens have been storage in the isothermal ethanal, the conditioning time increase, the stiffness will increase, as respectively.

3) The comparison between the front side and the back side

For the average stiffness in the -12 °C, the conditioning time is 1h, 24h, 72h, the stiffness and the time in logarithm scale, in order to do the comparison, the values of front side and back side have been put in the same table, as Table 14 shows:

Table 14 Front side & Back side-Average stiffness (MPa) in -12 °C

Average stiffness (MPa – log scale) in -6 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2	2.41	2.53	2.55
N2-opposite	2.38	2.50	2.52
N2-AO12	2.41	2.51	2.54
N2-AO12-opposite	2.38	2.48	2.50
P1	2.19	2.28	2.30
P1-opposite	2.15	2.26	2.28
P1-AO12	2.20	2.26	2.29
P1-AO12-opposite	2.15	2.24	2.25

Putting them in the same graph, as Figure 19 shows:

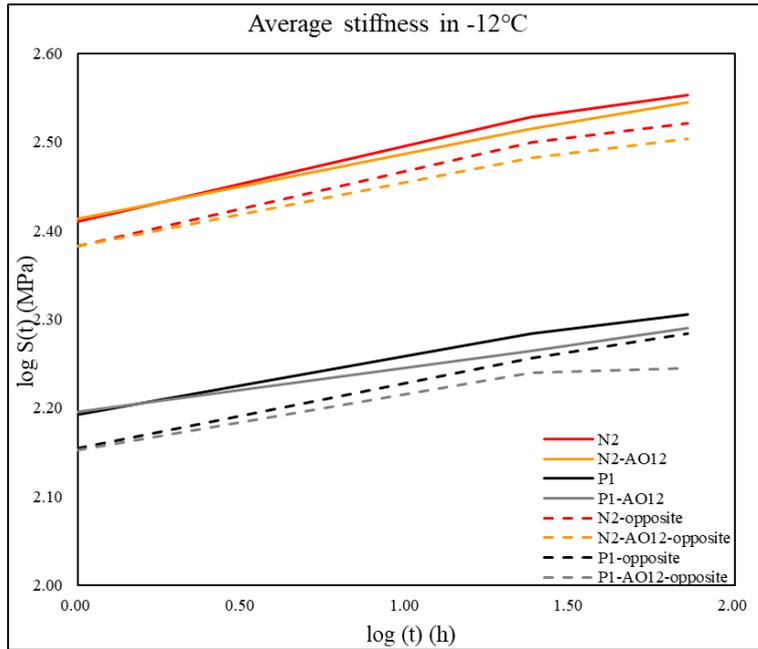


Figure 19 Front side & Back side-Average stiffness in -12 °C

According to Equation 9, the results have been shown in the Table 15.

Table 15 Front side & Back side-Difference average stiffness (%) in -12 °C

Difference average stiffness (%) in -12 °C			
Specimen type	Conditioning time (h)		
	1	24	72
N2 & N2-opposite	6.1	6.2	7.0
N2-AO12 & N2-AO12-opposite	6.8	7.2	9.1
P1 & P1-opposite	8.3	6.0	4.9
P1-AO12 & P1-AO12-opposite	9.4	5.4	9.8

The difference average stiffness (%) between front side and back side in -12 °C have been plotted in Figure 20.

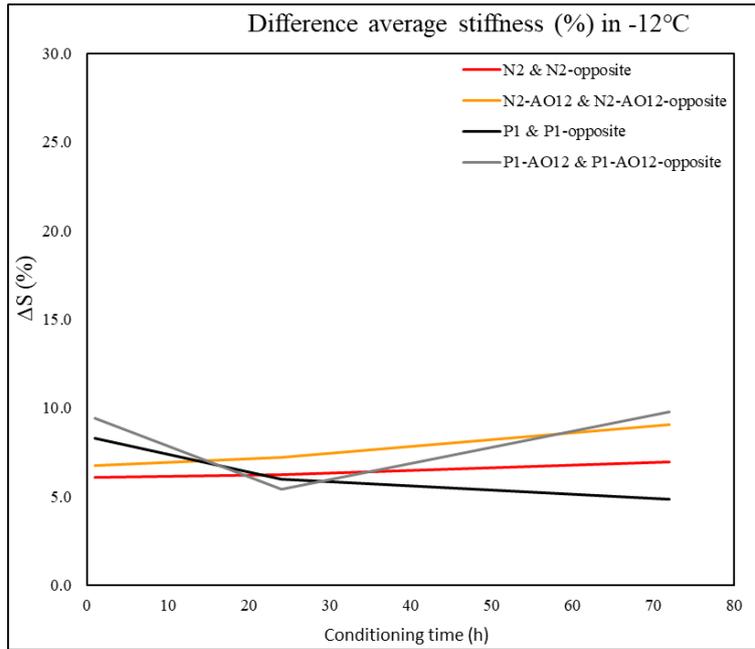


Figure 20 Front side & Back side difference average stiffness (%) in -12 °C

In Table 15, all the data are positive, which means the physical hardening load in front side of the specimen are more serious than load in the back side of the specimen; in the same conditioning temperature, as the conditioning time increase, the difference of the creep stiffness between front side and back side become larger, for the specimen N2 and N2-AO12; in the same conditioning temperature, as the conditioning time increase, the difference of the creep stiffness between front side and back side become smaller, for the specimen P1; in the same conditioning temperature, as the conditioning time increase, the difference of the creep stiffness between front side and back side is waving, for the specimen P1-AO12.

5.1.3. Comparison of stiffness between -6 °C and -12 °C

1) The front side

As we know, when the conditioning temperature decrease, the stiffness will increase, the relaxation parameter will decrease.

The temperature change from -6 °C to -12 °C, according to Equation 10, the results can be shown in the Table 16.

Table 16 Front side-Difference average creep stiffness (%) between -6 °C and 12 °C

Difference average-creep stiffness (%) between -6 °C and 12 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2	-12.25	-14.95	-15.22
N2-AO12	-16.13	-14.92	-15.50
P1	-11.47	-12.29	-12.84
P1-AO12	-17.56	-18.02	-18.03

The difference creep stiffness (%) between -6 °C and 12 °C in the front side can be plotted in Figure 21.

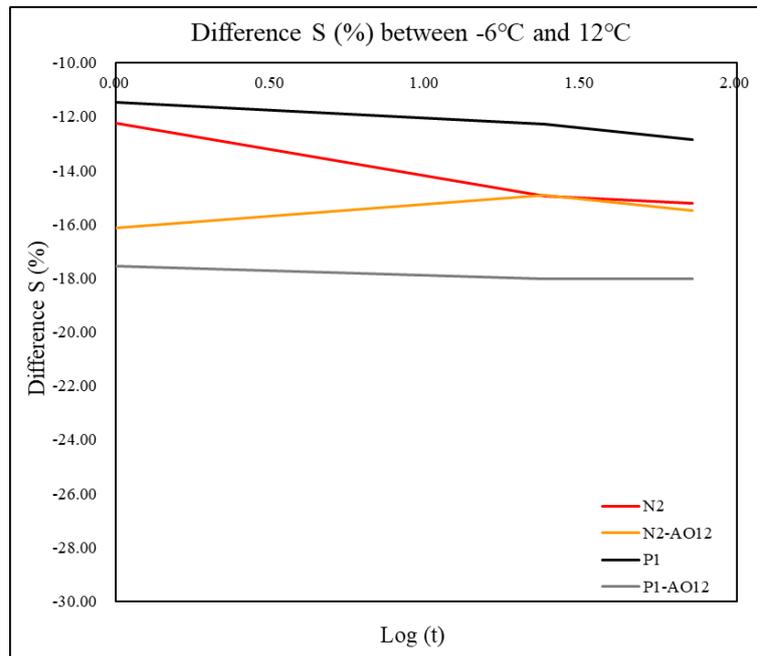


Figure 21 Front-Difference S (%) between -6 °C and 12 °C

In Table 16, all the data are negative, which means the physical hardening load in conditioning temperature -12 °C are more serious than load in the conditioning temperature -6 °C; in the same conditioning temperature, as the conditioning time increase, the difference of the creep stiffness between -6 °C and -12 °C become larger, same for the specimen N2, P1, and P1+AO12; but in the same conditioning temperature, as the conditioning time increase, the difference of the creep stiffness between -6 °C and -12 °C is waving, for the specimen N2+AO12.

2) The back side

In the back side, according to Equation 10, the results are shown in Table 17.

Table 17 Back side-Difference average creep stiffness (%) between -6 °C and 12 °C

Difference average-creep stiffness (%) between -6 °C and 12 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2-opposite	-17.16	-15.55	-15.04
N2-AO12-opposite	-15.95	-15.56	-15.14
P1-opposite	-15.78	-15.83	-13.27
P1-AO12-opposite	-18.77	-19.38	-18.09

The difference creep stiffness (%) between -6 °C and 12 °C in the front of side can be plotted in Figure 18 .

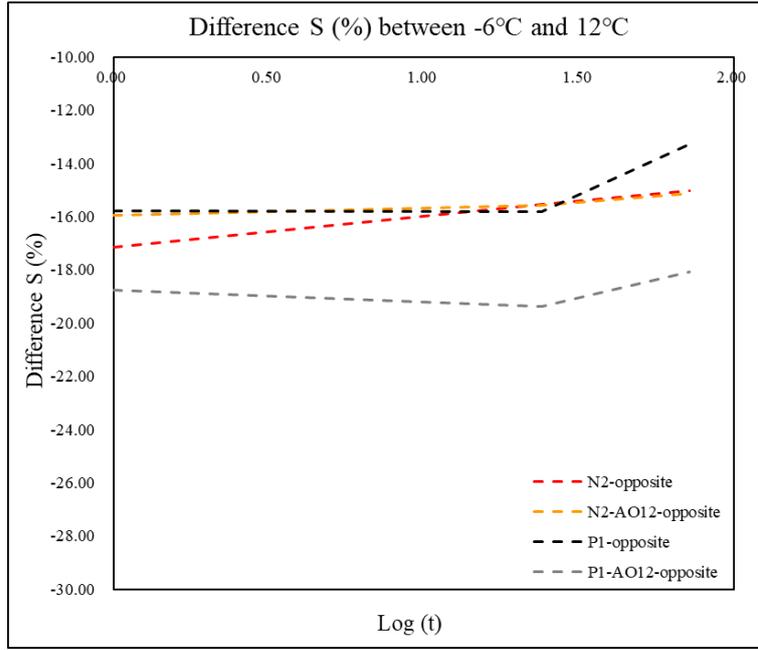


Figure 20 Back-Difference S (%) between -6 °C and 12 °C

In Table 17, all the data are negative, which means the physical hardening load in conditioning temperature -12 °C are more serious than load in the conditioning temperature -6 °C; in the same conditioning temperature, as the conditioning time increase, the difference of the creep stiffness between -6 °C and -12 °C become smaller, same for the specimen N2 and N2+AO12; but in the same conditioning temperature, as the conditioning time increase, the difference of the creep stiffness between -6 °C and -12 °C is waving, for the specimen P1 and P1+AO12.

