UNIVERSITÀ DEGLI STUDI DI PADOVA
SCUOLA DI INGEGNERIA
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LA CARATTERIZZAZIONE SPERIMENTALE DELL' INVECCHIAMENTO DEI BITUMI.

CASI DI STUDIO SU MISCELE A CALDO E A TIEPIDO

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UNIVERSITÀ DEGLI STUDI DI PADOVA
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Master Degree in Civil Engineering

EXPERIMENTAL CHARACTERIZATION OF BITUMEN'S AGING PROPERTIES

CASE STUDIES ON WARM AND HOT MIXES

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TABLE OF CONTENTS

TABLE OF CONTENTS

INTRODUCTION

Bitumen oxidation is one of the phenomena that contribute most to the deterioration of road pavements’ performances and it occurs both in the mixing process and during the service life of the infrastructure. The present work focuses on the laboratory reproduction of aging phenomena that take place only in the binder aging and on the experimental characterization of the initial and final binder’s properties in three different case studies.

Although asphalt has been used for more than a century to pave roads, the behaviour of its chemical, rheological and mechanical properties over time is not known yet. Moreover, in the past decades the heavy traffic has greatly increased and the need of economic and environmental-friendly disposal of waste material has arose, thus leading to the study of new materials and of methods for reclaiming materials from the aged pavement.

Hence, while on one hand the need of characterizing the behaviour of the whole bituminous pavement has arose, on the other studying the properties of its single components is getting more and more important. In particular, since the aging of the asphalt is mainly due to the aging of its organic component, studying the behaviour of the binder is the fundamental to start to understand the final properties of the mix and to improve them.

This work focuses mainly on binders aged according to standard laboratory procedures (*Rolling Thin Film Oven Test*, EN 12607-1, and *Preassure Aging Vessel*, EN 14769). The advanced experimental characterization of rheological properties is carried out by the *Dynamic Shear Rheometer* (EN 14770), while chemical properties are evaluated using both the infrared spectroscopy (*Fourier Transorm Infrared Sectroscopy*) and the size-exclusion chromatography (*Gel Permeation Chromatography*). Three case studies are analysed:

- ***Laboratory aging of warm mix asphalt:*** using warm mix asphalt instead of conventional hot mix asphalt the working temperature can be reduced, without decreasing the mix workability. The aim of this part of the study is to find a test procedure reflecting the binder aging in warm asphalt at the lower temperatures used in the production process that could replace the European standard EN 12607-1, developed for hot mix asphalt.
- ***Polymer degradation in polymer-modified binders:*** modifying the binder with chemical additives is a widespread technique to improve the final performances of a pavement. The aim of this part of the study is to analyse the polymer degradation caused by oxidation, estimating it by specific indexes, and to evaluate its rheological outcomes.
- ***Progressive oxidation in repeated recycling of pavement:*** the presence of road facilities paved with recycled asphalt raises the problem of recycling asphalt more than once. The aim of this part of the study is to understand the influence of the aged and several time recycled binder on the chemical and rheological properties of the final blend.

The thesis is divided in three ideal parts:

- ***Chapters from 1 to 3:*** theoretic introduction to bitumen, to its chemical and rheological properties and to the experimental procedures used for their evaluation.
- ***Chapter 4:*** preliminary tests.
- ***Chapters from 5 to 7:*** description of the projects, of their experimental development and of their results.

INTRODUZIONE

Uno dei fenomeni che più concorre a compromettere le prestazioni delle pavimentazioni stradali in conglomerato bituminoso è l’ossidazione del legante, sia durante la posa in opera che nel corso della vita utile dell’infrastruttura. Il presente lavoro di tesi si è focalizzato sulla riproduzione in laboratorio dei fenomeni di invecchiamento del bitume e sulla caratterizzazione sperimentale delle proprietà iniziali e finali dei leganti in tre distinti casi di studio.

Nonostante il conglomerato bituminoso sia usato da più di un secolo per la realizzazione di pavimentazioni stradali, non sono ancora completamente noti i processi di modifica delle sue caratteristiche chimico-fisiche e meccaniche nel corso del tempo. Negli ultimi decenni, inoltre, l’incremento di traffico e la necessità di disporre economicamente ed ecologicamente del materiale delle vecchie infrastrutture ha portato allo studio di nuovi materiali e metodi per riciclare il manto stradale.

Se, quindi, da un lato si è sviluppata l’esigenza di caratterizzare prestazionalmente il conglomerato nel suo insieme, dall’altro è sempre più necessario lo studio delle caratteristiche dei singoli componenti di questo. In particolare, essendo l’invecchiamento del conglomerato dovuto all’invecchiamento della sua parte organica, la ricerca sulle proprietà del solo legante è punto di partenza imprescindibile per comprendere le proprietà finali delle miscele e per migliorare le stesse.

Nel corso di questo lavoro si sono analizzati principalmente leganti invecchiati in laboratorio tramite procedure standard (*Rolling Thin Film Oven Test*, EN 12607-1, e *Pressure Aging Vessel*, EN 14769), la cui caratterizzazione sperimentale avanzata delle proprietà reologiche è stata effettuata tramite il *Dynamic Shear Rheometer* (EN 14770) mentre le proprietà chimiche sono state analizzate sia tramite spettrografia a luce infrarossa (*Fourier Transorm Infrared Sectroscopy*) che tramite cromatografia ad esclusione molecolare (*Gel Permeation Chromatography*). I tre casi di studio su cui si è focalizzata la ricerca sono i seguenti:

- ***Riproduzione dei fenomeni di invecchiamento nelle miscele a tiepido:*** l'impiego di miscele a tiepido consente di ridurre le temperature di lavorazione del conglomerato mantenendo la stessa lavorabilità delle miscele a caldo. Scopo di questa parte dello studio è determinare una procedura per l'invecchiamento a breve termine in laboratorio che rifletta le reali temperature di lavorazione di tale tecnologia e sostituisca lo standard europeo EN 12607-1, sviluppato per le miscele a caldo.
- ***Degradazione dei polimeri nei leganti modificati:*** l'additivazione/modifica dei leganti è pratica ormai molto diffusa per migliorare le prestazioni finali della pavimentazione. Scopo di questa parte dello studio è l'analisi della degradazione dei polimeri conseguente all'ossidazione, con quantificazione della stessa attraverso appositi indici, e analisi delle conseguenze reologiche di tale degradazione.
- ***Ossidazione progressiva nel riciclaggio oltre la seconda generazione:*** la presenza di infrastrutture stradali pavimentate con conglomerato parzialmente riciclato pone oggi il problema di investigare sul riciclaggio della pavimentazione oltre la seconda generazione. Scopo di questa parte dello studio è comprendere l'influenza del legante invecchiato e riciclato più volte sulle caratteristiche chimiche e reologiche del legante nel conglomerato finale.

La tesi si articola idealmente in tre parti:

- ***Capitoli da 1 a 3:*** introduzione teorica al materiale, alle sue proprietà chimico-fisiche e reologiche e alle procedure sperimentali per la determinazione delle stesse.
- ***Capitolo 4:*** test preliminari.
- ***Capitoli da 5 a 7:*** presentazione dei progetti di ricerca, del loro sviluppo sperimentale e dei risultati ottenuti.

CHAPTER 1: THE BITUMEN

1.1 INTRODUCTION

Bitumen is the most used binder for street paving, thanks to its adhesive and waterproofing properties. It is sticky, black and highly viscous liquid or semi-solid form of petroleum which can be found in “natural” form the pitch lakes or it can be a refined product.

1.1.1 EARLY USES

The first uses of *natural* bitumen date back to the third millennium B.C., when it was used by Middle Eastern populations as waterproofing and binding agent for water tanks. Later on, it has been used as waterproofing coat for boats, aqueducts and rooftops, as well as fuel for the Greek Fire, but it was not used for road paving until the half of the nineteen century.

Asphalt pavements started to be developed in France in the late 1830s, when natural deposit (pitch lakes and bituminous rocks) were found, and then the technique spread in the U.K. (1830s) and in the U.S.A. (1870s). However, only after the First World War asphalt concrete widespread worldwide and, as a consequence, bitumen started to be produced out of crude oil. Nowadays almost all of the bitumen used in the world is petroleum-derived.

1.1.2 MANIFACTURE

Crude oil is a mixture of hydrocarbons differing in molecular weight and in chain length: Alkanes or Paraffins (open chins of saturated hydrocarbons); Naphthenes (cyclic chain of saturated hydrocarbons); Aromatics (hydrocarbon with alternating double and single bonds between carbon atoms forming rings); Asphaltenes (complex mixtures containing hundreds or even thousands of atoms).

To extract the bitumen (and all the others petroleum-derived materials) out of the crude oil the latter is fractional distilled in tall steel towers known as distillation columns (Read, et al., 2003). The heavy hydrocarbons composing the bitumen flow out of the bottom on the column and, after other refining processes, over 20 different grades of bitumen can be obtained. The physical properties can be modified by changing temperature and pressure in the vacuum tower, as well as through other processes like air blowing.

After the production, bitumen can be stored in tanks and delivered at elevated temperatures, provided that it is handled properly and oxidizing conditions are avoided.

1.1.3 STRUCTURE AND CONSTITUTION

Bitumen is a *colloidal system consisting of high molecular weight asphaltene micelles dispersed or dissolved in lower molecular weight oily medium (martens)* (Read, et al., 2003). The colloidal nature is responsible for the time dependence of the deformations of this material.

Depending on the amount of resins and aromatics, the bitumen can have a SOL or a GEL structure (Figure 1). The first structure allows the bitumen to behave like a Newtonian fluid at high temperatures and as a viscous solid at low temperatures. On the contrary, the latter type of bitumen behaves like a non-Newtonian flow at high temperatures and as an elastic solid at low temperatures.

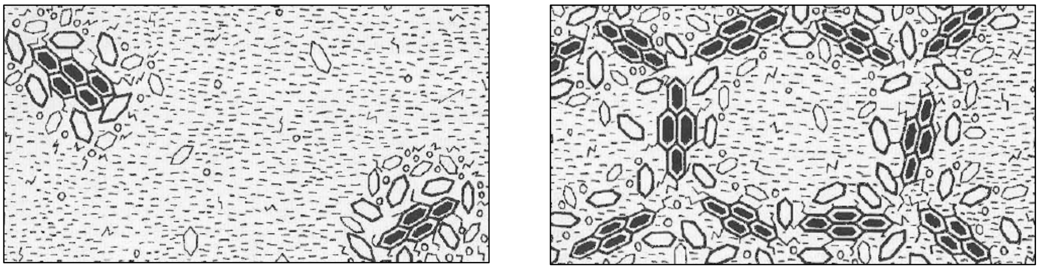

Figure 1: SOL (left) and GEL (right) type bitumen (Read, et al., 2003)

Most of the bitumen actually has an intermediate structure and their rheological properties are largely dependent on the asphaltenes concentration.

The bitumen behaviour is influenced also by the amount of saturated oils, because they enhance the solubility of the asphaltenes in the martens and help the flocculation of the formers.

From a chemical point of view, the bitumen is constituted by the following fractions:

element	percentage on the total weight
carbon	82-88%
hydrogen	8-14%
sulphur	0-8%
oxygen	0-2%
nitrogen	0-1.5%

The actual composition of the single binder depends on the source of the crude oil and on the production process.

A complete chemical description of this material is almost impossible, due to its complexity. Moreover, this complexity would make it impossible to correlate chemical aspects with rheological ones. Therefore, only a broad separation of the fractions is usually done and four of them are identified:

1. *Asphaltenes:* highly polar and complex aromatic materials of high molecular weight (600 to 300000mol, depending on the separation technique), constituting 5% to 25% in weight of the bitumen. These black or brown amorphous solids are insoluble in *n*-heptane and, apart from carbon and hydrogen, they can contain nitrogen, sulphur and oxygen. The higher the asphaltenes content, the higher are softening point and viscosity and the lower the penetration index.
2. *Aromatic martens:* non-polar carbon chains of low molecular weight (300 to 2000mol), constituting 40% to 65`% in weight of the bitumen. They are dark brown viscous liquids, with high dissolving ability for high weight hydrocarbons.
3. *Saturate maltens:* non-polar chains of aliphatic hydrocarbons, alkyl-naphthenes and alkyl-aromatics, with low molecular weight (300 to 2000mol). They are viscous oil with white colour and they form 5% to 20% in weight of the bitumen. Most of the paraffin wax in the bitumen belongs to these compounds, which give elasticity to the bitumen.
4. *Resins:* solid or semi-solid polar materials, with strong adhesive properties and medium molecular weight (500 to 50000mol). They are dark brown particles, soluble in *n*-heptane and with a chemical composition much alike the asphaltenes' one. They are dispersing or peptisers agents for the asphaltenes, governing the type character of the bitumen (SOL or GEL).

1.2 AGING

Exposition to oxygen, UV radiation and temperature changes affects the bitumen greatly, causing it to oxidise and lose volatile components. This process is named *aging* and it causes an alteration of chemical, physical and rheological properties, thus affecting the lifetime of the bitumen and of the asphalt: when aged, the binder is stiffer, but more fragile and keen to cracking and ravelling.

Two aging mechanism can be identified:

- *Irreversible aging:* it is the main responsible for the aging and it is due to changes in the chemical properties of the bitumen. The main causes of this process are: oxidation, loss of volatile components and exudation of the oils into the aggregates. As a result, polar molecules with high weight are produced out of non-polar lighter ones.
- *Reversible aging:* known also as physical hardening, it is due to the rearrangement of the molecular structure into the optimum state. If reheated, the bitumen can recover the original viscosity.

Aging occurs during the whole lifetime of the pavement, but begins before the construction progress: in fact, the first aging step occurs during the mixing (Figure 2).

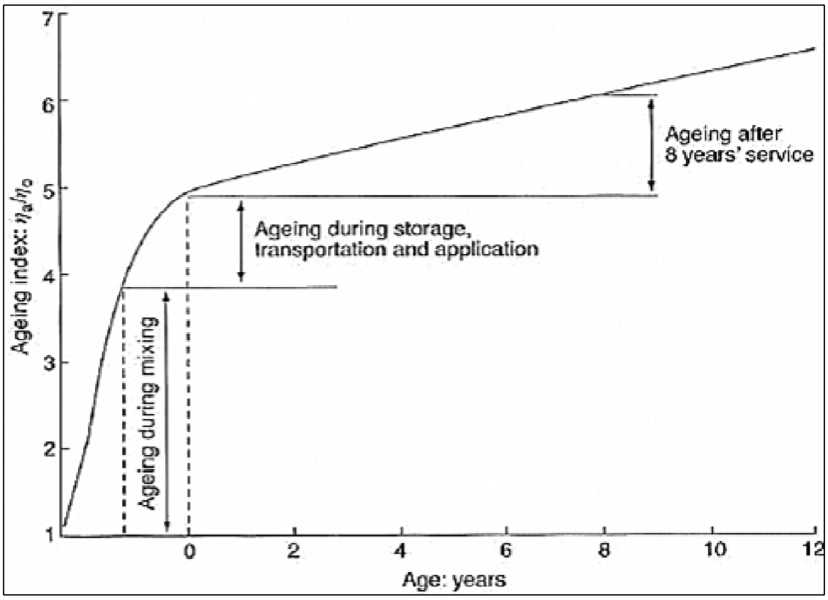

Figure 2: aging process (aging index is a ratio of two values)
(Read, et al., 2003)

The first phase is faster and, thanks to the high temperature of the process involved, it leads to chemical changes in the bitumen. The mix with aggregates, in fact, occurs at high temperatures, where the oxidation and loss of volatiles are enhanced.

The second phase, on the contrary, is slow and does not affect greatly the chemical composition. Only the surface layer is seriously damaged, because directly exposed to oxygen, radiations and chemical agents. As for the deeper layers, the magnitude of long term aging is mainly related with the porosity of the asphalt and its void content.

1.2.1 LABORATORY AGING

To simulate the field aging a number of tests have been studied. The aging speed is enhanced increasing the temperature, decreasing the bitumen film thickness and increasing the oxygen pressure(Lu, et al., 2002).

The tests can be broadly classified as tests over the bitumen and tests over the asphalt mixture. In this study only two tests of the first kind have been used and, thus, will be described.

1.2.1.1 ROLLING THIN FILM OVEN TEST (RTFOT)

This test is used to simulate the short-term aging. It “was developed by the California Division of Highways and involves rotating eight glass bottles each containing 35g of bitumen in a vertically rotating shelf (15 rev/min), while blowing hot air (4000ml/min) into each sample bottle at its lowest travel position. During the test, the bitumen flows continuously around the inner surface of each container in relatively thin films of 1.25 mm at a temperature of 163°C for 75 min. ” (Airey, 2003).

During the process the high temperatures combined with the forced oxygen flows cause the oxidation of the bitumen and the loss of volatile components. The latter can be quantified by weighting the material before and after the RTFOT, while the first one can be revealed by the rheological, physical and/or chemical tests.

The conditions simulated by this test are not the same of the practical ones, but can be reasonably well correlated.

1.2.1.2 PRESSURE AGING VESSEL (PAV)

This test is used to simulate the long-term aging and usually is performed after the RTFOT: 50g of binder aged with the RTFOT are poured in a 140 mm diameter pan (≅3.2 mm binder film); the pan is then placed in a heated vessel, pressurized with air to 2.10 MPa for 20 h at 100°C. Thanks to the not very high temperature and the high pressure, the conditions that this test simulates are comparable to 5-10 years of field aging. After the PAV, the material can be tested for rheological, chemical and physical properties.

CHAPTER 2: RHEOLOGICAL CHARACTERIZATION OF BITUMINOUS BINDERS

2.1 INTRODUCTION

Since the late eighties, empirical tests over the binders’ properties have proved to be unable to completely characterize the bitumen behaviour. In fact, these tests focus more on some mechanical performances then on rational (and correlated to real life) parameters and they are not sufficient to characterize modified binders or non-conventional asphalts. Thus, the need for a better description and for pavement’s life forecasts has led to the implementation of a new set of tests, which outputs are fundamental rheological parameters.

Rheology is the *science of deformation and flow of matter* (Barnes, et al., 1989), a discipline that studies the stress-strain interaction in the materials and it allows to forecasts its behaviour under well-defined conditions. Together with chemical inquiries and large-scale tests, the study of bitumen rheology is central in the project of long-life pavements.

2.2 RHEOLOGY

Bitumen is a viscous elastic material, owning both “solid” (elastic) and “liquid” (viscos) properties.

The elastic materials, when stressed, suffer some deformation but, in the process, they develop some potential energy which allows them, when the stress is taken off, to gain back the original shape . On the contrary, liquid materials own no shape and their deformation is completely irreversible.

As said, bitumen owns both natures and the predominance of one over the other is temperature dependent: at high temperature the bitumen reacts like a liquid, allowing to be poured and mixed whit aggregates, while at low temperature it stiffens to a solid, bounding the aggregates together to the asphalt.

The following paragraphs describe the rheological laws of ideal solid, ideal liquid materials and of their ideal combinations. The basic hypothesis behind these laws is that the material is continuous, homogenous and isotropic.

2.2.1 IDEAL ELASTIC SOLID

The behaviour of on elastic matter was described for the first time by Robert Hooke: *Ut tension, sic vis*[1] (As the extension, so the force). This law, nowadays know as Hooke law of elasticity, is manly used for describing the spring behaviour and can be represented by the following equation:

$$F = k \cdot x \qquad (1)$$

where: F = force

k = stiffness constant

x = extension

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[1] Hooke, Robert. *Lectures de Potentia Restitutiva, or of spring explaining the power of springing bodies*. John Martyn, 1931.

For common application in civil engineering, this law has been modified to the following one, where the main parameters are stress and strain:

$$\sigma = \varepsilon \cdot E \tag{2}$$

where: E = Young tensile modulus [N/mm2]

ε = tensile strain

σ = tensile stress

Meanwhile, elastic solids follow another law, known as Poisson effect[2]:

$$\frac{d\varepsilon_{transverse}}{d\varepsilon_{axial}} = \nu \tag{3}$$

where: ν = Poisson ratio

$d\varepsilon_{transverse}$ = transverse strain

$d\varepsilon_{axial}$ = axial stress

Eventually, joining model (2) and (3), for homogenous and isotropic materials the following equations can be written:

$$\begin{gathered}
\varepsilon_x = \frac{1}{E}[\sigma_x - \nu(\sigma_y + \sigma_z)] \\
\varepsilon_y = \frac{1}{E}[\sigma_y - \nu(\sigma_x + \sigma_z)] \\
\varepsilon_z = \frac{1}{E}[\sigma_z - \nu(\sigma_x + \sigma_z)] \\
\gamma_{xy} = \frac{\tau_{xy}}{G} \\
\gamma_{xz} = \frac{\tau_{xz}}{G} \\
\gamma_{yz} = \frac{\tau_{yz}}{G}
\end{gathered} \tag{4}$$

where: $G = \frac{E}{2(1+\nu)}$

In these solids, when the force is removed, the strain is completely recovered.

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[2] When a material is compressed in one direction, it usually tends to expand in the other two directions perpendicular to the direction of compression (Wiki)

2.2.2 IDEAL VISCOUS LIQUID

The viscosity of a fluid represents its attitude to dissipate energy when a force is applied to it. This dissipation is caused by friction between parcels that are moving at different velocities in different layer of the flow. Due to the energy dissipation, the strain can not be recovered when the force that caused it is removed.

The shear-driven flow is often illustrated by the Couette flow (Figure 3) and described by the differential Newton law:

$$\tau = \eta \cdot \dot{\gamma} \tag{5}$$

where: τ = shear stress

η = dynamic viscosity [Pa · s]

$\dot{\gamma}$ = shear rate (the speed of the strain)

When to a viscous flow a normal stress is applied the Newton law becomes:

$$\sigma = \eta_e \cdot \dot{\varepsilon} \tag{6}$$

where: σ = normal stress

η_e = extensional viscosity [Pa · s]

$\dot{\varepsilon}$ = strain rate (the speed of the strain)

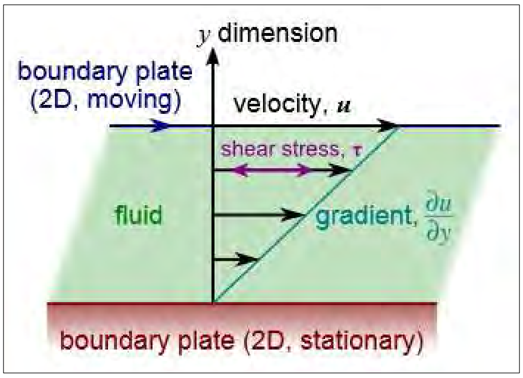

Figure 3: Couette configuration using two infinite flat plates (Wiki)

In a pure viscous fluid (also known as Newtonian fluid) the magnitude of η is strain-independent and this parameter is the slope of the flow curve in the τ- η plane. While this is the ideal fluid behaviour, there are many non-Newtonian fluids:

- Bingham plastics (viscoplastic): material that behaves as a rigid body at low stresses but flows as a viscous fluid at high stress

- Shear thickening (dilatant): the viscosity increases with the shear rate
- Shear thinning (pseudoplastic): the fluid viscosity decrease as the shear rate rises

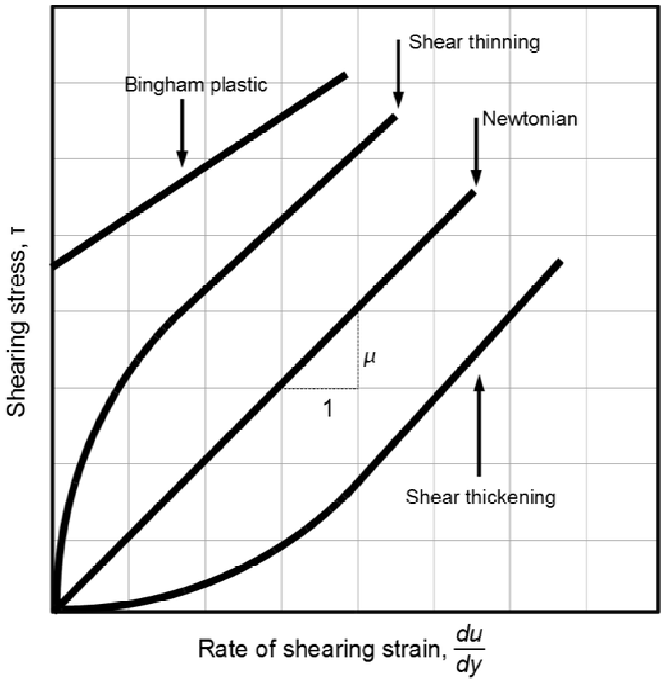

Figure 4: viscosity in different materials (Wiki)

2.2.3 VISCO-ELASTIC MATERIALS

In these materials the stress depends both on the strain and on the strain rate, thus combining the viscose and the elastic properties. When, in addition, both the modulus and the viscosity are independent from the stress application conditions, the material are labelled as *linear viscoelastic*[3].

The viscoelastic behaviour can be described through many different models, made up from basic mechanical elements like dampers and springs. The two main models are the Maxwell and the Kelvin-Voigt ones: the first one describes the *delayed elasticity* with unrecoverable strains, while the second one describes the *creep* with asymptotic recovery of the strain. The bitumen behaviour can be described superposing these two basic models.

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[3] § 2.4

2.2.3.1 *MAXWELL MODEL*

Maxwell has modelled the viscoelastic behaviour as a connection in series of purely viscose dumper and of a purely elastic spring (Figure 5).

The differential equation that represents the model is:

$$\left(\frac{d\gamma}{dt}\right)_{tot} = \frac{1}{G}\frac{d\tau}{dt} + \frac{\tau}{\eta} \qquad (7)$$

where: $\frac{1}{G}\frac{d\tau}{dt}$ = spring component

$\frac{\tau}{\eta}$ = dumper component

The spring component reacts as soon as the stress is applied and relaxes immediately when the stress is removed. On the other hand, the dumper component grows exponentially during the application of the stress and it exponentially relaxes as the stress is taken back.

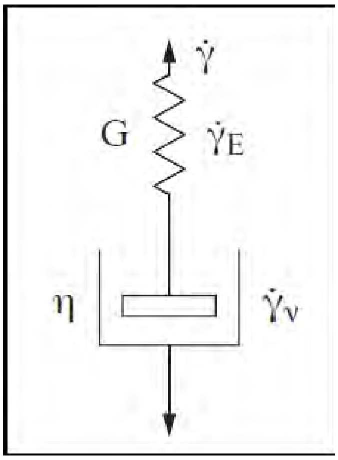

Figure 5: Maxwell model

This model allows predicting the results of a stress relaxation test[4], while it cannot predict accurately the creep[5] results.

2.2.3.2 *KELVIN-VOIGT MODEL*

This model consists of a purely viscose dumper and of a purely elastic spring connected in parallel (Figure 6).