5.2. Analysis of average m-value

Since all the sample were tested on both sides, in order to have a good comparison, we can make a difference of relaxation parameter, showing in Equation 11.

Equation 11 Difference of relaxation parameter between act on Front & Back side

$$\Delta m_{N2 \& N2\text{-opposite}} = \frac{m_{N2} - m_{N2\text{-opposite}}}{m_{N2}} \times 100$$

$$\Delta m_{N2\text{-AO12} \& N2\text{-AO12}\text{-opposite}} = \frac{m_{N2\text{-AO12}} - m_{N2\text{-AO12}\text{-opposite}}}{m_{N2\text{-AO12}}} \times 100$$

$$\Delta m_{P1 \& P1\text{-opposite}} = \frac{m_{P1} - m_{P1\text{-opposite}}}{m_{P1}} \times 100$$

$$\Delta m_{P1\text{-AO12} \& P1\text{-AO12}\text{-opposite}} = \frac{m_{P1\text{-AO12}} - m_{P1\text{-AO12}\text{-opposite}}}{m_{P1\text{-AO12}}} \times 100$$

The temperature changes from -6 °C to -12 °C, a comparison can be done, relaxation is linear scale, and conditioning time is in logarithm scale, same for test act on front side and back side, showing in Equation 12.

Equation 12 Difference relaxation parameter between -6 °C and -12 °C

$$\Delta m_{N2(-6^{\circ}\text{C} \& -12^{\circ}\text{C})} = \frac{m_{N2(-6^{\circ}\text{C})} - m_{N2(-12^{\circ}\text{C})}}{m_{N2(-6^{\circ}\text{C})}} \times 100$$

$$\Delta m_{N2-AO12(-6^{\circ}\text{C} \& -12^{\circ}\text{C})} = \frac{m_{N2-AO12(-6^{\circ}\text{C})} - m_{N2-AO12(-12^{\circ}\text{C})}}{m_{N2-AO12(-6^{\circ}\text{C})}} \times 100$$

$$\Delta m_{P1(-6^{\circ}\text{C} \& -12^{\circ}\text{C})} = \frac{m_{P1(-6^{\circ}\text{C})} - m_{P1(-12^{\circ}\text{C})}}{m_{P1(-6^{\circ}\text{C})}} \times 100$$

$$\Delta m_{P1-AO12(-6^{\circ}\text{C} \& -12^{\circ}\text{C})} = \frac{m_{P1-AO12(-6^{\circ}\text{C})} - m_{P1-AO12(-12^{\circ}\text{C})}}{m_{P1-AO12(-6^{\circ}\text{C})}} \times 100$$

5.2.1. Results of the test at -6 °C

1) The front side

For the average m-value in the -6 °C, the conditioning time is 1h, 24h, 72h, the m-value is in linear scale and the conditioning time is in logarithm scale, as the Table 18 shows below:

Table 18 Front side-Average m-value (-) in -6 °C

Average-m-value (-) in -6 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2	0.338	0.298	0.288
N2-AO12	0.327	0.295	0.284
P1	0.304	0.281	0.276
P1-AO12	0.326	0.304	0.301

According to upper data, Figure 22 is illustrating the diagrams of m-value in linear scale and time in logarithmic scale for each of the samples.

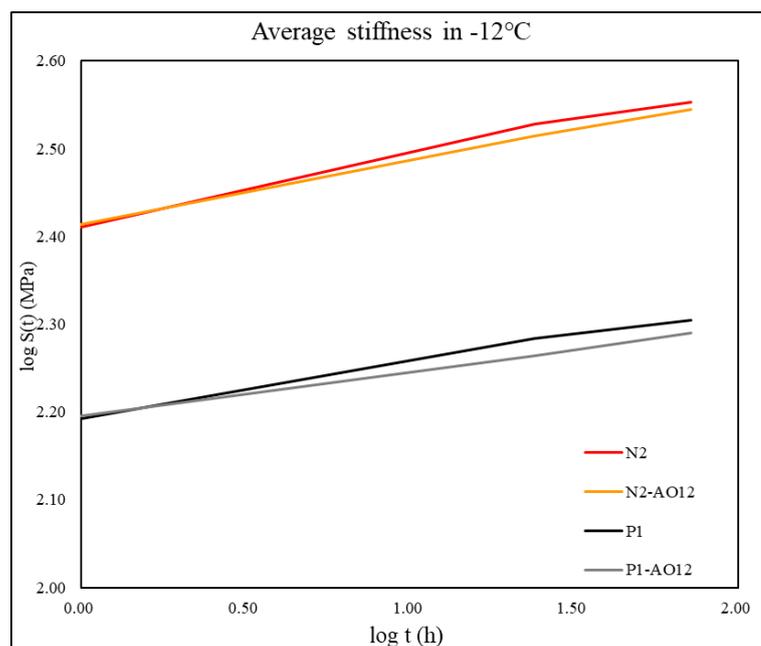


Figure 22 Average m-value in -6 °C

In the -6 °C, in the isothermal conditioning, the specimens have been storage in the isothermal ethanal, as the conditioning time increase, the m-value will decrease, as respectively.

2) The back side

For the average stiffness in the -6 °C, the conditioning time is 1h, 24h, 72h, the m-value in linear scale and the time in logarithm scale, as Table 19 shows below:

Table 19 Back side-Average m-value (-) in -6 °C

Average-m-value (-) in -6 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2-opposite	0.365	0.321	0.311
N2-AO12-opposite	0.355	0.325	0.317
P1-opposite	0.356	0.329	0.308
P1-AO12-opposite	0.355	0.338	0.337

For average m-value for the opposite side at the -6 °C (with the same conditioning times), the m-value in linear scale and the time in logarithm scale, as Figure 23 shows below:

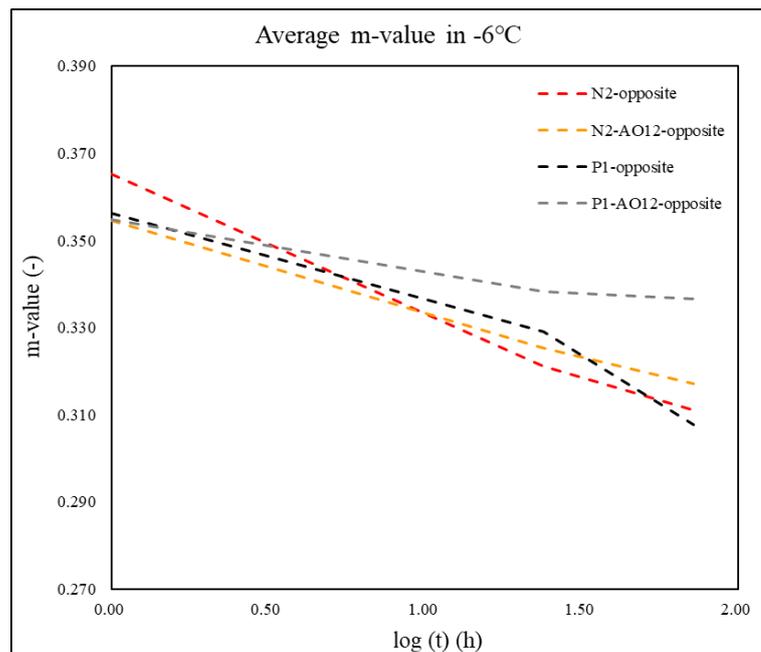


Figure 23 Back side-Average m-value in -6 °C

In the -6 °C, in the isothermal conditioning, the specimens have been storage in the isothermal ethanal, as the conditioning time increase, the m-value will be decrease, as respectively.

3) The comparison between the front side and the back side

For the average m-value in the -6 °C, the conditioning time is 1h, 24h, 72h, the m-value in linear scale and the time in logarithm scale, in order to do the comparison, the value of front side and back side have been put in the same table, as Table 20 shows below:

Table 20 Front side & Back side-Average m-value (-) in -6 °C

Average-m-value (-) in -6 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2	0.338	0.298	0.288
N2-opposite	0.365	0.321	0.311
N2-AO12	0.327	0.295	0.284
N2-AO12-opposite	0.355	0.325	0.317
P1	0.304	0.281	0.276
P1-opposite	0.356	0.329	0.308
P1-AO12	0.326	0.304	0.301
P1-AO12-opposite	0.355	0.338	0.337

Plotting them in the same graph, as Figure 24 shows below:

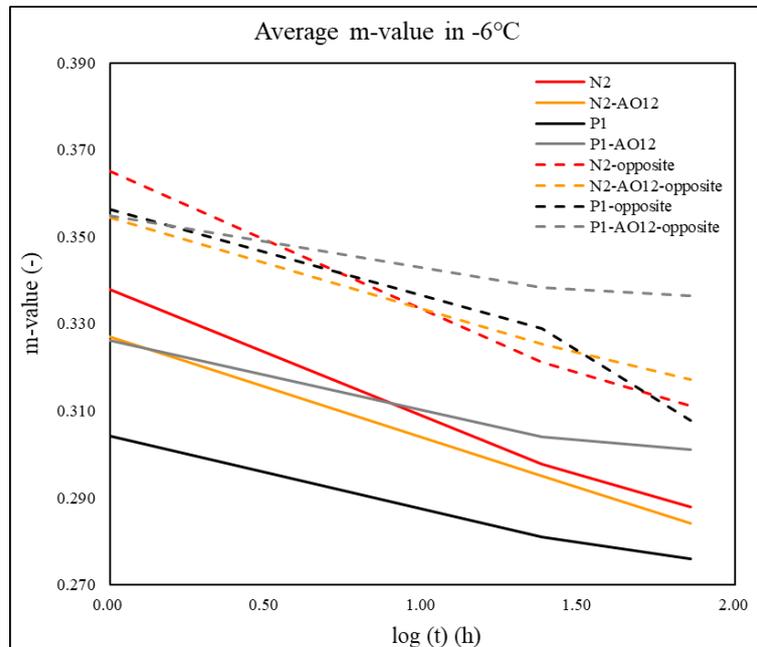


Figure 24 Front side & Back side-Average m-value in -6 °C

According to Equation 11, the results can be shown in Table 21.