The differential equation that represents the model is:

$$\tau = \gamma \cdot G + \eta\frac{d\gamma}{dt} \qquad (8)$$

where: $\gamma \cdot G$ = stress on the spring

$\eta\frac{d\gamma}{dt}$ = stress on the dumper

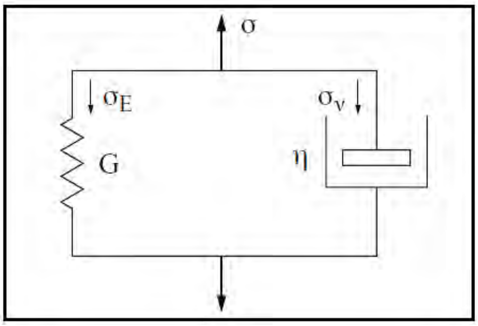

Figure 6: Kevin-Voigt model

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[4] A sudden strain is applied and kept still for the whole test. As a result, the stress will decay.

[5] A sudden stress is applied and kept still for the whole test. As a result, the strain will increase and, at the end, there will be some non-reversible deformations.

Through this model a viscoelastic strain affecting a solid can be represented. When the constant stress is applied, the material deforms at a decreasing rate, asymptotically approaching the steady-state strain. When the stress is released, the material gradually relaxes to its previous shape.

This model allows predicting the results of a creep test, while it can not predict accurately the stress relaxation results

In the following table (Table 1) are shown the viscoelastic functions for both models

	Maxwell	Kevin-Voigt
$J(t) = \frac{1}{G(t)}$	$J_i + \frac{t}{\eta_i}$	$J_i \cdot \left[1 - \mathrm{e}^{-\frac{\mathrm{t}}{\lambda_\mathrm{i}}}\right]$
$G(t)$	$G_i \cdot \left[1 - \mathrm{e}^{-\frac{\mathrm{t}}{\lambda_\mathrm{i}}}\right]$	G_i
$G'(\omega)$	$\frac{G_i \cdot \omega^2 \lambda_i^2}{1 + \omega^2 \lambda_i^2}$	G_i
$G''(\omega)$	$\frac{G_i \cdot \omega \lambda_i}{1 + \omega^2 \lambda_i^2}$	$\omega \cdot \eta_i$
$J'(\omega)$	J_i	$\frac{J_i}{1 + \omega^2 \lambda_i^2}$
$J''(\omega)$	$\frac{1}{\omega \eta_i}$	$\frac{J_i \cdot \omega \lambda_i}{1 + \omega^2 \lambda_i^2}$

Table 1: Maxwell & Kevin-Voigt equations

where: $\lambda_i = \frac{\eta_i}{G_i}$

2.2.3.3 *GENERALIZED MODELS*

Describing real life materials needs more complex rheological models than the ones previously seen. However, as it has already been stated, the basic elements are always springs and dumpers somehow connected. The main generalized models are the extension of Maxwell’s and Kelvin-Voigt’s.

The first one is used when strain cannot be described as the combination of a single strain and of a single dumper. The model, therefore, is made of many simple Maxwell elements, assembled in parallel (Figure 7).

The second one, on the other hand, describes a material in which relaxation occurs at a distribution of times. It is made of several Kelvin-Voigt elements, connected in series (Figure 8).

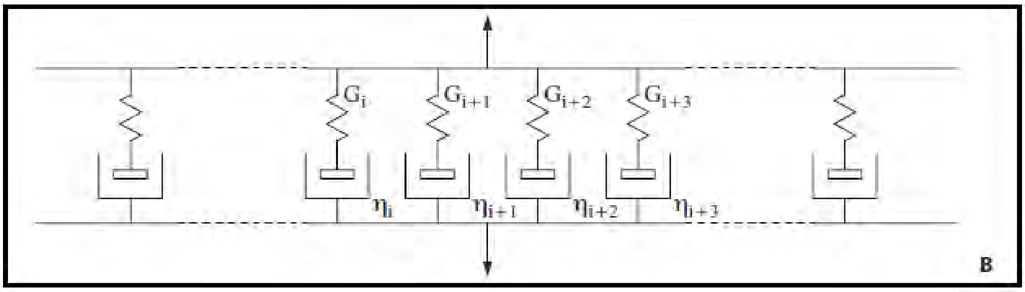

Figure 7: generalized Maxwell model (Mazzotta, 2011/2012)

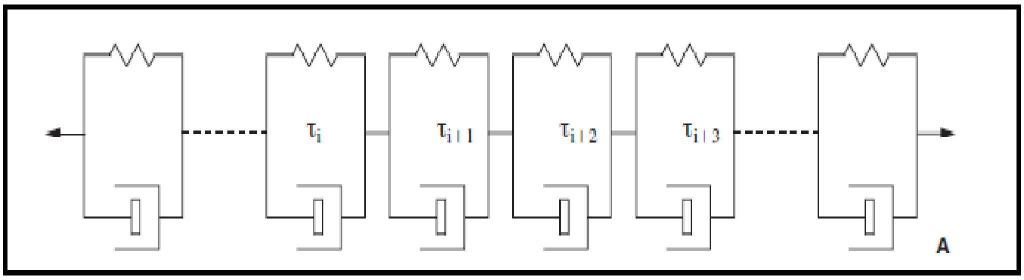

Figure 8: generalized Kelvin-Voigt model (Mazzotta, 2011/2012)

2.3 DYNAMIC ANALYSIS

Rheological properties of a bitumen system are determined by measuring its viscosity at different rates of shear for a given temperature, shear stress and time (Loeber, et al., 1998). The measures can be done with stead-state tests or with dynamic tests.

While creep and relaxation tests are convenient for studying the material response for a long time load, the *short time* response can be evaluated only through dynamic tests, in which the stress (or strain) resulting from a sinusoidal strain (or stress) is measured. These tests can provide the Master Curve of a material in a wide range of frequencies (10^{-9} – 10^{9}) and in a relatively short time (at most a couple of hours).

2.3.1 RHEOLOGICAL PARAMETERS

When a viscoelastic material is subjected to a sinusoidal varying stress, a state will eventually be reached in which the resulting strain is also sinusoidal, having the same angular frequency but retarded in phase by an angle δ (Roylance, 2001), known as *phase angle*. This is true even when the strain is the controlled variable. By knowing the value of the phase angle, the rheology of a material can be easily defined (Figure 9):

- in-phase ( ): ideal elastic materials;
- out-of-phase ( ): viscous liquids;
- : viscoelastic materials.

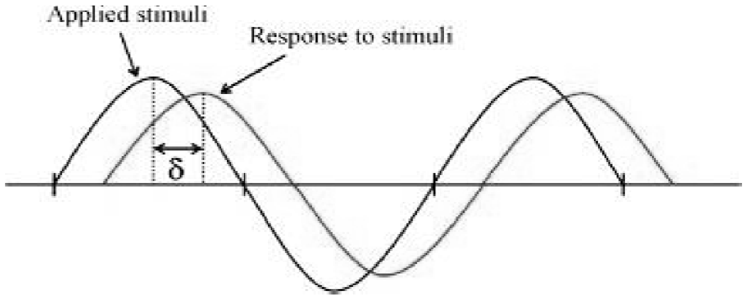

Figure 9: schematic representation of viscoelasticity

Selecting the origin along the time axis to coincide with a time at which the strain has its maximum, the strain and stress functions can be written as:

(9)

where: ,

= maximum stress, = maximum strain

= phase angle, = frequency

Once the parameters above are known, it is possible to define the absolute value of the *complex modulus*:

– (10)

This modulus is defined as complex because it can be represented properly in the complex plane (Figure 10): using an algebraic manoeuvre common in the analysis of reactive electrical circuits and other harmonic systems, it is convenient to write as a complex quantity whose real part is in phase with the strain and whose imaginary part is 90° out of phase with it:

(11)

where: is the *storage modulus*

is the *loss modulus*[6]

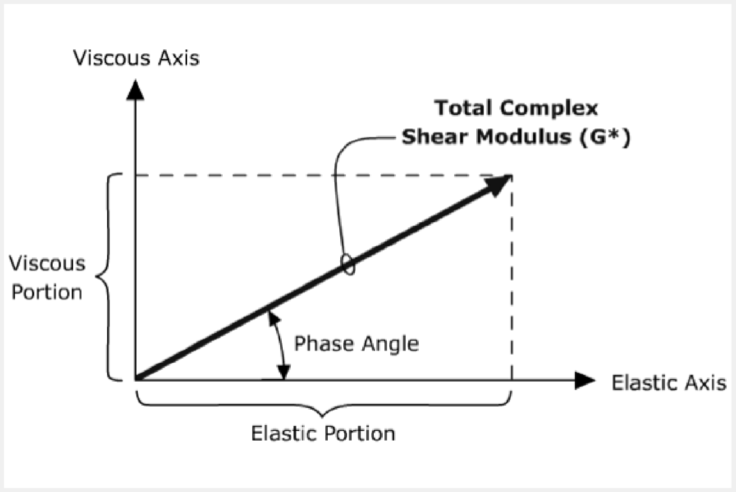

Figure 10: G* in the complex plane (Interactive, 2011)

Similarly, the *complex compliance* (mutual of the complex modulus) can be defined as:

—

(12)

However, while G* and J* are mutual, this is not true for their real and imaginary part.
From the equations above, the following one can be deducted:

(13)

Moduli and phase angle are frequency dependent, although the explicit dependence has been omitted in this paragraph, for the sake of simplicity.

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[6] "These terms are sometimes misinterpreted as the elastic and viscous moduli; in reality, the elastic component of the response only represents part of the storage modulus, and the viscous response only part of the loss modulus. In addition to the elastic and viscous response, most real viscoelastic materials exhibit a significant amount of delayed elastic response that is time-dependent but completely recoverable. In interpreting the storage and loss moduli, it should be kept in mind that both these parameters reflect a portion of the delayed elastic response" (Anderson, et al., 1994)

2.3.2 TIME-TEMPERATURE SUPERPOSITION

Temperature has a dramatic influence on rates of viscoelastic response, and in practical work it is often necessary to adjust a viscoelastic analysis for varying temperature. Time-temperature superposition (TTS, also known as method of reduced variables) is a procedure frequently applied:

- To determine the temperature dependence of the rheological behaviour of a viscoelastic material
- To expand the time or frequency regime at a given temperature at which the material behaviour is studied

This is due to the fact that the various relaxation times belonging to a given relaxation process have the same temperature dependence: the effect of lowering the temperature is simply to shift the viscoelastic response (plotted against log time) to the right without change in shape (Roylance, 2001) & (Van Gurp, et al., 1998).

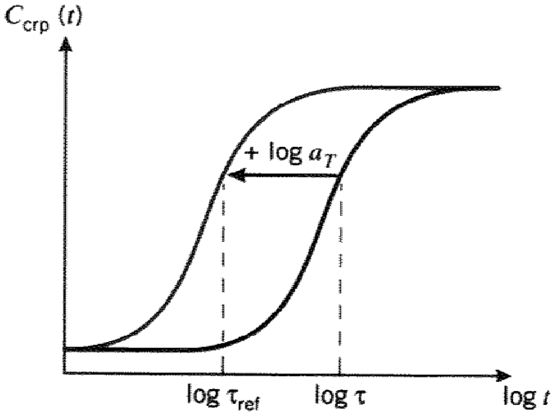


Figure 11: T.T.S. shifting factor

A reference temperature T_{REF} being given, the *time-temperature shift factor* is defined as the horizontal shift that must be applied to a response curve (C_{RESP}), measured at an arbitrary temperature T, in order to move it to the curve measured at T_{REF} (Figure 11).

It is theoretically assumed that the same shift factor can be applied to every viscoelastic property.

Some popular models for are the following ones:

- Arrhenius (mainly used for the glassy range of temperatures):

$$\log a_T = \frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{T_{REF}}\right) \qquad (14)$$

where: E_A = activation energy

R = gas constant

- Williams-Landel-Ferry (for temperatures near or above the glass temperature)

$$\log a_T = -\frac{C_1(T-T_0)}{C_2+T-T_0} \qquad (15)$$

where C_1 and C_2 are positive constants that depend on material and reference temperature

The theoretical aspects of this phenomenon has been firs investigated by Prince E. Rouse in his *A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers* (published in 1953); there, he described the viscose material as a system made of beads connected by polymeric harmonic springs, in which each bead suffers from random thermal forces and drag forces.

However, while for the simpler material only the horizontal shift factor a_T is needed, for more complex ones another factor must be evaluated: the *vertical shift factor* b_T. This depends mainly on the high density variations that occur to some materials while the temperature changes, but also on other hardly identifiable parameters. For this reason, b_T has not been properly modelled yet, and it is often neglected in the bitumen study.

2.3.3 THE MASTER CURVE

A series of creep or relaxation data taken over a range of temperatures can be converted to a single *master curve* via this horizontal shifting. The curve usually represents the trend of a viscoelastic variable, plotted against time or frequency.

Thanks to the TTS principle, the master curve at a reference temperature can represent a range of frequency (or application time) wider than the experimental one.

When the data are gained by sinusoidal oscillatory analysis, the master curve can be evaluated through the *reduced frequency*:

$$\overline{\omega}(T_r) = a_T \cdot \omega(T) \qquad (16)$$

Along with the master curve, the a_T vs. temperature behaviour is plotted, in log scale.