Table 21 Front side & Back side-Difference average m-value (%) in -6 °C

Difference average-m-value (%) in -6 °C			
Specimen type	Conditioning time (h)		
	1	24	72
N2 & N2-opposite	-8.0	-7.8	-8.0
N2-AO12 & N2-AO12-opposite	-8.4	-10.3	-11.6
P1 & P1-opposite	-17.1	-17.1	-11.5
P1-AO12 & P1-AO12-opposite	-8.8	-11.3	-11.8

The difference average m-value (%) between front side and back side in -6 °C have been plotted

in Figure 25.

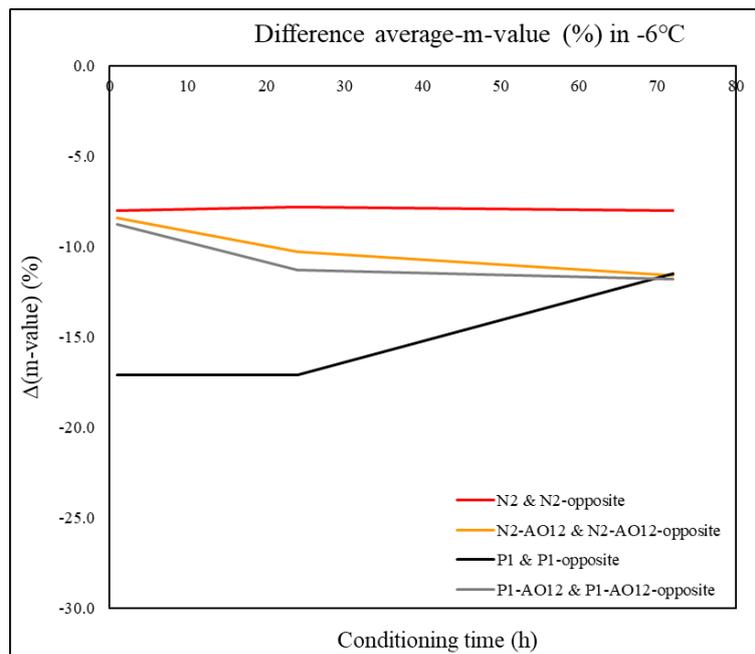


Figure 25 Front side & Back side difference average m-value (%) in -6 °C

In Table 21, all the data are negative, which means the physical hardening load in front side of the specimen are more serious than load in the back side of the specimen; in the same conditioning temperature, as the conditioning time increase, the difference of the m-value between front side and back side become smaller, except the bitumen type N2, the difference is waving.

5.2.2. Results of the test at -12 °C

1) The front side

For the average m-value in the -12 °C, the conditioning time is 1h, 24h, 72h, the m-value is in linear scale and the conditioning time is in logarithm scale, as Table 22 shows below:

Table 22 Front side-Average m-value (-) in -12 °C

Average m-value (-) in -12 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2	0.284	0.245	0.235
N2-AO12	0.282	0.236	0.230
P1	0.279	0.249	0.241
P1-AO12	0.270	0.247	0.241

For the average m-value in the -12 °C, the conditioning time is 1h, 24h, 72h, the m-value is in linear scale and the conditioning time is in logarithm scale, as Figure 26 shows below:

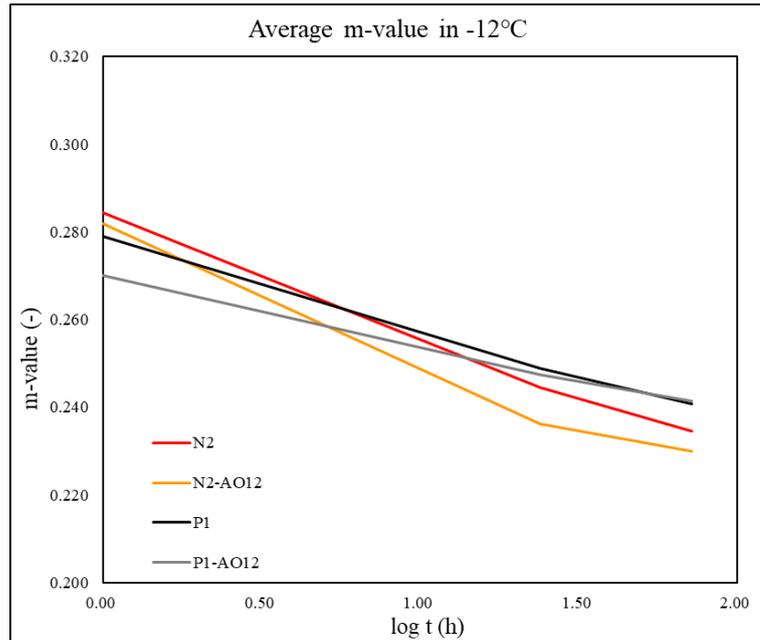


Figure 26 Front-Average m-value in -12 °C

In the -12 °C, in the isothermal conditioning, when the specimens have been storage in the isothermal ethanal, as the conditioning time increase, the m-value will be decrease, as respectively.

2) The back side

For average m-value for the opposite side at the -12 °C (with the same conditioning times), the m-value in linear scale and the time in logarithm scale, as Figure 23 shows below:

Table 23 Back side-Average m-value (-) in -12 °C

Average-m-value (-) in-12 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2-opposite	0.314	0.269	0.262
N2-AO12-opposite	0.306	0.271	0.268
P1-opposite	0.317	0.281	0.279
P1-AO12-opposite	0.308	0.276	0.275

For the average m-value in the -12 °C, the conditioning time is 1h, 24h, 72h, the m-value in linear scale and the time in logarithm scale, as Figure 27 shows below:

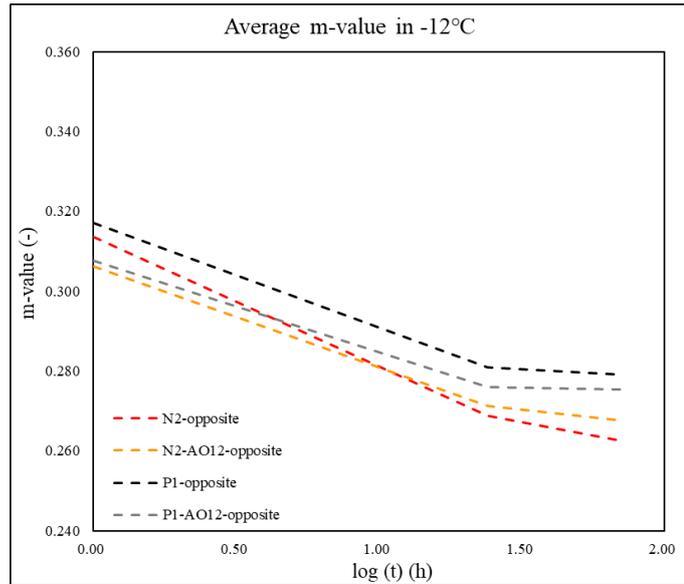


Figure 27 Back side-Average m-value in -12 °C

In the -12 °C, in the isothermal conditioning, when the specimens have been storage in the isothermal ethanal, as the conditioning time increase, the m-value will be decrease.

3) The comparison between the front side and the back side

For the average m-value in the -12 °C, the conditioning time is 1h, 24h, 72h, the m-value in linear scale and the time in logarithm scale, in order to do the comparison, the value of average m-value have been put in the same table, both for the front side and back side, as Table 24 shows below:

Table 24 Front side & Back side-Average m-value (-) in -12 °C

Average-m-value (-) in-12 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2	0.284	0.245	0.235
N2-opposite	0.314	0.269	0.262
N2-AO12	0.282	0.236	0.230
N2-AO12-opposite	0.306	0.271	0.268
P1	0.279	0.249	0.241
P1-opposite	0.317	0.281	0.279
P1-AO12	0.270	0.247	0.241
P1-AO12-opposite	0.308	0.276	0.275

Plotting them in the same graph, as Figure 28 shows below:

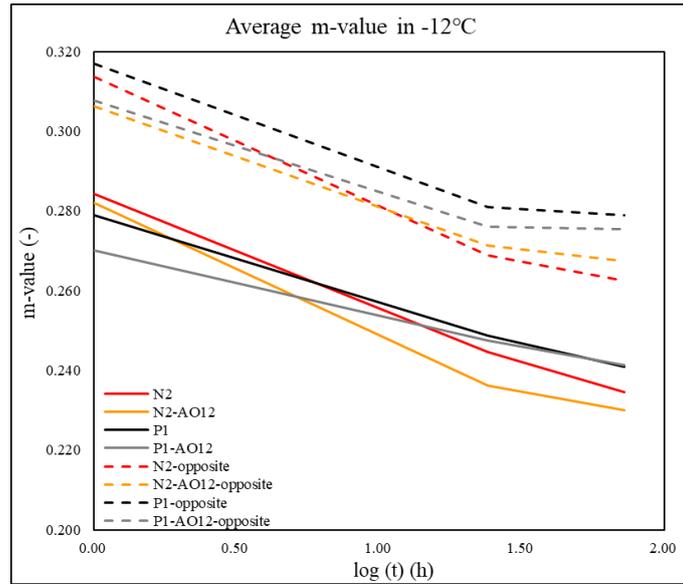


Figure 28 Front side & Back side-Average m-value in -12 °C

According to Equation 11, the results show in Table 25:

Table 25 Front side & Back side-Difference average m-value (%) in -12 °C

Specimen type	Difference average-m-value (%) in -12 °C		
	Conditioning time (h)		
	1	24	72
N2 & N2-opposite	-10.3	-9.9	-11.9
N2-AO12 & N2-AO12-opposite	-8.6	-14.9	-16.3
P1 & P1-opposite	-13.6	-12.9	-15.8
P1-AO12 & P1-AO12-opposite	-14.0	-11.6	-14.1

The difference average m-value (%) between front side and back side in -12 °C have been plotted in Figure 29.