The mostly used master curve is the one where complex shear modulus $G^*(\omega)$ and the phase angle δ are plotted against frequency on a log-log scale. The behaviour of this curve is material-dependent, but can always be described by some parameters:

- *Glassy modulus (G_g):* at low temperatures and high frequencies entropic motions are frozen and only elastic bond deformations are possible. It is a relatively high modulus on the order of 1 GPa.
- *Steady-state viscosity (η_0):* at high temperatures and low frequencies the stiffness decreases of two orders of magnitude. Where the rubbery state is reached, the *zero-shear rate viscosity* (value of apparent viscosity in resting fluid) can be evaluated as $\eta_{ss} = \lim_{\omega\to 0}\frac{G^*}{\omega}$ and, for very low frequencies, $\eta_0 = \eta_{ss}$.
- *Crossover frequency (ω_c) and crossover time (t_c):* the frequency, at a given temperature, where $\tan\delta = 1$. At this point, the storage and loss moduli are equal. For bitumen, the crossover frequency is nearly equal to the point at which the viscous asymptote intersects the glassy modulus. The crossover time is the reciprocal of the crossover frequency $t_c = \frac{1}{\omega_c}$.
- *Rheological index (R):* the difference between the glassy modulus and the dynamic complex modulus at the crossover frequency, $R = G_g - G^*(\omega_c)$. The rheological index is directly proportional to the width of the relaxation spectrum and is a measure of the shear-rate dependency of bitumen.

The parameters for the master curve, as described above, are meant to be clearly definable characteristic parameters, as opposed to statistically determined parameters that may or may not truly reflect the mechanical properties of bitumen (Anderson, et al., 1994).

2.4 LINEAR VISCOELASTIC CONDITIONS IN BITUMEN

The viscoelastic parameters seen can be defined properly only in the linear-viscoelastic region of response, where the stress-strain relationship is not influenced by the magnitude of one of them (Airey, et al., 2004). Thus, the first investigation over a material must be the linearity test, performed through stress/strain sweep tests using a Dynamic Shear Rheometer (DSR).

The linearity of bitumen has already been investigated and modelled by various researchers. The main work in literature is the study published in 1994 by the Strategic Highway Research Program, which will be summarized in the following paragraph.

The complex mechanical behaviour of viscoelastic materials such as asphalt cement is a result of the interaction of both time and temperature dependence. In the mathematical modelling of the LVE behaviour of bitumen, these effects must be treated separately. Time dependency is reflected in the location (t_c or ω_c) and shape (R) of the master curve; temperature dependency is indicated by the plot of $\log a(T)$ vs. temperature.

2.4.1 S.H.R.P. MODEL

The linear strain limit is *arbitrarily established as the strain at which the storage modulus decreases at the 95% of its maximum value* (Anderson, et al., 1994). It has been seen that the LVE (Linear Viscoelastic) limit increases with temperature.

So, for the region within the previous limit, it was found that the following series of equations can well approximate the empirical master curves.

$$G^*(\omega) = G_g \left[1 + \left(\frac{\omega_c}{\omega}\right)^{log2/R}\right] - \frac{R}{log2}$$

$$\delta(\omega) = \frac{90}{1} + \left(\frac{\omega_c}{\omega}\right) log2R \qquad (17)$$

$$R = \log 2 \cdot \frac{\log\left(\frac{G^*(\omega)}{G_g}\right)}{\log\left(1 - \frac{\delta}{90}\right)}$$

where: $G^*(\omega)$ = complex modulus [Pa]

$\delta(\omega)$ = phase angle

ω = given frequency [rad/s]

G_g = glassy modulus (usual 1GPa[7])

ω_c = crossover frequency [rad/s]

R = rheological index

The equations (17) can be manipulated to get the shear stress and strain LVE limits as a function of the complex modulus (Airey, et al., 2004):

$$\gamma_{LVE} = \frac{12.0}{G^{*0.29}}$$
$$\tau_{LVE} = 0.12G^{*0.71} \qquad (18)$$

where: γ_{LVE} = shear strain at the limit of the LVE

τ_{LVE} = shear stress at the limit of the LVE

$G^*(\omega)$ = complex modulus [Pa]

2.4.2 EUROPEAN STANDARD

In 2012 the European Committee for standardization published the latest norm about the Dynamic Shear Rheometer: *EN 14770, Bitumen and bituminous binders - Determination of complex shear modulus and phase angle - Dynamic Shear Rheometer (DSR).*

In the Annex C the procedure for the determination of the viscoelastic linear range is carried out (CEN, 2012):

- The determination of the linear region should be done for each selected geometry
- For a given geometry, determination of the linear region on the all selected temperature ranges shall consist, at least, of carrying out:
- strain (or stress) sweep at the lowest temperature and at the highest frequency
- strain (or stress) sweep at the highest temperature and at the lowest frequency
  in order to select the adequate strain level.

---

[7] (Anderson, et al., 1994)

- To remain in the linear range, the value of G’ and G’’ must not differ by more than 5 % of the initial value over the stress or strain range chosen. The initial value can be taken as the intercept of a regression line fitted to the first measured values.

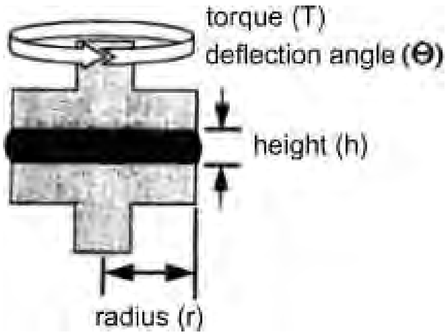
2.4.3 ASTM STANDARD

In the Annex X1 of the D7175–08 norm (ASTM, 2008) is provided the test method for proving the linearity of a binder through the DRS tests. The determination is based on the change in complex shear modulus at 10 rad/s when the strain is increased from 2% to 12%.

To define the linear region the test is carried on by producing a strain sweep at constant frequency (10 rad/s, which is assumed to be the frequency of a normal street). Then, the *modulus ratio* is calculated as the complex shear modulus at 12% strain divided by the complex shear modulus at 2% strain.

According to this norm, the measurement was performed in the non-linear range of the material if the modulus ratio is < 0.900 and linear if is > 0.900.

2.5 DYNAMIC SHEAR RHEOMETER TESTS



The aim of this dynamic test is to evaluate the complex modulus and the phase angle of the tested bitumen. It is performed by rotating the upper plate in an alternating clockwise and counter-clockwise position (oscillating).

If the bitumen test specimen is seen as a series of circular layers, rotating one with respect to another. The shear strain is defined as the distance the point rotates divided by the specimen thickness. Therefore, the shear strain is zero at the centre and it increases to the maximum at the outer edge of the specimen, where, also, most of the shear resistance is developed.

The complex modulus G* is evaluated by a set of equation whose main assumption is the linearity of the material. If the modulus varies with the magnitude of the shear strain, the previous assumption is not valid and the measured modulus could be in error. Given that, the test must be applied only to the LVE region, which can be estimated by testing a sample in a wide range of strains. Once obtained the whole G*/strain curve, the linear region can be easily identified as the one in which the value of G* is constant.

The load (being it strain or stress controlled) can be applied mainly in four different ways:

1. Repeated loading from zero to the peak and back to zero, with the load changing at a linear rate.
2. Step load: sudden application of a load, which is held constant for a finite period of time (creep test).
3. Repeated creep: repeated application of a step load with the load always applied so that the upper plate moves in one direction when loaded.
4. Sinusoidal loading pattern: repeated application of a sinusoidal load that causes the plate to move back and forth about the zero position.

This last method is used to evaluate modulus and phase angle in the DSR test, whether stress or strain controlled. The curve of strain and the one of stress are not synchronized with each other, the first one lagging behind the second. This lag is also known as *phase angle* and it express the attitude of the material to recover deformation: a low value (gained at low temperature or at high frequencies) represents a very elastic behaviour, while a value of about 90° represents a completely viscose behaviour without recovery of the strain.

2.5.1 SAMPLING AND TESTING PROCEDURE

The following tests have been executed according to the E.U. standards EN14770:2012 and EN 12594:2007. The rheometer used was *Physica MCR 301* by *Anton Paar*.

2.5.1.1 PREPARATION OF THE RHEOMETER

According to the manufacturer’s instructions, before switching on the equipment the water and the air flow must be opened up, so that they can start the temperature-control system. After the switch on of both the equipment and the software, the selected testing geometry must be mounted and the plates must be cleaned properly. Then, the *zero gap* between plates is set with both plates nominally at the same reference temperature as required for the first test temperature.

2.5.1.2 SAMPLE PREPARATION

Given the small amount of bitumen needed for the testing, it has been followed the procedure at the point 7.1.1 of the EN 12594.

The binder has been poured in a small container which has been placed in the oven for 15 to 20 minutes at a temperature related to the kind of bitumen and to its aging conditions (Table 2).

	Unaged bitumen	Aged bitumen
20/30	145°C	155°C
30/45	142°C	152°C
35/50	140°C	150°C
40/60	138°C	148°C
50/70	136°C	146°C
70/100	133°	143°C
100/150	129°C	139°C
160/220	125°C	135°C
250/330	120°C	130°C
Polymer modified	190±10°C	190±10°C

Table 2: table of the temperatures used in oven heating

Then, the container has been removed from the oven and the melted sample has been stirred, allowing air bubbles to escape and, especially for polymer modified binders, to ensure homogeneity. Afterwards the container has been placed again in the oven for some minutes (less than 5).

The shape needed for the DSR test has been gained by pouring the melted binder into silicone moulds, allowing them to be overfilled in order to prevent the volume loss due to the temperature induced shrinkage. The entire procedure (melting, homogenising and moulding) has been carried out within 30 minutes. The following minimum and maximum storage durations before the de-moulding and testing procedure have been followed:

- Minimum delay: 2 h for pure bitumen; 12 h for PmBs.
- Maximum delay: 3 days whatever the binder.

Just before the measurement, the excess of bitumen of the samples has been cut to the mould height using a hot knife. The moulds with the samples, then, have been placed in the refrigerator for 5 to 10 minutes. In the meantime, to ensure adhesion between sample and plates, the latter have been heated at 80°C to 90°C for 5 to 10 minutes. Then, the binder sample has been removed from the mould and placed to the lower plate (for the 8mm geometry) or the mould has been pushed closed to the upper plate till the sample stuck on it (for the 25mm geometry).

Immediately after mounting the test specimen, the plates have been brought to the selected testing gap plus 0.025 mm (this addition was automatically performed by the rheometer). Maintaining the bonding temperature, the excess binder has been trimmed with the aid of a hot spatula. Care has been taken so that the sample covered the whole measuring plates and that the trimming tool did not dig into the specimen between plates. Then, the plates have been brought to the exact testing gap of 1 mm (25 mm plate) or 2 mm (8 mm plate).

2.5.1.3 TESTING PROCEDURE

Before starting the test, the starting temperature has been set and held constant for 10 to 20 minutes, in order to gain a thermal equilibrium state of the sample.

The rheometer has been set to perform the tests in the oscillatory mode, to ensure dynamic response, always in the strain control mode. The parameters that have been set were: frequency (single value or sweep), strain (single value or sweep), number of registering points, temperature (single value or multiple).

2.5.1.4 CLEANING

When the test is finished, the temperature of the plates must be raised to 80°C-90°C and kept still for some minutes in order to remove the binder. Only after this heating the plates can be raised and the bitumen can be easily taken off with the aid of soft cleaning cloth or paper.

Then, the plates must be removed from the equipment and cleaned first with toluene, to dissolve bitumen, and afterward with acetone, to dissolve any residuals of the toluene.

CHAPTER 3: CHEMICAL CHARACTERIZATION OF BITUMINOUS BINDERS

3.1 INTRODUCTION

Along with the rheological characterization of the bitumen, in the past twenty years their chemical characterization has become more and more important. This is due to increasing use of polymeric additives in the binders and to the need of better understanding the aging mechanisms: with time passing by, in fact, the binders suffer from oxidation and loss of volatile components, while it has been observed a reduction of the polymers (Lu, et al., 2002).

For the purposes of this thesis, two different techniques have been used:

- Fourier Transform Infrared Spectroscopy: it combines a user-friendly approach to the test with reliable and repeatable results regarding aliphaticity, aromaticity and oxygenation rate.
- Gel Permeation Chromatography: it allows to characterize the polymers according to their molecular size and to easily estimate their aging condition.

3.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

The infrared spectroscopy is an analytic technique used in both organic and inorganic chemistry to get the infrared spectra of absorption, emission or photoconductivity.

In fact, every atom in a molecule absorbs a specific frequency that is characteristic of his structure and the frequency of the absorbed radiation is associated with a particular normal mode of motion and a particular bond type.

This kind of spectroscopy deals with the infrared region of the electromagnetic spectrum, analysing wavelengths[8] from 0,8 μm to 1000 μm (14000 to 10 cm^{-1}), and its divided in three regions:

- Near-Infrared: 14000-4000 cm^{-1}
- Mid-Infrared: 4000-400 cm^{-1}, used to study the fundamental vibrations and associated rotational-vibrational structure.
- Far-Infrared: 400-10 cm^{-1}, used for rotational spectroscopy

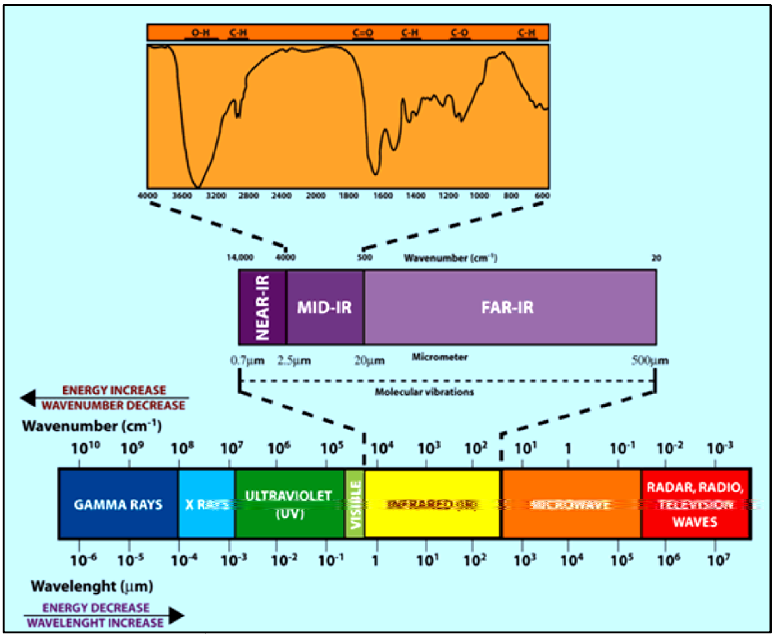


Figure 12: electromagnetic spectrum, with emphasis on the infrared region and on the mid-infrared one

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[8] Usually, instead of the wavelength the wavenumber is used. This is the mutual of the wavelength or the number of waves existing in a specified distance which, in spectroscopy is cm. Thus, the unit for the wavenumber is cm-1.

The FTIR (Fourier Transform Infra-Red) technique collects samples from the second region (with increasing interferences at the lower limit) (Figure 12). Unlikely other type of spectroscopies, the FTIR collects samples from a wide spectral range at once: the light beam contains many frequencies, but at every step it is modified to a different combination of frequency. Eventually, a computer infers the data backwards to get the absorption level for every wavenumber.

3.2.1 THE INTERFEROMETER

The combination of frequencies in the light beam is changed at every step through the use of the Michelson Interferometer (Figure 13): the beam splitter is partially reflective and divides the beam in two beams, which will be reflected by the mirrors (M1 and M2). Then both beams will recombine again on the splitter and, depending on the difference between the distances from splitter to mirrors, the interference will be constructive or destructive.

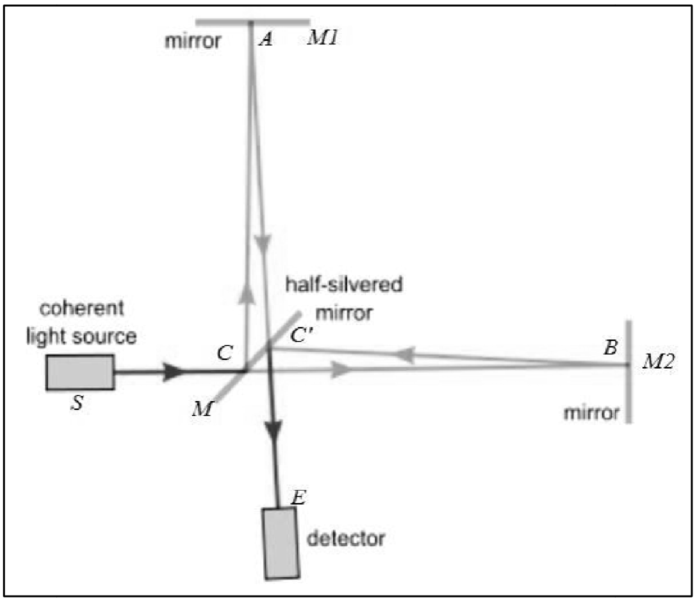

Figure 13: Michelson interferometer

The interferometer implemented in the FTIR equipment has a moving mirror, so that for its every position different frequencies are destructed in the interference. At the detector, an interferogram is generated by making measurements of the signal at many discrete positions of the moving mirror.

Then, the interferogram is converted in an actual spectrum by a Fourier Transform.

3.2.2 THE SPECTRUM EXTRACTION

The total intensity at the detector is a function of the path length difference and of the wavelength:

$$I(x) = \int_0^\infty I(x,\bar{v})\,d\bar{v} = \frac{1}{2}\int_0^\infty I(\bar{v})[1+\cos(2\pi\bar{v}x)]d\bar{v} \qquad \forall x$$

$$I(\bar{v}) = \int_0^\infty I(x,\bar{v})\,dx = 4\int_0^\infty \left[I(p) - \frac{1}{2}I\,(p=0)\right]\cos(2\pi\bar{v}x)\,dx \qquad \forall x \qquad (19)$$

where $I(x)$ = spectrum

$\bar{v}$ = wavenumber

x = path length difference

The two functions in (19) can be interconverted by using a Fourier transform

3.2.3 ATTENUATED TOTAL REFLACTANCE

In this study the Attenuated Total Reflectance (ATR) technique has been used to collect the FTIR spectra. This method allows examining a material without further preparation, simply by placing it on the ATR crystal, because it measures the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample (Figure 14).

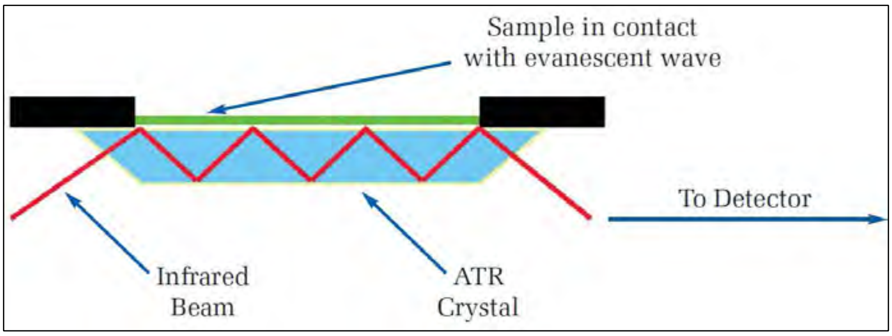

Figure 14: schematic representation of the ATR crystal

The beam of light is directed into a dense crystal (germanium, KRS-5, zinc selenide and diamond) with a reflective index higher than the one of the testing material. The internal reflectance produces an evanescent infrared wave that extends for 0.5-5 μm into the surface of the sample. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered.

3.2.4 SPECTRUM ANALYSIS

Every single organic material owns a specific spectrum, which depends on the molecular structure of the material itself. During this project work the absorbance spectrum has been used in the analysis, where absorbance (at a specific wavelength) is defined as:

$$A(\lambda) = -\log\frac{I_1}{I_0} \tag{20}$$

where I_0 = intensity of the radiation falling upon a material

I_1 = intensity of the radiation transmitted through the material

Within the mid-infrared spectrum two regions can be defined:

- *Functional groups area*: it stretches between 4000 and 1500 cm^{-1}. The functional groups are groups of atoms or bonds within molecules that are responsible for the characteristic chemical reactions of molecules of that specific group.
- *Fingerprint area*: it stretches between 1500 and 700 cm^{-1}. In this area, each different material produces a unique pattern.

Once the spectrum is given, it is compared with known spectra measured under the same conditions to uniquely identify the compound. Moreover, the peaks in the fingerprint area can be used to evaluate some indexes that should give some quantitative information about the material.

3.2.4.1 BITUMEN SPECTRUM

The bitumen absorbance spectrum is characterized by the following peaks:

- 2870 cm^{-1} and 2920 cm^{-1}: methyl and methylene bonds (C-H)
- 1709 cm^{-1}: carbonyl stretching vibration (C=O)
- 1460 cm^{-1}: asymmetric vibration of ethylene bonds (CH_2)
- 1375 cm^{-1}: bending vibration of methyl bonds (CH_3)
- 1030 cm^{-1}: sulfoxide stretching vibration (S=O)

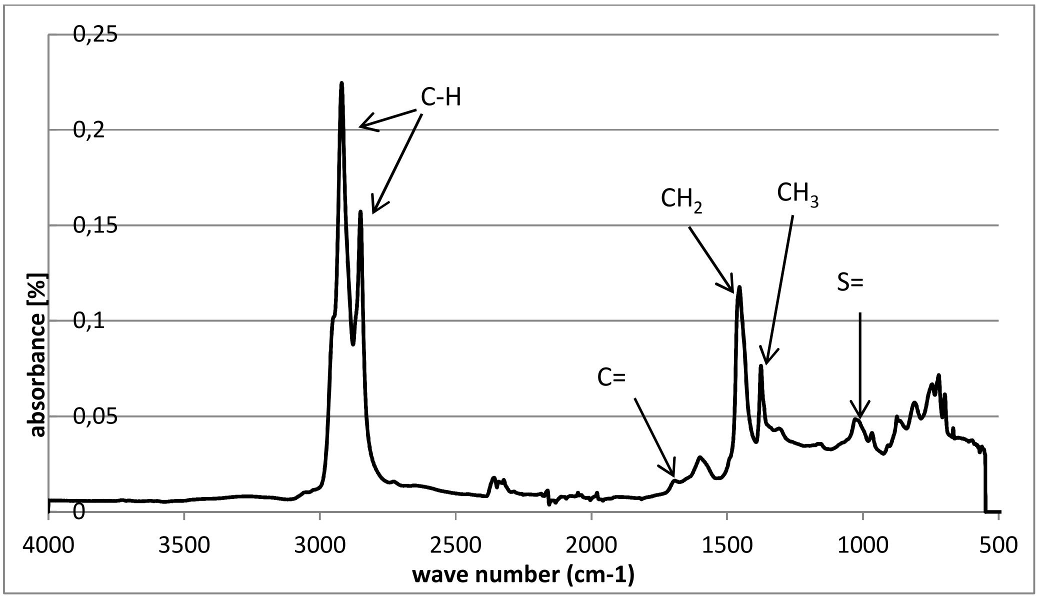

Figure 15: FTIR bitumen spectrum

3.2.4.2 INDEXES

The oxidation of the bitumen causes the formation of new C=O and S=O bonds, while no change is applied to the CH_2 and to the CH_3 peak. Hence, the Oxidation Indexes have been defined as:

$$Carbonyl\ Index\ (CI) = \frac{A_{ico}}{A_{CH_2}+A_{CH_3}}$$

$$Sulfoxide\ Index\ (SI) = \frac{A_{iso}}{A_{CH_2}+A_{CH_3}} \qquad (21)$$

where A_{ico} = area centred on the carbonyl peak

A_{iso} = area centred on the sulfoxide peak

$A_{CH_2} + A_{CH_3}$ = reference area, centred around the CH_2 ant the CH_3 peaks

As integration limits for the area calculation the valley values (deepest inflexion points) at each side of the peak has been taken (Poulikakos, et al., 2014) (Figure 16). In general, the following limits have been found:

- carbonyl area: around 1660 cm^{-1} and 1725 cm^{-1}
- sulfoxide area: around 985 cm^{-1} and 1045 cm^{-1}
- CH_2 area: around 1330 cm^{-1} and 1393 cm^{-1}
- CH_3 area: around 1393 cm^{-1} and 1513 cm^{-1}

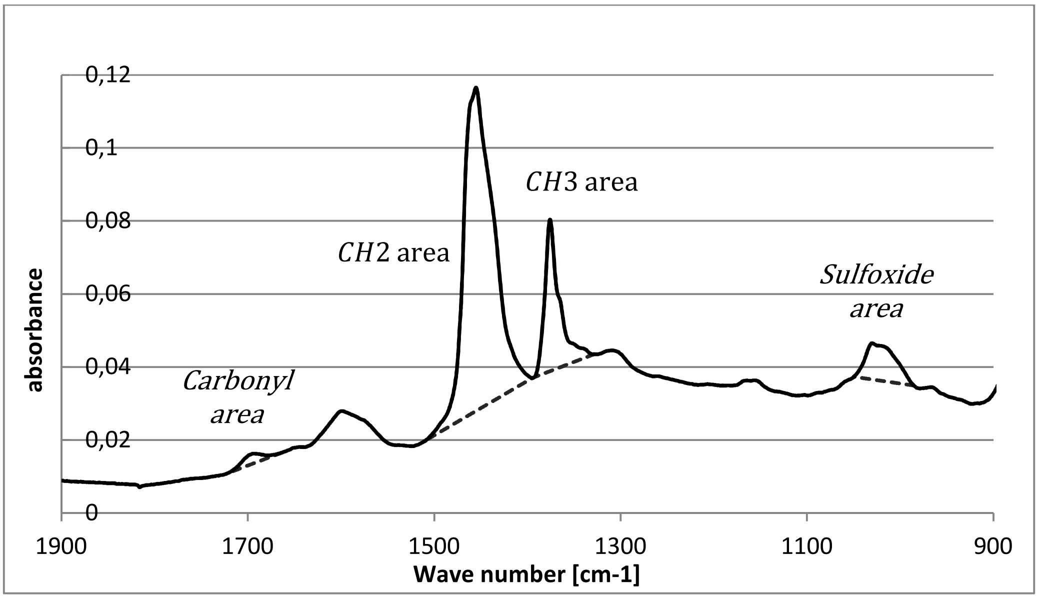

Figure 16: peaks' limits

3.2.5 SAMPLING AND TESTING PROCEDURE

3.2.5.1 PREPARATION OF THE FTIR

In this study the Nicolet iS5 FTIR with iD5 ATR from Thermo Scientific has been used (Figure 17). The equipment requires no operation but the switch on for being ready to collect the spectrum.

Once it is switched on, along with its computer software, it is necessary to collect a sample of the background (spectrum absorbed by the crystal) which will be later (and automatically) subtracted from the sample's spectra. Then, a couple of "empty" spectra should be collected, in order to check for the actual cleanliness of the crystal.