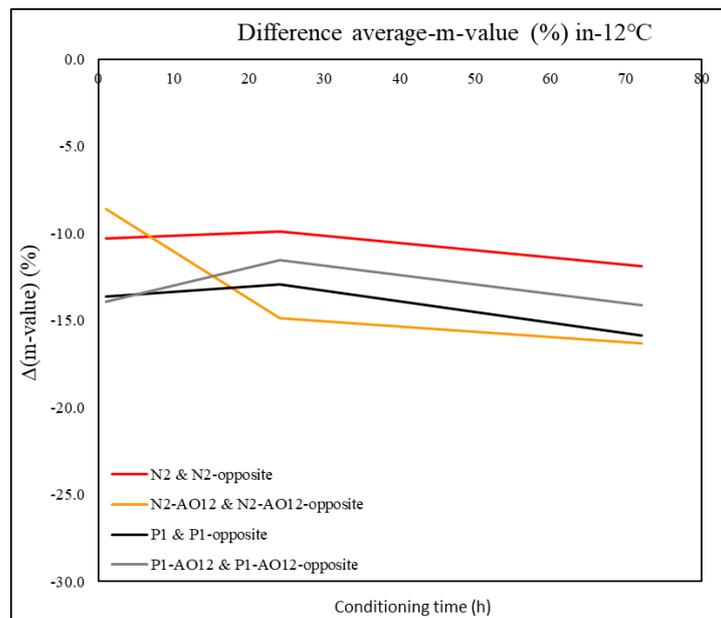


Figure 29 Front side & Back side difference average m-value (%) in -12 °C

In Table 25, all the data are negative, which means the physical hardening load in front side of the specimen are more serious than load in the back side of the specimen; in the same conditioning temperature, as the conditioning time increase, the difference of the m-value between front side and back side become smaller, for bitumen type N2-AO12, except the bitumen type N2, P1, P1-AO12, the difference is waving.

5.2.3. Comparison of m-value between -6 °C and -12 °C

1) The front side

The temperature change from -6 °C to -12 °C, according to Equation 12, the results show in Table 26.

Table 26 Front side-Difference average-m-value (%) between -6 °C and 12 °C

Difference average-m-value (%) between -6 °C and 12 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2	15.88	17.86	18.58
N2-AO12	13.75	19.93	19.09
P1	8.32	11.46	12.74
P1-AO12	17.23	18.62	19.82

The difference of m-value (%) between -6 °C and -12 °C in the front side is plotted in Figure 30.

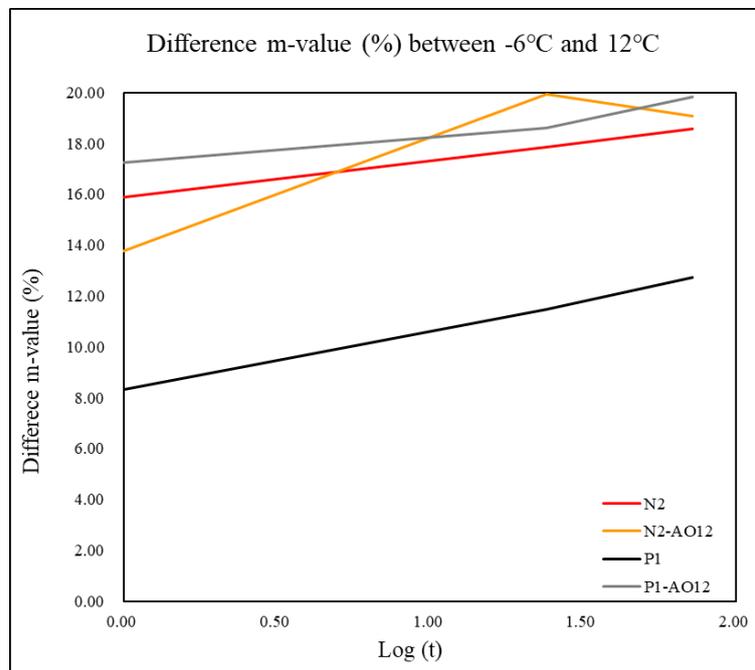


Figure 30 Front-Difference m-value (%) between -6 °C and 12 °C

In Table 26, all the data are positive, which means the physical hardening load in conditioning temperature -12 °C are more serious than load in the conditioning temperature -6 °C; in the same conditioning temperature, as the conditioning time increase, the difference of the m-value between -6 °C and -12 °C become larger, same for the specimen N2, P1, and P1+AO12; but in

the same conditioning temperature, as the conditioning time increase, the difference of the m-value between -6 °C and -12 °C is waving, for the specimen N2+AO12.

2) The back side

The temperature change from -6 °C to -12 °C, according to Equation 12, the results show in Table 27.

Table 27 Back side-Difference average m-value (%) between -6 °C and 12 °C

Difference average-m-value (%) between -6 °C and 12 °C			
Specimen type	Conditioning time (h- log scale)		
	0.00	1.38	1.86
N2-opposite	14.10	16.30	15.64
N2-AO12-opposite	13.62	16.60	15.66
P1-opposite	11.04	14.59	9.36
P1-AO12-opposite	13.29	18.42	18.16

The difference m-value (%) between -6 °C and -12 °C in the back side have been plotted in Figure 31.

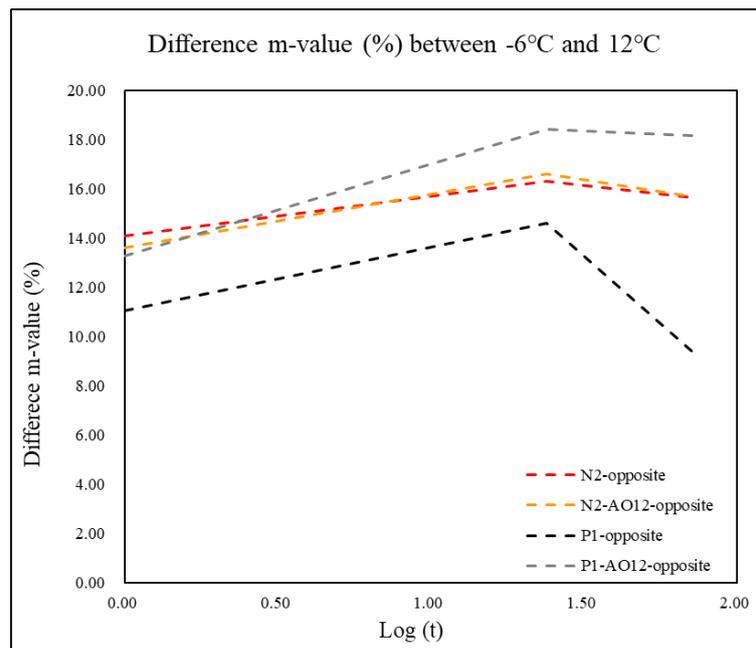


Figure 31 Back-Difference m-value (%) between -6 °C and 12 °C

In Table 27, all the data are positive, which means the physical hardening load in conditioning temperature -12 °C are more serious than load in the conditioning temperature -6 °C; in the same conditioning temperature, as the conditioning time increase, the difference of the m-value between -6 °C and -12 °C is waving, same for the four different specimens N2, N2+AO12, P1 and P1+AO12.

5.3. Influence of antioxidant in low temperature

According to the difference of the base bitumen used in polymer modified sample (P1) and the

neat sample (N2), the effect of polymer modification cannot be assessed and the analysis of the influence of antioxidant has been done independently for each of these two samples.

In the case of creep stiffness:

In Table 10 (-6 °C), compare N2 and N2+AO12, P1 and P1+AO12, in front side, both the creep stiffness is decrease, which means the antioxidant improves the performance of neat bitumen and polymer modified bitumen. In the back side, the data is waving.

In Table 14 (-12 °C), compare N2 and N2+AO12, P1 and P1+AO12, in front side, in the conditioning time 24 h and 72 h, both the creep stiffness is decrease, which means the antioxidant improves the performance of neat bitumen and polymer modified bitumen, but in the conditioning time 1 h, the data is waving. In the back side, both creep stiffness is decrease, which means the antioxidant improves the performance of neat bitumen and polymer modified bitumen.

For the relaxation parameter:

In Table 20 (-6 Celsius), in the front side, compare N2 and N2+AO12, the relaxation parameter is still decrease, which means the antioxidant have neglectable effects on the neat bitumen. Compared to P1 and P1+AO12, the relaxation parameter is increase, which means the antioxidant improve the performance of polymer modified bitumen. In the back side, both data are waving.

In Table 24 (-12 Celsius), in the front side, compare N2 and N2+AO12, compared to P1 and P1+AO12, the data are waving. In the back side, compare N2 and N2+AO12, the data is waving. Compared to P1 and P1+AO12, the relaxation parameter is still decrease, which means the antioxidant have neglectable effect on polymer modified bitumen.

According to what discussed above, these conclusions can be drawn:

At -6 °C, for P1, the antioxidant has a positive effect both in creep stiffness and relaxation parameter, it improves polymer modified bitumen performance. But for N2, it only has a positive effect in creep stiffness.

At -12 °C, for N2, in different conditioning time, the antioxidant has different effect for creep stiffness, both negative and positive. Have negative effect for relaxation parameter both with N2 and P1.

This kind of antioxidant only have positive effect on polymer modified bitumen at -6 °C.

5.4. Determination of the limiting grade

According to section 3.2, we can determine both the stiffness critical temperature $T_{S(300\text{ MPa})}$ and the relaxation parameter critical temperature $T_{m(0.300)}$, and the warmer limiting low temperature has been chosen as the limiting grade, T_L .

5.4.1. Determining the limiting temperature for creep stiffness

According to the methodology, the limiting low temperature for creep stiffness $T_{S(300\text{ MPa})}$ in front side was determined in Table 28.

Table 28 Stiffness limiting temperature ($^{\circ}\text{C}$) for the front side of the beam

Sample	Storage time (h)	S(-6 $^{\circ}\text{C}$) (MPa)	S(-12 $^{\circ}\text{C}$) (MPa)	$T_{S(300\text{MPa})}$ ($^{\circ}\text{C}$)	$T_{c,S}$ ($^{\circ}\text{C}$)
N2	1	140.3	257.2	-13.5	-23.5
	24	158.2	337.2	-11.1	-21.1
	72	164.2	356.8	-10.7	-20.7
N2-AO12	1	119.7	259	-13.3	-23.3
	24	154.2	327	-11.3	-21.3
	72	159.8	350.8	-10.8	-20.8
P1	1	92.6	155.7	-19.6	-29.6
	24	108	192	-16.7	-26.7
	72	110.3	201.8	-15.9	-25.9
P1-AO12	1	73.7	156.8	-17.2	-27.2
	24	82.8	183.6	-15.6	-25.6
	72	87.1	194.8	-15.2	-25.2

The upper data have been plotted in Figure 32, the temperature is linear scale, the conditioning time is logarithm scale:

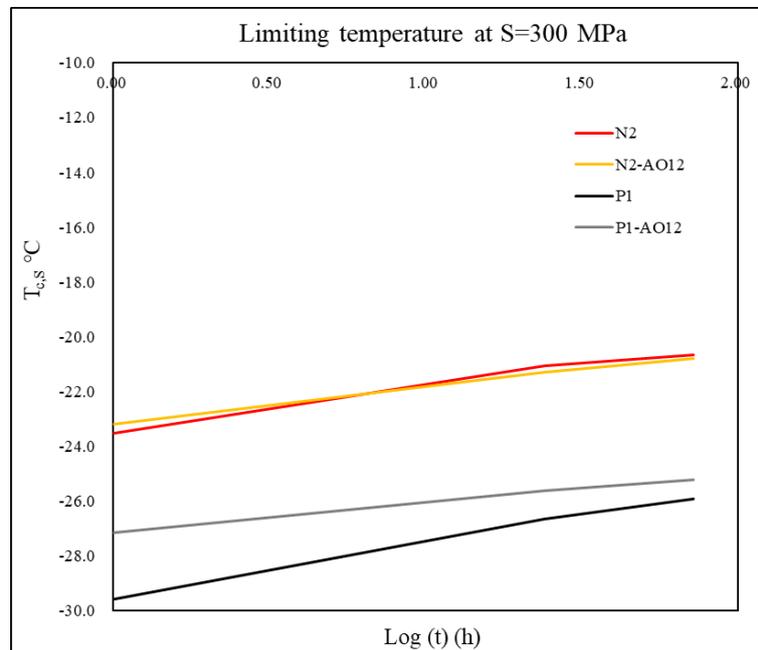


Figure 32 Front-Limiting temperature at $S=300$ ($^{\circ}\text{C}$)

It shows that in the same material, as the conditioning time increase, the limiting temperature increases.

The same calculation has been performed for the back side of the beam which are presented in Table 29 and Figure 33.

Table 29 Back-Value of stiffness limiting temperature (°C)

Sample	Storage time (h)	S(-6 °C) (MPa)	S(-12 °C) (MPa)	T _{S(300MPa)} (°C)	T _{c,S} (°C)
N2-opposite	1	108.1	241.5	-13.6	-23.6
	24	145.7	316.2	-11.6	-21.6
	72	155.4	332.0	-11.2	-21.2
N2-A012-opposite	1	113.5	241.5	-13.8	-23.8
	24	140.5	303.3	-11.9	-21.9
	72	149.5	319.0	-11.5	-21.5
P1-opposite	1	72.6	142.8	-18.6	-28.6
	24	88.7	180.5	-16.3	-26.3
	72	103.7	192.0	-16.3	-26.3
P1-A012-opposite	1	64.9	142.0	-17.7	-27.7
	24	75.2	173.7	-16.0	-26.0
	72	79.6	175.8	-16.0	-26.0

Upper data have been plotted in Figure 33, the temperature is linear scale, the conditioning time is logarithm scale:

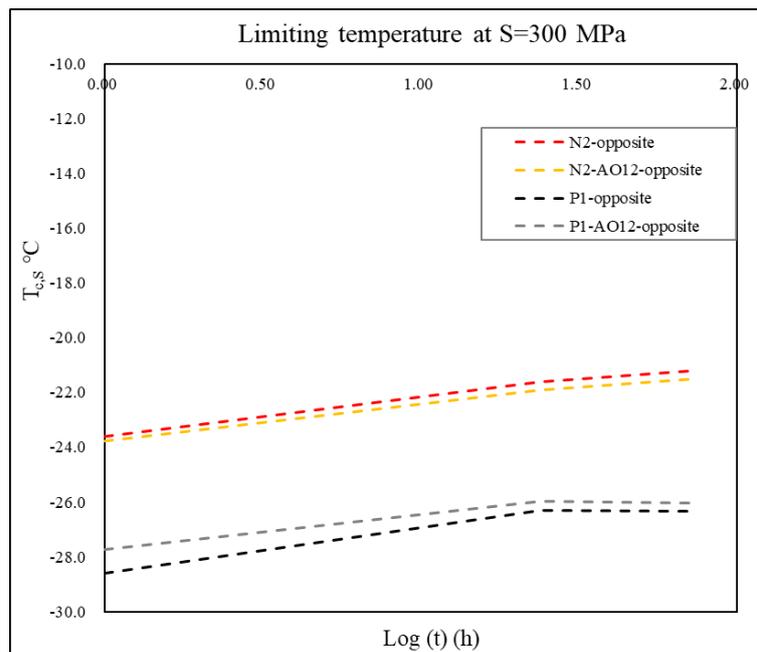


Figure 33 Back-Limiting teperature at S=300 (°C)

In the same material, as the conditioning time increases, the limiting temperature increases.

5.4.2. Comparison of the T_s between Front & Back

A comparison has been made between the front side and back side, which shows in Table 30.

Table 30 Front & Back side-Difference of the limiting temperature for creep stiffness

Difference limiting temperature at S=300 (%)			
Sample	Conditioning time (h)		
	1	24	72
N2 & N2-opposite	-0.4	-2.5	-2.6
N2-AO12 & N2-AO12-opposite	-2.5	-2.8	-3.4
P1 & P1-opposite	3.3	1.4	-1.6
P1+AO12 & P1-AO12-opposite	-2.1	-1.3	-3.3

If Table 30 value is positive, which means the condition in front side is serious than the back side, but from the Table 30, as the conditioning time increase, the data is waving, such conclusion cannot be got.

4) Determining the limiting temperature for m-value in front side

According to the methodology, the limiting low temperature for creep stiffness in front side was determined in Table 31.

Table 31 Front-Value of m-value limiting temperature (°C)

Sample	Storage time (h)	m (-6 °C)	m (-12 °C)	T _{m(0.300)} (°C)	T _{c,m} (°C)
N2	1	0.338	0.284	-10.2	-20.2
	24	0.298	0.245	-5.8	-15.8
	72	0.288	0.235	-4.7	-14.7
N2-AO12	1	0.327	0.282	-9.6	-19.6
	24	0.295	0.236	-5.5	-15.5
	72	0.284	0.230	-4.3	-14.3
P1	1	0.304	0.279	-7.0	-17.0
	24	0.281	0.249	-2.5	-12.5
	72	0.276	0.241	-1.9	-11.9
P1-AO12	1	0.326	0.270	-8.8	-18.8
	24	0.304	0.247	-6.5	-16.5
	72	0.301	0.241	-6.1	-16.1

Upper data can be plotted in Figure 34, the temperature is linear scale, the conditioning time is logarithm scale:

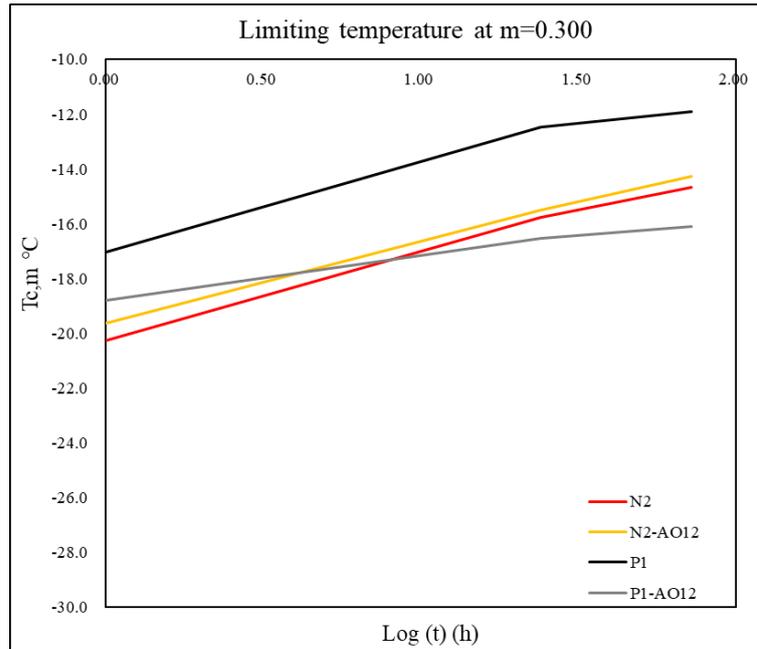


Figure 34 Front-Limiting teperature at m=0.300 (°C)

In the same material, as the conditioning time increases, the limiting temperature increases.

5) Determining the limiting temperature for m-value in back side

The same calculation has been performed for the back side of the beam which are presented in Table 32 and Figure 35.