Figure 17: Nicolet iD5 and iS5

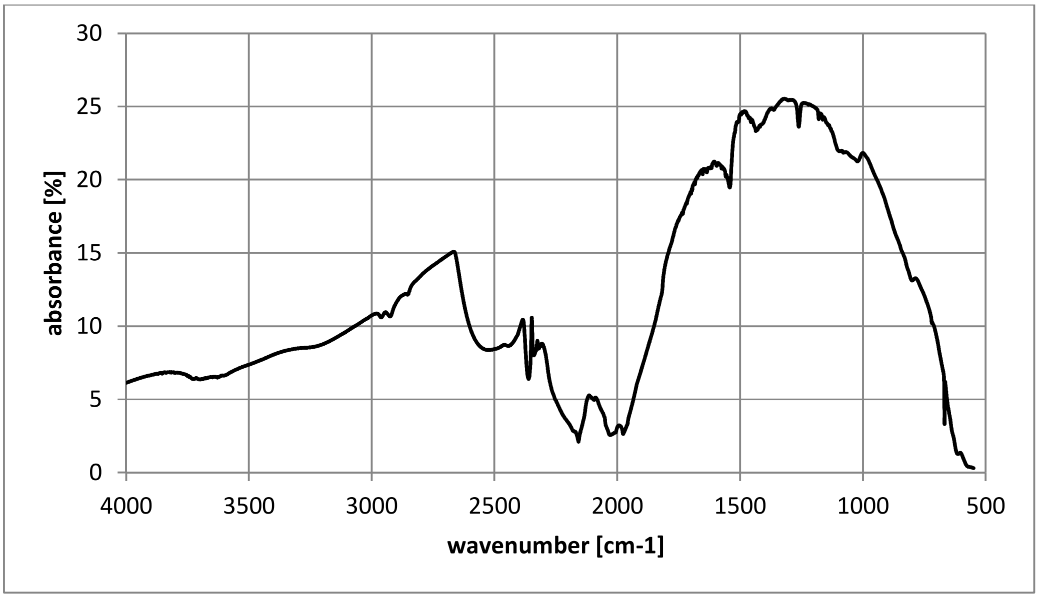

Figure 18: background spectrum

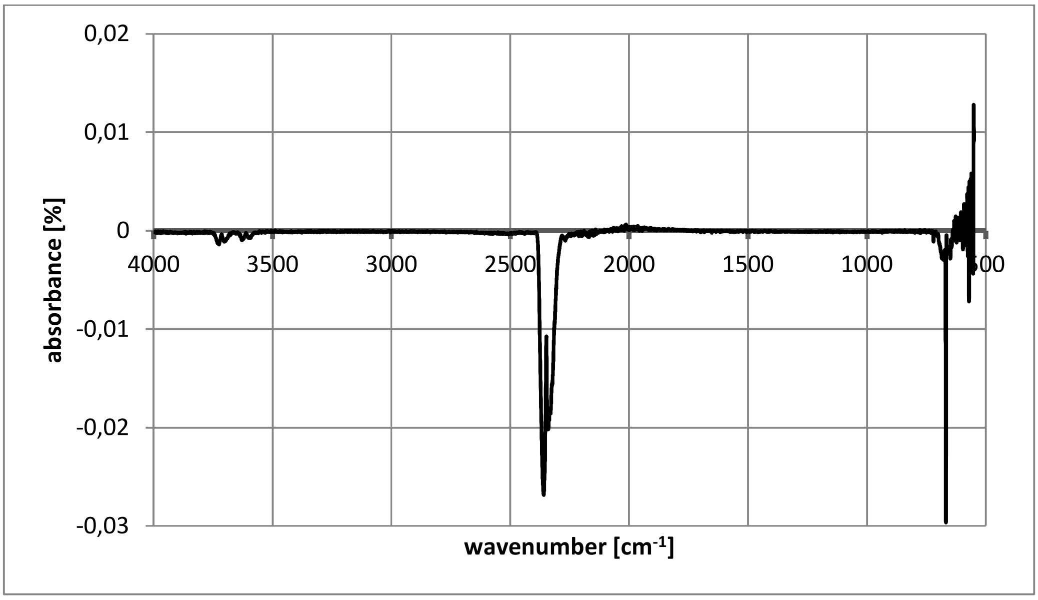

Figure 19: "empty" spectrum

The peak situated around 2355 cm^{-1} is typical of the crystal (diamond) used for this ATR-FTIR. Anyhow, it doesn't affect the measurements, since no bitumen characteristic peak is situated at that point.

3.2.5.2 SAMPLE PREPARATION

The bitumen needed for the test (roughly 0.1-0.2g) is extracted from its container using a small spatula.

First of all, the layer of material directly exposed to air has to be discarded (given the unknown oxidation process that it might have suffered of). Then, a small amount must be placed onto the crystal surface, so that it completely covers the latter (Figure 20).

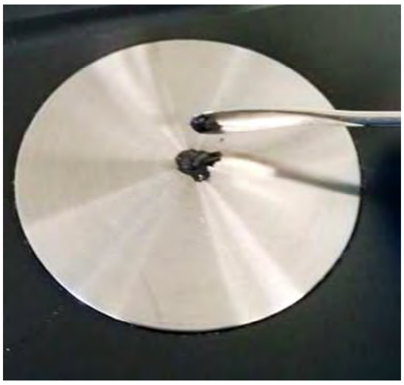

Figure 20: FTIR sample preparation

3.2.5.3 TESTING PROCEDURE

The test is automatically run by the software (Ominc 7, provided by Thermo Scientific). The operator can only choose the number of points, of steps and the wavenumber limits.
Eventually, the spectrum will be measured and it saved in a file compatible with Excel.

3.2.5.4 CLEANING

When the test is finished, the binder is removed using toluene and, afterwards, acetone. Then, the effective cleanliness must be assessed performing another empty test.

3.3 GEL PERMEATION CHROMATOGRAPHY

Chromatography is the generic name of a large set of laboratory techniques used for the separation of mixtures (*analytes*). In general, the mixture is dissolved in liquid phase (*mobile phase*) and forced to pass through a structure holding another material (*stationary phase)*. The separation is based upon the differential interaction of the analyte with the mobile and stationary phases.

In this study the Gel Permeation Chromatography (GPC) has been used. This technique is a type of the Size Exclusion Chromatography, where the molecules are separated by their size which is related to the molecular weight (Figure 22).

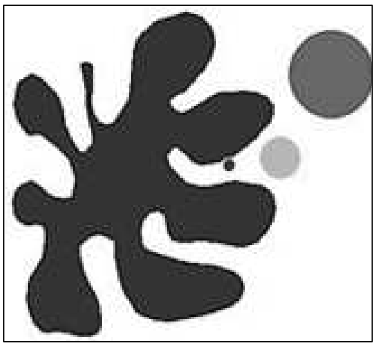
Figure 21: pore vs analytes

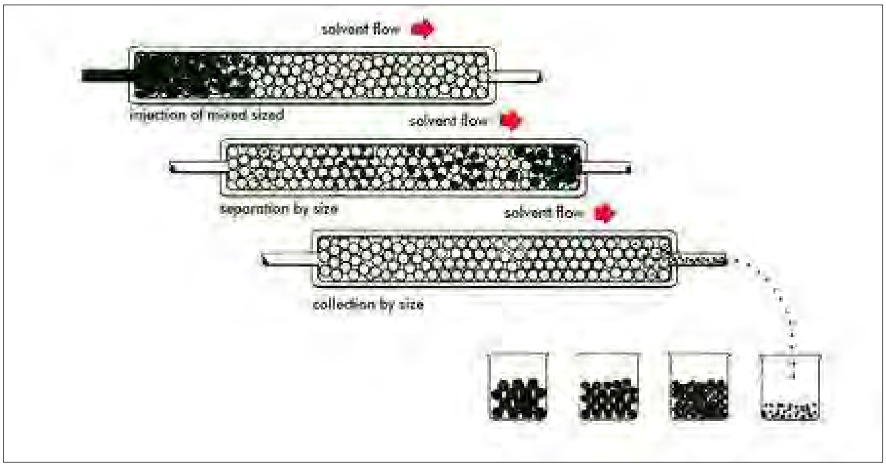

Figure 22: Molecules of various sizes elute from the column at different rates.

The main advantage of GPC is that there is almost no chemical or polar interaction between the stationary phase and the analytes, but the separation is obtained via the use of porous beads packed in a column: the porous surface of the beads retains the smaller particles longer than the bigger ones (Figure 22).

There is a limited range of molecular weights that can be separated by each column depending on the pore size of the packing material. Therefore the size of the pores for the packing should be chosen according to the range of molecular weight of analytes to be separated. In fact, the molecules bigger than the pores are completely un-retained, while smaller ones might be retained for an extremely and excessive long time.

In the picture below (Figure 23) the main components of the used GPC system are shown (Agilent Technologies, 2014):

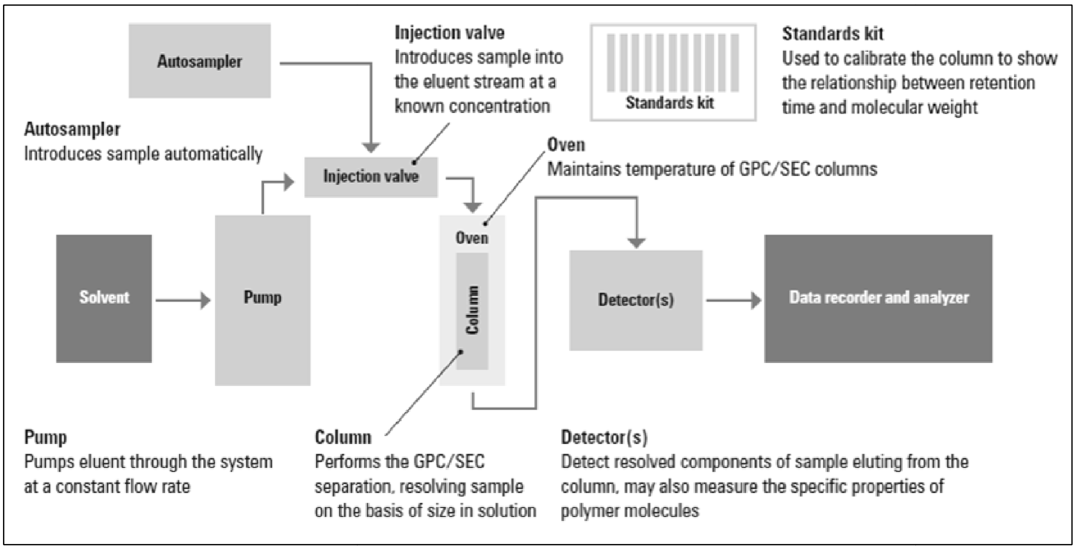

Figure 23: main components of a GPC/SEC system

In this study two detectors were used: Ultra violet detector (UV-detector, it measures the absorption of UV light) and a refractive index detector (RI-detector, it assesses the difference in refractive index between the dissolved analyte and the pure solvent).

3.3.1 BITUMEN CHROMATOGRAM

The results of GPC analysis are chromatogram, where the intensity (molecular volume) detected by the detector is plotted against the retention time (Figure 24). As it has been said, the retention time is dependent on the molar mass of the single molecule: the shorter the RT, the higher the molar weight of the molecule.

The bitumen chromatogram obtained with the GPC system is characterized by the following peaks:

- Asphaltene's peak: it occurs at about 15.6 minutes for the RI detector and at about 15.4 minutes for the UV detector.
- Maltene's peak: it occurs at about 17.7 minutes for both the detectors.

The two peaks are actually partially overlapping, so a quantification of the single compound is almost impossible.

The modification of the binder with polymers leads to the appearance of new peaks. Because of the higher molar mass of the polymers, these peaks occur before the bitumen's ones and, because of their high sensitivity to oxidation, tend to disappear after aging.

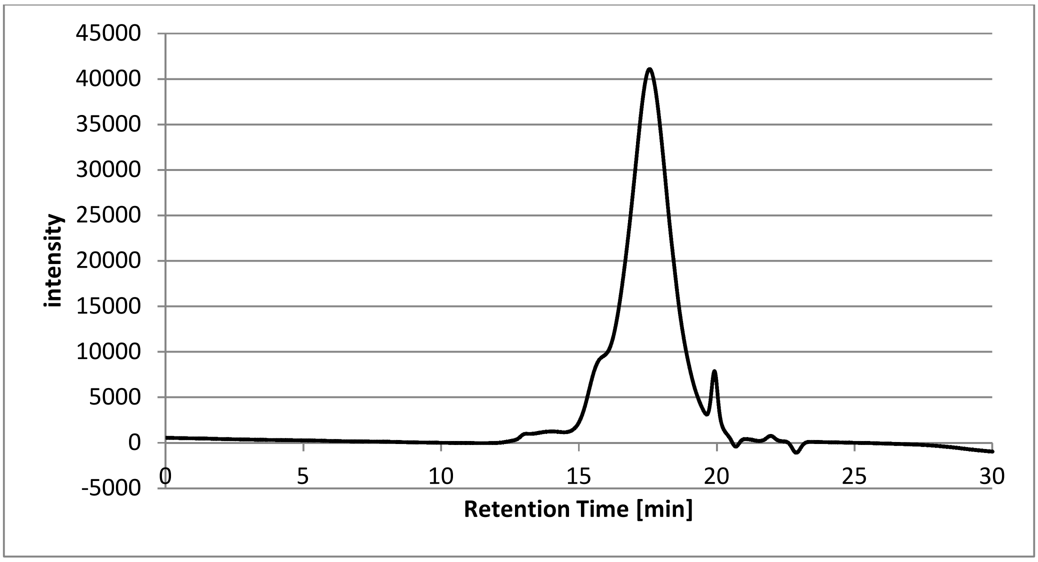

Figure 24: Chromatogram of Polymer Modified Bitumen.