Table 32 Back-Value of m-value limiting temperature (°C)

Sample	Storage time (h)	m(-6 °C)	m(-12 °C)	$T_{m(0.300)}$ (°C)	$T_{c,m}$ (°C)
N2-opposite	1	0.365	0.314	-13.6	-23.6
	24	0.321	0.269	-8.4	-18.4
	72	0.311	0.262	-7.4	-17.4
N2-A012-opposite	1	0.355	0.306	-12.8	-22.8
	24	0.325	0.271	-8.8	-18.8
	72	0.317	0.268	-8.1	-18.1
P1-opposite	1	0.356	0.317	-14.6	-24.6
	24	0.329	0.281	-9.6	-19.6
	72	0.308	0.279	-7.6	-17.6
P1-A012-opposite	1	0.355	0.308	-13.0	-23.0
	24	0.338	0.276	-9.7	-19.7
	72	0.337	0.275	-9.6	-19.6

Upper data can be plotted in Figure 35, the temperature is linear scale, the conditioning time is logarithm scale:

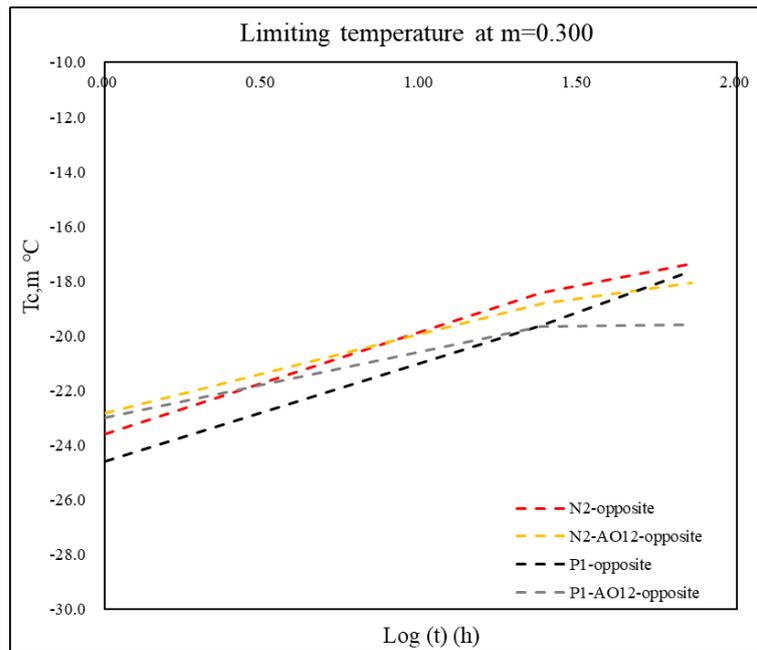


Figure 35 Back-Limiting teperature at m=0.300 (°C)

In the same material, as the conditioning time increases, the limiting temperature increases.

6) *The comparison of the m-value limiting temperature between front & back side*

A comparison has been made between the front side and back side, which shows in Table 33.

Table 33 Front & Back side-Difference of the limiting temperature for m-value

Difference limiting temperature at m=0.300 (%)			
Sample	Conditioning time (h)		
	1	24	72
N2 & N2-opposite	-16.5	-17.0	-18.5
N2-AO12 & N2-AO12-opposite	-16.3	-21.5	-26.8
P1 & P1-opposite	-44.4	-57.5	-48.0
P1+AO12 & P1-AO12-opposite	-22.2	-19.0	-21.6

The values show in Table 33 is negative, which means the condition in front side is serious than the back side.

7) *Determining the limiting grade in front side*

From the previous part, the limiting temperature have been already calculated, according to these data, the limiting grade can be calculated, as Table 34 shows below:

Table 34 Front-Limiting grade (°C)

Sample	Storage time (h)	T _{c,s} (°C)	T _{c,m} (°C)	ΔT (°C)	T _L (°C)
N2	1	-23.5	-20.2	-3.3	-20.2
	24	-21.1	-15.8	-5.3	-15.8
	72	-20.7	-14.7	-6.0	-14.7
N2-AO12	1	-23.2	-19.6	-3.6	-19.6
	24	-21.3	-15.5	-5.8	-15.5
	72	-20.8	-14.3	-6.5	-14.3
P1	1	-29.6	-17.0	-12.6	-17.0
	24	-26.7	-12.5	-14.2	-12.5
	72	-25.9	-11.9	-14.0	-11.9
P1-AO12	1	-27.2	-18.8	-8.4	-18.8
	24	-25.6	-16.5	-9.1	-16.5
	72	-25.2	-16.1	-9.1	-16.1

According to upper part data, limiting grade in front side can be plotted in Figure 36.

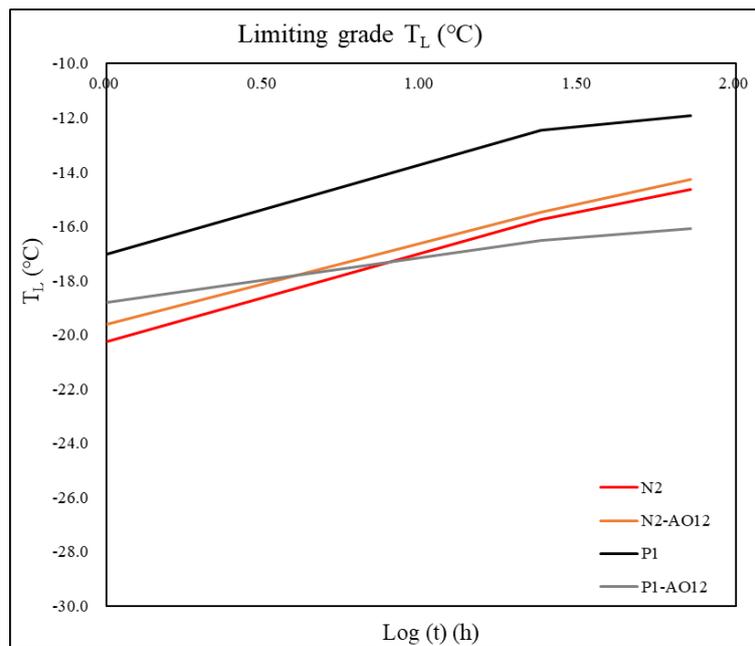


Figure 36 Front-Limiting grade T_L (°C)

The limiting grade dominants by relaxation parameter, antioxidant improves the performance of polymer modified bitumen.

8) Determining the limiting grade in back side

From the previous part, the limiting temperature have been already calculated, according to these data, the limiting grade can be calculated and shows in Table 35.

Table 35 Back-Limiting grade ($^{\circ}\text{C}$)

Sample	Storage time (h)	$T_{c,s}$ ($^{\circ}\text{C}$)	$T_{c,m}$ ($^{\circ}\text{C}$)	ΔT ($^{\circ}\text{C}$)	T_L ($^{\circ}\text{C}$)
N2-opposite	1	-23.6	-23.6	0.0	-23.6
	24	-21.6	-18.4	-3.2	-18.4
	72	-21.2	-17.4	-3.8	-17.4
N2-A012-opposite	1	-23.8	-22.8	-1.0	-22.8
	24	-21.9	-18.8	-3.1	-18.8
	72	-21.5	-18.1	-3.4	-18.1
P1-opposite	1	-28.6	-24.6	-4.0	-24.6
	24	-26.3	-19.6	-6.7	-19.6
	72	-26.3	-17.6	-8.7	-17.6
P1-A012-opposite	1	-27.7	-23.0	-4.8	-23.0
	24	-26.0	-19.7	-6.3	-19.7
	72	-26.0	-19.6	-6.5	-19.6

According to upper part data, the limiting grade for front side can be plotted in Figure 37:

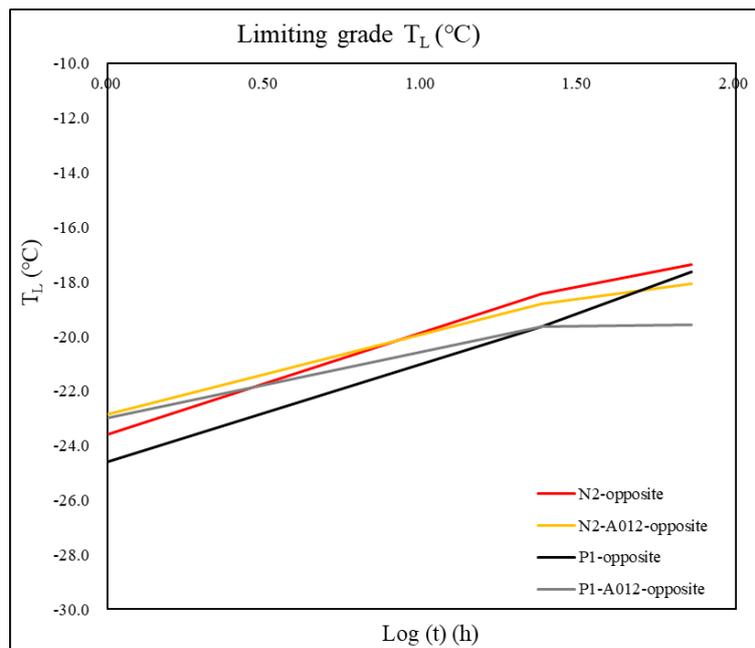


Figure 37 Back-Limiting grade T_L ($^{\circ}\text{C}$)

The limiting grade dominants by relaxation parameter, antioxidant have neglectable effects both on neat and polymer modified bitumen.

9) The comparison of the limiting grade between the front side and back side.

A comparison between the front side and back side have been made, which shows Table 36.

Table 36 Front & Back-Difference of Limiting grade (%)

Sample	Conditioning period (h)	Difference of Limiting grade (%)
N2 & N2-opposite	1	-16.5
	24	-17.0
	72	-18.5
N2-AO12 & N2-AO12-opposite	1	-16.3
	24	-21.5
	72	-26.8
N2-AO12 & P1-opposite	1	-44.4
	24	-57.5
	72	-48.0
N2-AO12 & P1-AO12-opposite	1	-22.2
	24	-19.0
	72	-21.6

The values presented in Table 36 are all negative, which means the condition in front side is serious than the back side, in the back side, the limiting grade have higher tolerance.

5.5. Hardening and Relaxation indexes

According to the analysis method explained in section 3.4., a hardening index, S_i/S_0 , defined as the ratio of the creep stiffness, S (60 s), a relaxation index, m_i/m_0 , defined as the ratio of the relaxation parameter, m (60 s).

In hardening indexes, for the relative completeness physical hardening under the conditioning time of 24h, Equation 13 can be used:

Equation 13 Relative completeness for hardening index

$$\Delta S = \frac{S_{24}/S_1}{S_{72}/S_1} \times 100$$

In relaxation index, for the relative completeness physical hardening under the conditioning time of 24h, Equation 14 can be used:

Equation 14 Relative completeness for relaxation index

$$\Delta m = 100 - \frac{m_{24}/m_1}{m_{72}/m_1} \times 100$$

1) The front side

First, there are the average stiffness and average m-value both -6 °C and -12 °C in Table 37.