3.3.1.1 CALIBRATION

When the molar weight of the compounds is needed, a calibration procedure must be run: the retention time of a monodispersed polymer standard is evaluated and the known molar weights of its peaks are plotted in the software to obtain the calibration curve (Figure 25).

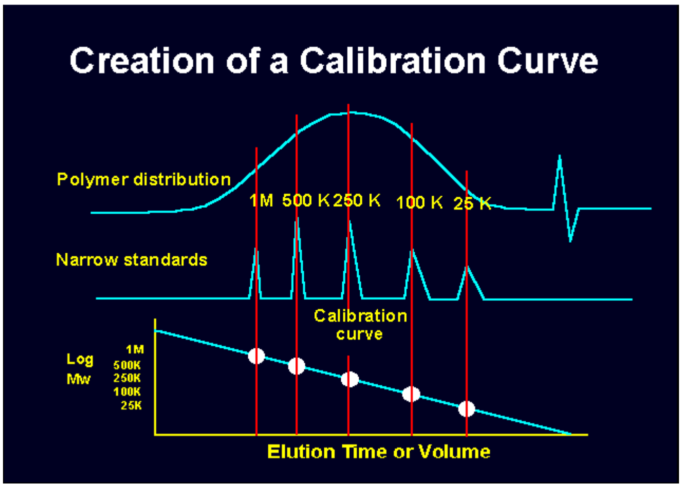

Figure 25: creation of a calibration curve.

The calibration curve, then, can be used to evaluate the actual molar weight[9] of the samples' peaks and the concentration of every single compound.

3.3.2 SAMPLING AND TESTING PROCEDURE

3.3.2.1 SAMPLE PREPARATION

The bitumen needed for the test (about 200mg) is extract from the container with the aid of a spatula or of a cutter without heating and put in a small 25 ml glass flask. Then, the sample is dissolved in Tetrahydrofuran (THF, $(CH_2)_4O$) to obtain the required concentration of approximately 10 mg/ml (Figure 26).

---

[9] Several definition of average molecular weight can be used to characterize the nature of a polymer:

- Number average molar mass: $M_n = \frac{\sum M_i N_i}{\sum N_i}$
- Mass average molar mass (formerly called weight average): $M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$
- Viscosity average molar mass: $M_v = \left[\frac{\sum M_i^{1+a} N_i}{\sum M_i N_i}\right]^{\frac{1}{a}}$, where a is an exponent that relates intrinsic viscosity and molecular mass.
- Z average molar mass: $M_z = \frac{\sum M_i^3 N_i}{\sum M_i^2 N_i}$

Figure 26: solutions of bitumen and THF

Once the bitumen is completely dissolved, the solution is diluted to 2 mg/ml. The accurate concentration is calculated from the mass of bitumen and THF, which have been weighed before with a precision of 1 mg. For the injection sample, about 2ml of the solution are taken up with a syringe, and filtered through a 0.45 um PTFE-Filter into a 2ml flask. Eventually, the labelled flasks are placed in the sample tray of the automatic sampler of the GPC-system (Figure 27).

Figure 27: sample tray and automatic sampler

3.3.2.2 TESTING PROCEDURE

The test is automatically run by the software Agilent GPC, provided by the manufacturer. Through the software the components of the equipment can be switched on and the test parameters (solvent flow in the system, sampling time, temperature, etc.) can be set.

In this study the followings parameters have been used:

- solvent flow: 1.00 ml/min.
- sampling time: 30 minutes.
- RI temperature: 35°C.
- UV wavelength: 215 nm

3.3.3 DATA ANALYSIS

The analysis of the chromatogram can be performed in two ways:

- Through the software itself: once a standard material has been tested and the molecular weight of its components registered, the calibration procedure is run by the software. As a result, the molecular weight of the peaks will be given.
- Analysing the changes in the retention time of the chromatogram peaks or the area of the peaks in a spreadsheet like MS-EXCEL.

CHAPTER 4: PRELIMINARY TESTS

4.1 DYNAMIC SHEAR RHEOMETER

4.1.1 LINEAR VISCO-ELASTIC (LVE) DOMAIN

The linear viscoelastic domain has been determined in conformity to the standard presented in the paragraph 2.4. The bitumen analysed was a styrene-modified bitumen 13/80 produced in 1996.

In the following charts the G*-strain curves are displayed, at different test temperature.

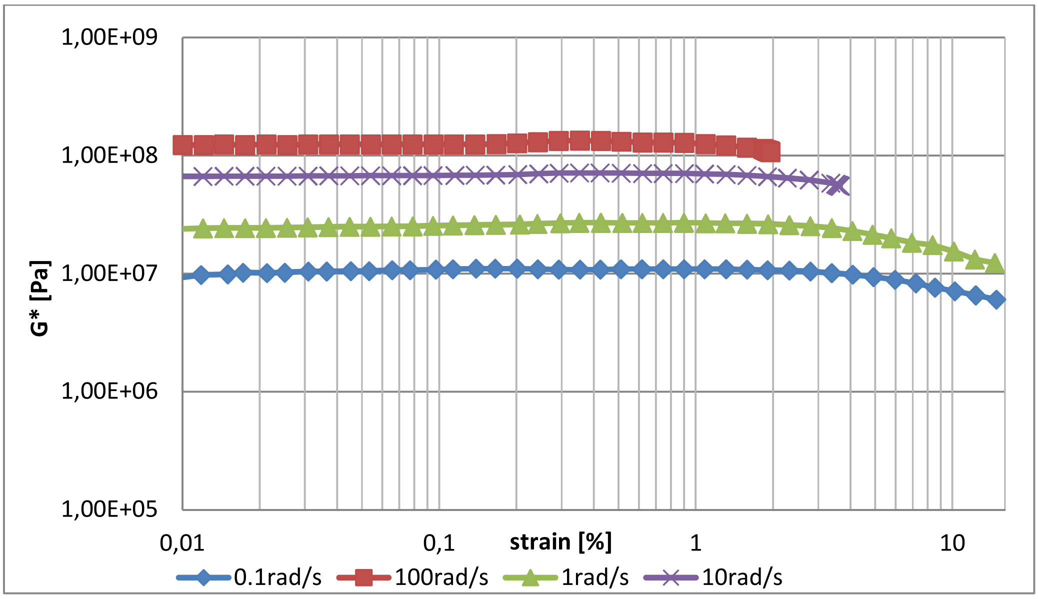

Figure 28: complex modulus vs strain at 0°C.

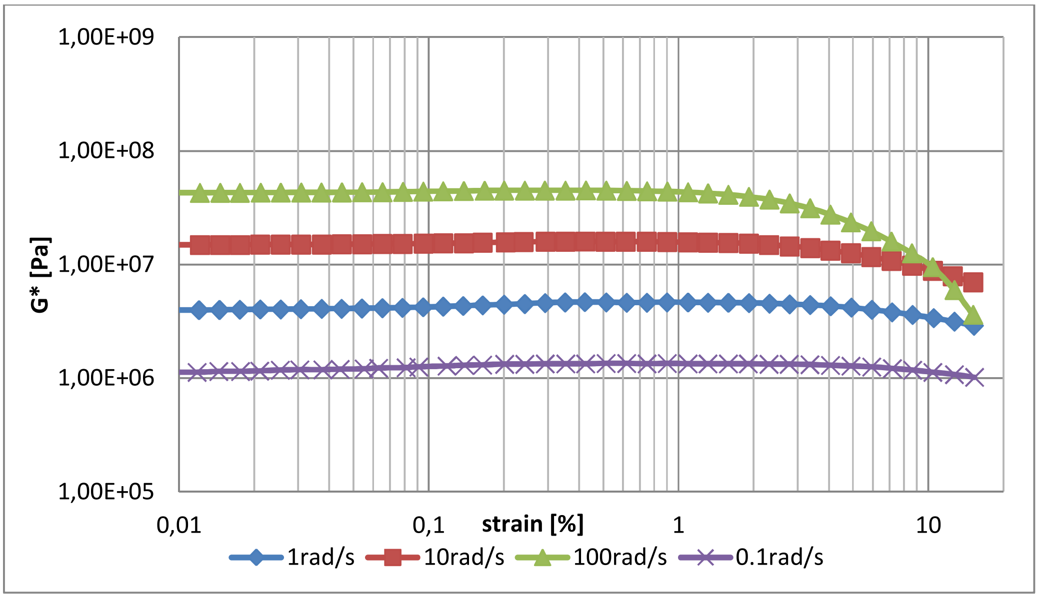

Figure 29: complex modulus vs strain at 10°C.

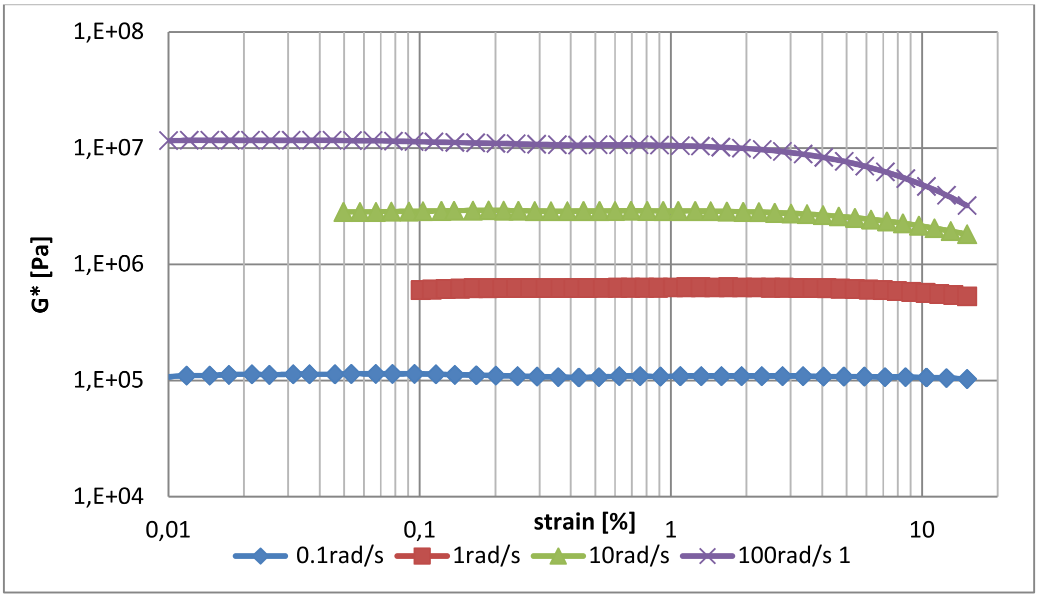

Figure 30: complex modulus vs strain at 20°C.

The results of the analysis fit the prediction of the SHRP model (see §2.4.1), with a LVE strain limit that decreases with both increasing frequency and decreasing temperature. As expected, the complex modulus at the LVE strain limits increases with both increasing frequency and decreasing temperature.

The strain limit is very low in all the study cases, leading to the following conclusions:

- the material has a limited linear region, very sensitive to temperature and frequency
- the testing condition must be studied carefully before carrying on further tests

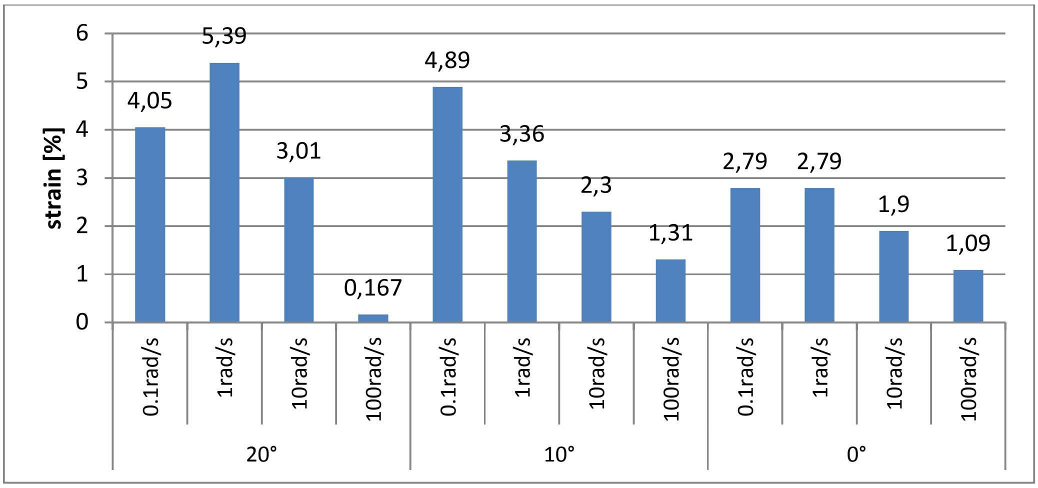

Figure 31: SHRP Linear ViscoElastic Limit

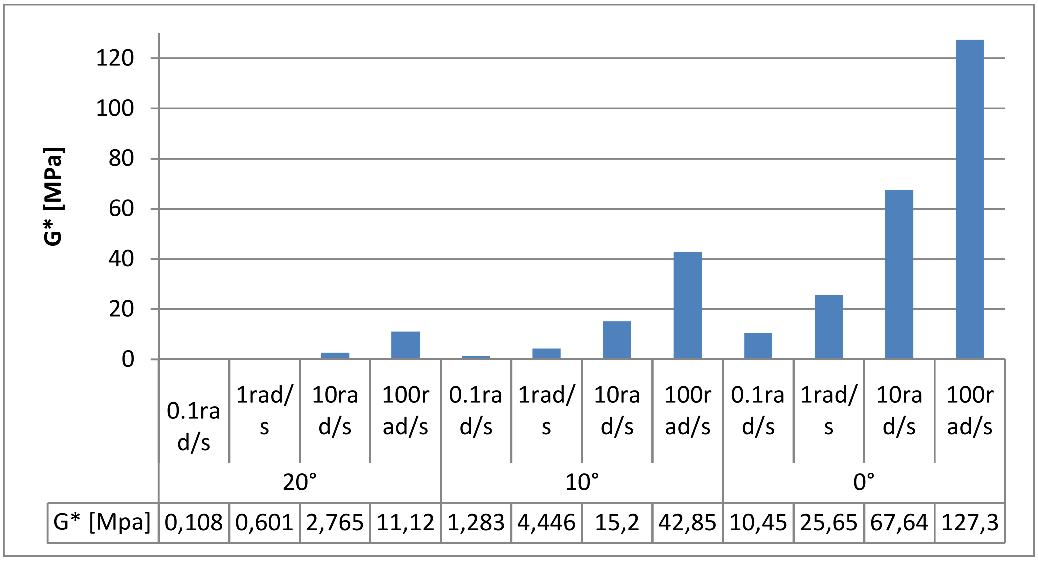

Figure 32: Complex Modulus in correspondence of the SHRP LVE Limit

The EU standard (§2.4.2) requires using the value of the modulus for zero strain, which is a value that cannot be straight evaluated. In this case, it has been calculated as the mean value within the ones produced by a strain lower than the 1%.