Table 37 Front-The average stiffness and average m-value both in -6 °C and in -12 °C

Temperature	Bitumen	S (MPa)			m (-)		
(°C)		1h	24h	72h	1h	24h	72h
-6	N2	140.3	158.2	164.2	0.338	0.298	0.288
	N2+AO12	119.7	154.2	159.8	0.327	0.295	0.284
	P1	92.6	108	110.3	0.304	0.281	0.276
	P1+AO12	73.7	82.8	87.1	0.326	0.304	0.301
-12	N2	257.2	337.2	356.8	0.284	0.245	0.235
	N2+AO12	259	327	350.8	0.282	0.236	0.23
	P1	155.7	192	201.8	0.279	0.249	0.241
	P1+AO12	156.8	183.6	194.8	0.27	0.247	0.241

Hardening indexes (S_i/S_0) for the entire long-term aged binders at -6 °C and -12 °C ($t_0=1h$) and the relative degree of physical hardening under a condition time of 24h (ΔS) has been calculated by use of Equation 12; these results are presented in Table 38.

Table 38 Front-Hardening indexes

Temperature	Sample	S_i/S_0		ΔS
		$t_i=24h$	$t_i=72h$	
-6	N2	1.13	1.17	96.35
	N2+AO12	1.29	1.33	96.50
	P1	1.17	1.19	97.89
	P1+AO12	1.12	1.18	95.12
-12	N2	1.31	1.39	94.50
	N2+AO12	1.26	1.35	93.23
	P1	1.23	1.30	95.13
	P1+AO12	1.17	1.24	94.23

According to the results presented in Table 38, the physical hardening leads to a significant increase in creep stiffness in the first 24h, followed with a milder increasing, suggesting that effect of physical hardening is mainly occurring in the first 24h. based on a close observation of the degree of completeness of physical hardening in Table 39, all the values are in a range between 93.23% to 97.89%. The antioxidant improves the ability to dissipated energy on polymer modified bitumen.

Relaxation indexes for the entire long-term aged binders at -6 °C and -12 °C ($t_0=1h$) and the relative degree of physical hardening under a condition time of 24h has been calculated by use of Equation 14, these results are presented in Table 39.

Table 39 Front-Relaxation indexes

Temperature (°C)	Sample	m_i/m_o^*		Δm
		$t_i=24h$	$t_i=72h$	
-6	N2	0.88	0.85	96.71
	N2+AO12	0.90	0.87	96.36
	P1	0.92	0.91	98.22
	P1+AO12	0.93	0.92	99.01
-12	N2	0.86	0.82	95.87
	N2+AO12	0.84	0.82	97.38
	P1	0.89	0.86	96.80
	P1+AO12	0.92	0.89	97.55

According to the results presented in Table 39, the physical hardening leads to a significant decrease in m-value in the first 24h, followed with a milder decreasing, suggesting that effect of physical hardening is mainly occurring in the first 24h. based on a close observation of the degree of completeness of physical hardening in Table 40, all the values are in a range between 95.87% to 99.01%.

2) The back side

First, there are average stiffness and average m-value both -6 °C and -12 °C in Table 40.

Table 40 Back-The average stiffness and average m-value both in -6 °C and in -12 °C

Temperature (°C)	Sample	S (MPa)			m (-)		
		1h	24h	72h	1h	24h	72h
-6	N2-opposite	108.1	145.7	155.4	0.365	0.321	0.311
	N2-AO12-opposite	113.5	140.5	149.5	0.355	0.325	0.317
	P1-opposite	72.6	88.7	103.7	0.356	0.329	0.308
	P1-AO12-opposite	64.9	75.2	79.6	0.355	0.338	0.337
-12	N2-opposite	241.5	316.2	332.0	0.314	0.269	0.262
	N2-AO12-opposite	241.5	303.3	319.0	0.306	0.271	0.268
	P1-opposite	142.8	180.5	192.0	0.317	0.281	0.279
	P1-AO12-opposite	142.0	173.7	175.8	0.308	0.276	0.275

According to the results presented in Table 41, the hardening indexes for the entire long-term aged binders at -6 °C and -12 °C ($t_0=1h$) and the relative degree of physical hardening under a condition time of 24h. we can use Equation 13, these results are presented in Table 41.

Table 41 Back-Hardening indexes

Temperature (°C)	Sample	S_i/S_o^*		ΔS
		$t_i=24h$	$t_i=72h$	
-6	N2-opposite	1.35	1.44	93.76
	N2-AO12-opposite	1.24	1.32	93.98
	P1-opposite	1.22	1.43	85.57
	P1-AO12-opposite	1.16	1.23	94.41
-12	N2-opposite	1.31	1.37	95.24
	N2-AO12-opposite	1.26	1.32	95.09
	P1-opposite	1.26	1.35	94.01
	P1-AO12-opposite	1.22	1.24	98.79

According to the results presented in Table 41, the physical hardening leads to a significant increase in creep stiffness in the first 24h, followed with a milder increasing, suggesting that effect of physical hardening is mainly occurring in the first 24h. based on a close observation of the degree of completeness of physical hardening in Table 42, all the values are in a range between 85.57% to 98.79%.

Relaxation indexes for the entire long-term aged binders at -6 °C and -12 °C ($t_0=1h$) and the relative degree of physical hardening under a condition time of 24h. we can use Equation 14, the results show in Table 42:

Table 42 Back-Relaxation indexes

Temperature (°C)	Bitumen	m_i/m_o^*		Δm
		$t_i=24h$	$t_i=72h$	
-6	N2-opposite	0.88	0.85	96.86
	N2-AO12-opposite	0.92	0.89	97.50
	P1-opposite	0.92	0.86	93.56
	P1-AO12-opposite	0.95	0.95	99.46
-12	N2-opposite	0.86	0.84	97.62
	N2-AO12-opposite	0.89	0.87	98.59
	P1-opposite	0.89	0.88	99.29
	P1-AO12-opposite	0.90	0.90	99.78

According to the results presented in Table 42, the physical hardening leads to a significant decrease in m-value in the first 24h, followed with a milder decreasing, suggesting that effect of physical hardening is mainly occurring in the first 24h. based on a close observation of the degree of completeness of physical hardening in Table 33, all the values are in a range between 93.56% to 99.78%.

5.6. Dissipated energy

As it was explained in Section 3.3., the dissipated energy is related to the ratio of relaxation parameter and creep stiffness, m/S . By use of Equation 4, the dissipated energy has been assessed

for both sides of each samples. For ease of comparison, first, these results are presented in two separate sections for each side, then the comparison of the sides is discussed.

1) *The front side*

According to the upper formula, the results can be gotten in Table 43.

Table 43 Front-The ratio between m-value and creep stiffness m/S

Temperature (°C)	Sample	m/S (‰)		
		1	24	72
-6	N2	2.409	1.882	1.754
	N2+AO12	2.732	1.914	1.779
	P1	3.287	2.602	2.502
	P1+AO12	4.427	3.670	3.456
-12	N2	1.106	0.725	0.657
	N2+AO12	1.089	0.722	0.656
	P1	1.792	1.296	1.193
	P1+AO12	1.722	1.347	1.239

The ratio between relaxation parameter and creep stiffness is plotted in Figure 38.

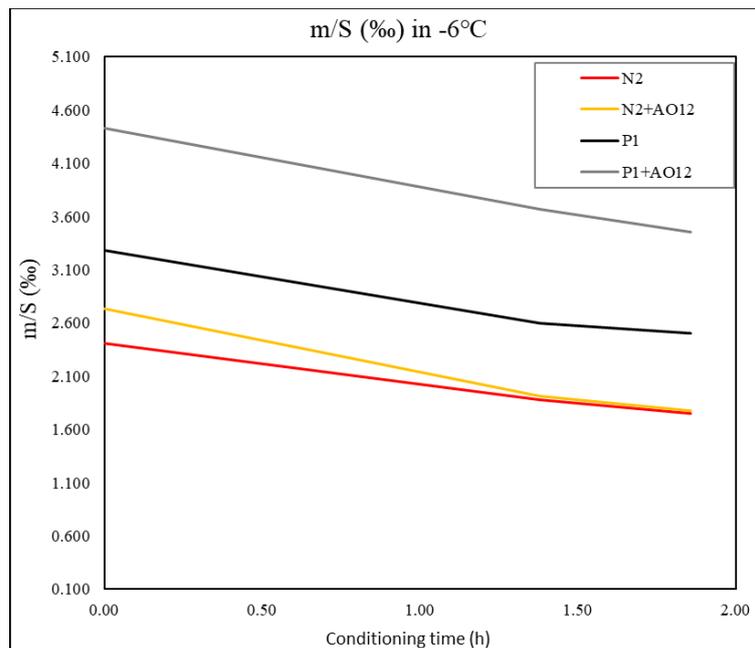


Figure 38 Front-Difference of m/S (%) in -6 °C

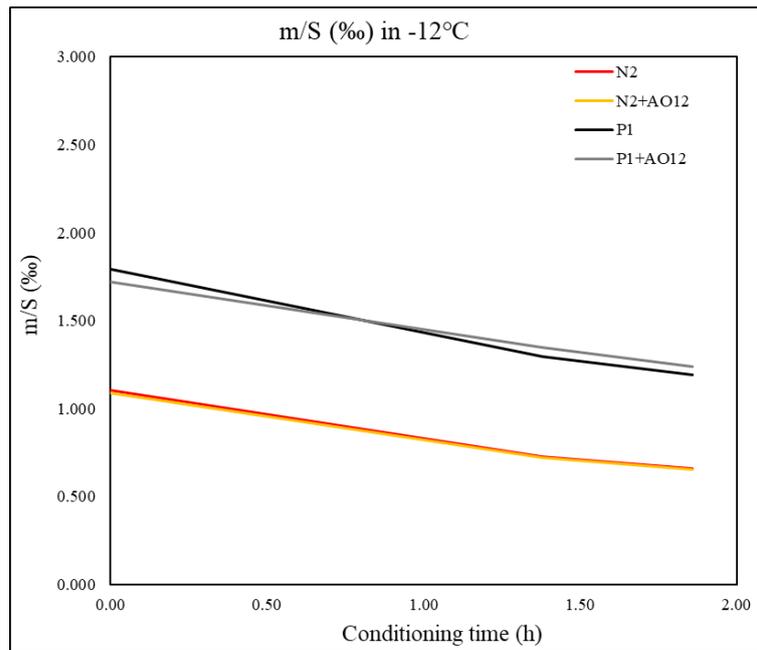


Figure 39 Front-Difference of m/S(%) in -12 °C

From the Table 43, as the conditioning time increase, the dissipated energy decreases; at test temperature -6 °C, antioxidant improves the ability to dissipated energy both on neat and polymer modified bitumen; at test temperature -12 °C, the data more or less the same, antioxidant effects can be neglected.

2) The back side

The ratio of relaxation parameter and creep stiffness on the back side is calculated in Table 44.

Table 44 Back-The ratio between m-value and creep stiffness m/S

Temperature (°C)	Sample	m/S (%)		
		1	24	72
-6	N2-opposite	3.378	2.204	2.002
	N2-AO12-opposite	3.122	2.316	2.122
	P1-opposite	4.908	3.708	2.968
	P1-AO12-opposite	5.469	4.5	4.226
-12	N2-opposite	1.299	0.85	0.79
	N2-AO12-opposite	1.268	0.895	0.839
	P1-opposite	2.221	1.557	1.453
	P1-AO12-opposite	2.167	1.589	1.567

The ratio between relaxation parameter and creep stiffness is plotted in Figure 40 and Figure 41 for both temperatures (-6 °C and -12 °C).

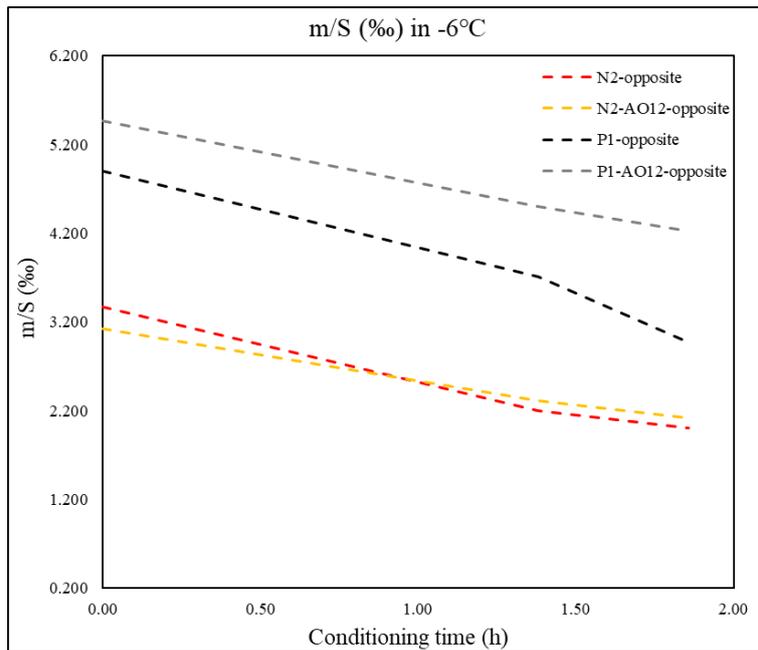


Figure 40 Back-Difference of m/S (%) in -6 °C

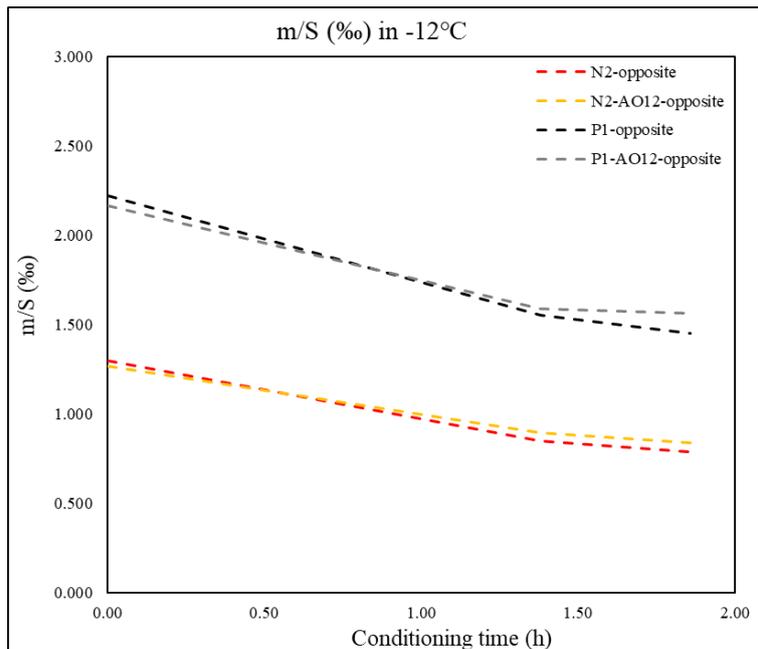


Figure 41 Back-The Difference of m/S(%) in -12 °C

According to Table 44, as the conditioning time increase, the dissipated energy decreases; at test temperature -6 °C, antioxidant improves the ability to dissipated energy on polymer modified bitumen.

3) The comparison between the front side and back side

In order to have a good comparison, a difference can be made between the load act at the front side of specimen and the load act at the back side of specimen. The formula shows below:

Equation 15 Different dissipated energy between the front side and back side

$$\Delta\left(\frac{m}{S}\right)_{N2 \& N2\text{-opposite}} = \frac{\left(\frac{m}{S}\right)_{N2} - \left(\frac{m}{S}\right)_{N2\text{-opposite}}}{\left(\frac{m}{S}\right)_{N2}} \times 100$$

$$\Delta\left(\frac{m}{S}\right)_{N2\text{-AO12} \& N2\text{-AO12-opposite}} = \frac{\left(\frac{m}{S}\right)_{N2\text{-AO12}} - \left(\frac{m}{S}\right)_{N2\text{-AO12-opposite}}}{\left(\frac{m}{S}\right)_{N2\text{-AO12}}} \times 100$$

$$\Delta\left(\frac{m}{S}\right)_{P1 \& P1\text{-opposite}} = \frac{\left(\frac{m}{S}\right)_{P1} - \left(\frac{m}{S}\right)_{P1\text{-opposite}}}{m_{P1}} \times 100$$

$$\Delta\left(\frac{m}{S}\right)_{P1\text{-AO12} \& P1\text{-AO12-opposite}} = \frac{\left(\frac{m}{S}\right)_{P1\text{-AO12}} - \left(\frac{m}{S}\right)_{P1\text{-AO12-opposite}}}{\left(\frac{m}{S}\right)_{P1\text{-AO12}}} \times 100$$

According to abovementioned formulas, the results show in Table 45.

Table 45 Front side & Back side-Difference m/S (%)

Temperature (°C)	Sample	m/S (%)		
		1	24	72
-6	N2 & N2-opposite	-40.248	-17.079	-14.119
	N2-AO12 & N2-AO12-opposite	-14.307	-21.01	-19.238
	P1 & P1-opposite	-49.342	-42.504	-18.655
	P1-AO12 & P1-AO12-opposite	-23.526	-22.618	-22.253
-12	N2 & N2-opposite	-17.473	-17.192	-20.268
	N2-AO12 & N2-AO12-opposite	-16.469	-23.837	-27.88
	P1 & P1-opposite	-23.901	-20.138	-21.781
	P1-AO12 & P1-AO12-opposite	-25.827	-17.941	-26.471

In Table 45, all the data are negative, which means the physical hardening load in front side of the specimen are more serious than load in the back side of the specimen; in the same conditioning temperature, as the conditioning time increase, the difference of the m-value between front side and back side is waving.

CHAPTER 6.

CONCLUSION

In the study presented in this thesis the effects of physical hardening on the low temperature behaviour of bitumen were explored through a laboratory investigation, in which four bitumen types (neat, neat + antioxidant, polymer modified, polymer modified + antioxidant) by performing BBR creep tests at different temperatures and conditioning times.

The main findings of this thesis can be summarized as follows:

- When considering the limiting grade, the effects of the antioxidant on neat bitumen were found to be negligible, while an increase in performance was observed in the case of polymer modified binder.
- By analysing the relative completeness hardening index, it was interesting to highlight that the antioxidant did not affect significantly the evolution in time of the physical hardening phenomenon
- By considering the m/S parameter, it was found that the antioxidant had the potential to enhance the energy dissipation capability of both neat and modified binders.

TERMINOLOGY

Bitumen: Includes both modified and unmodified bitumen. Modifiers added to the bitumen are restricted to non-particulate organic modifiers with largest dimension no greater than 250 μm .

Linear: Refers to a modulus or mechanical property when the mechanical property is independent of load, i.e., a constant ratio between stress and strain.

Viscoelastic: A type of material behaviour that includes both viscous and elastic behaviour. The moduli for viscoelastic materials are time dependent.

Physical hardening: Reversible stiffening of a bitumen that occurs below room temperature; reversed by heating to room temperature.

Short-term ageing: Ageing that occurs in a bitumen at above ambient temperatures as a result of mixing, transport and storage, laydown, and compaction.

Long-term ageing: Refers to the ageing of bitumen that occurs in the field during service over five or more years.

Fatigue cracking: Cracking caused by repeated loading at stress levels lower than those that cause cracking under a single load application.

Rutting: Permanent deformation in a pavement caused by repeated traffic loads and an HMAC mixture with inadequate shearing resistance. Evidenced by the formation of ruts in the wheel path.

Thin film: A relative term used to define the thickness of a bitumen film. The film created in the rotating RTFO bottles is considered to be a thin film. A several millimetre thick residue in the bottom of a container would be considered a thin film. For the purposes of handling procedures, thin describes a bitumen layer that is sufficiently thin so that oxygen can readily diffuse into and saturate the bitumen and thereby contribute to oxidation.

$T_{S(300\text{MPa})}$: The calculated temperature where the creep stiffness (S) at 60s loading equals 300 MPa

$T_{m(0.300)}$: The calculated temperature where the m-value at 60 s loading equals 0.300

$T_{c,s}$: Limiting temperature for creep stiffness, 10 °C colder than $T_{S(300\text{MPa})}$.

$T_{c,m}$: Limiting temperature for m-value, 10 °C colder than $T_{m(0.300)}$.

T_L : Limiting grade, the warmer of the limiting temperatures.

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