As the following chart reports, the linear region defined by the EU standard is limited too.

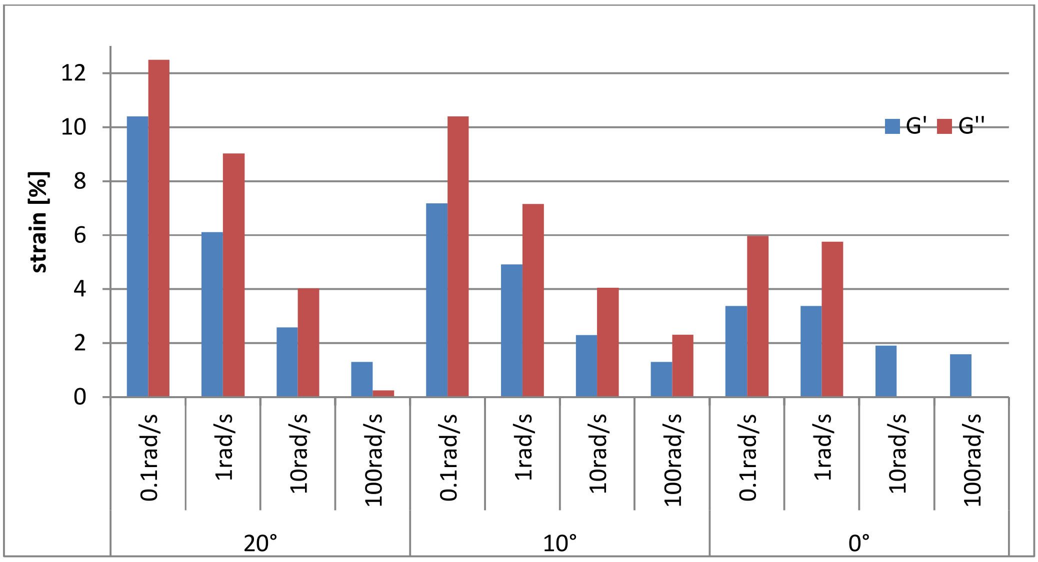

Figure 33: EU Linear ViscoElastic Limit

Comparing the results gained with the EU and the SHRP standards, it can be seen that the second one is more binding than the first and, for safety’s sake, should be used when testing this type of binder.

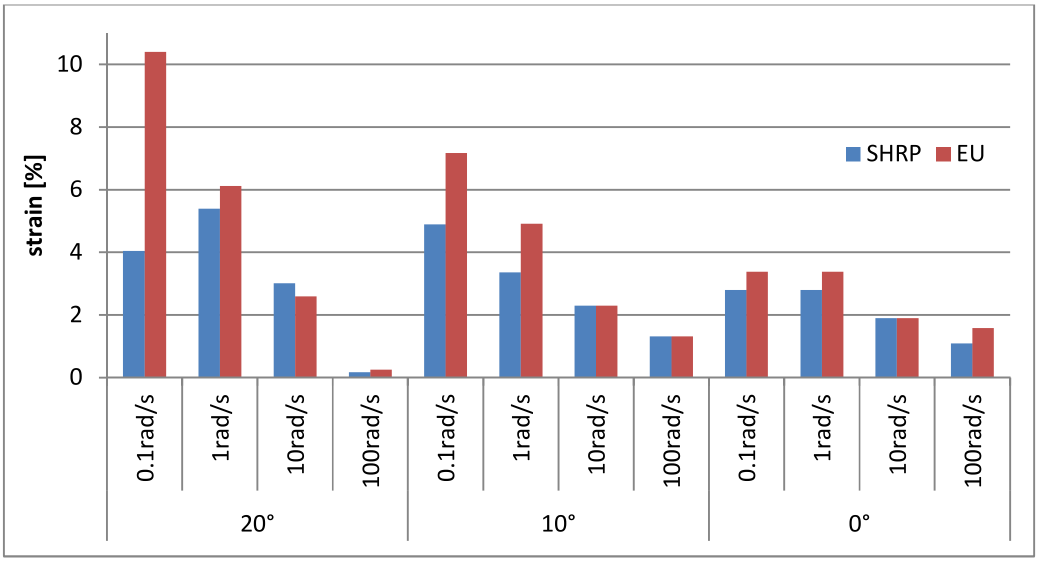

Figure 34: LVE - SHRP vs EU standards

As a consequence of the limited linear region, if the linearity test is carried out according to the ASTM standard (§2.4.3), 11 out of 12 samples should be rejected as *non-linear*, having a modulus ratio smaller than 0.9. Moreover, in 2 tests the 12% of deformation could not been reached, due to equipment limits.

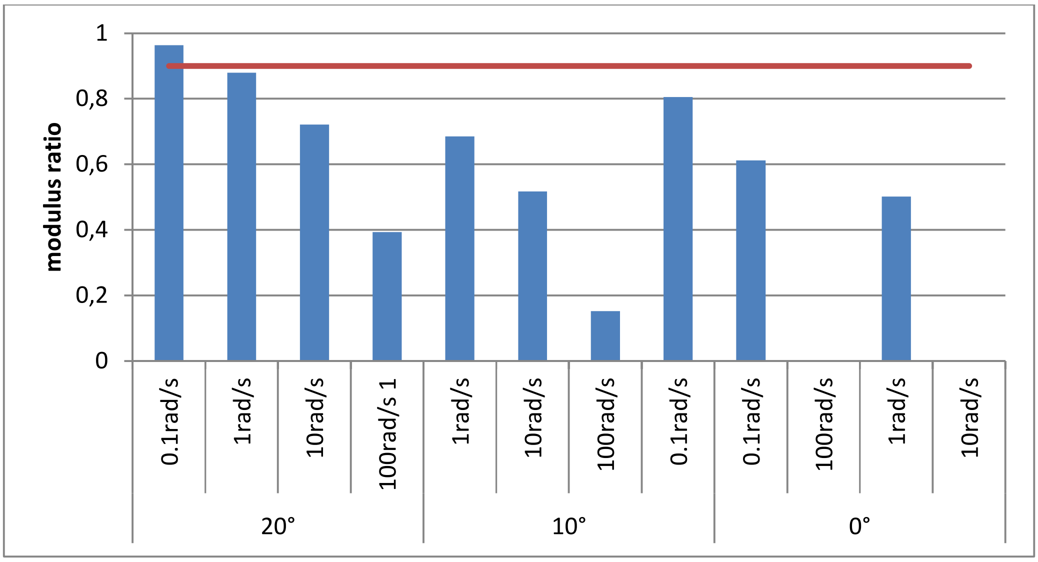

Figure 35: ASTM Linearity Test

4.1.2 REPEATABILITY

In order to assess the test repeatability six samples of bitumen 40/50 have been tested under the same conditions:

- frequency sweep from 1 to 100 rad/s
- fixed strain at 0.1%
- fixed temperature at 40°C
- 25mm plate and 1mm gap

As stated in the European Standard (CEN, 2012), *the precision of this test method has not yet been established*. However, the same standard suggests meeting at least the following criteria:

- The complex modulus should not differ from the mean by more than the 15%
- The phase angle should not differ from the mean by more than 3°

In the charts below the average of the complex modulus and of the phase angle are shown, where the error bars represent the maximum difference between values and average for a given frequency.

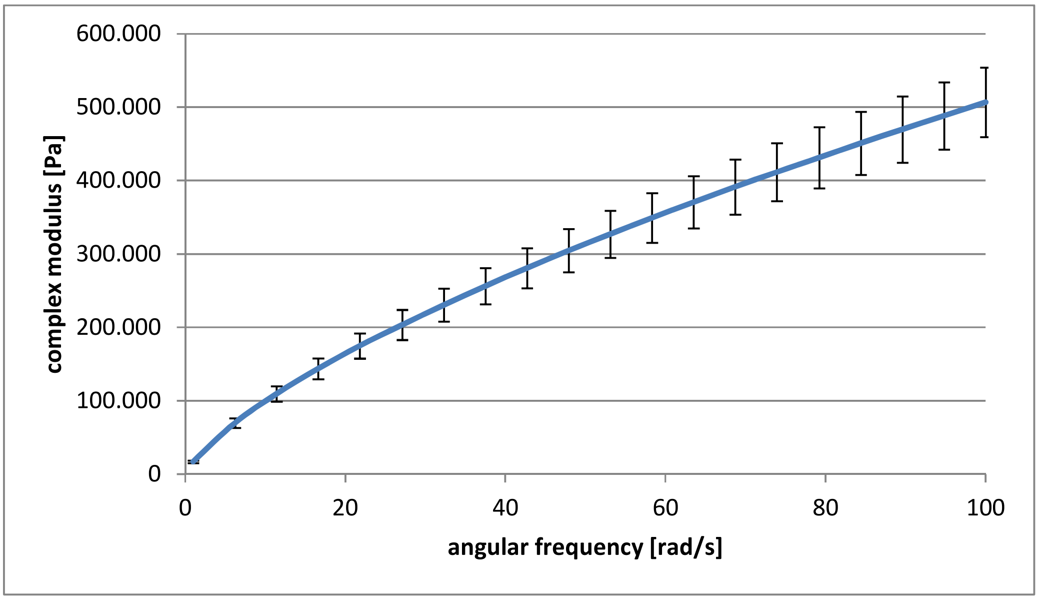

Figure 36: repeatability. Complex modulus.

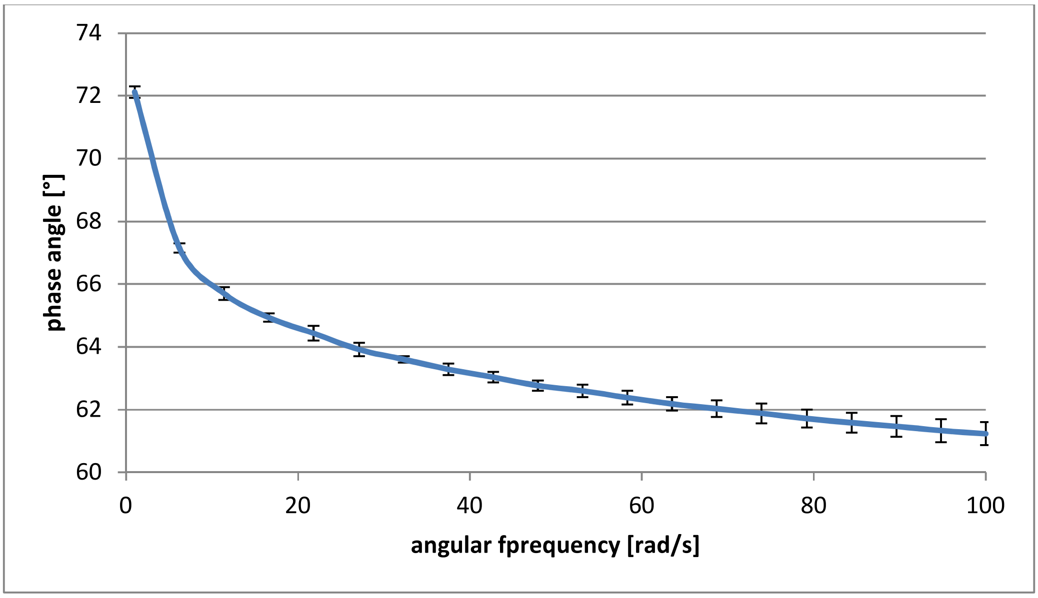

Figure 37: repeatability. Phase angle [°]

Thanks to this test, it has been proved that both the equipment and the procedure meet the EU suggestions: the maximum difference between G^* and the average for every given frequency is about 10%, far less than the recommended 15%, while the maximum difference between phase angle and the average for every given frequency is about 0.23°, far less than the recommended 3°.

4.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

4.2.1 NOISE

The noise in the fingerprint region has been evaluated as the bigger peak-to-valley distance (Figure 38). Three different “empty” spectra have been analysed and, as a result, it was chosen to discard as noise the fluctuations smaller than 0.0005%.

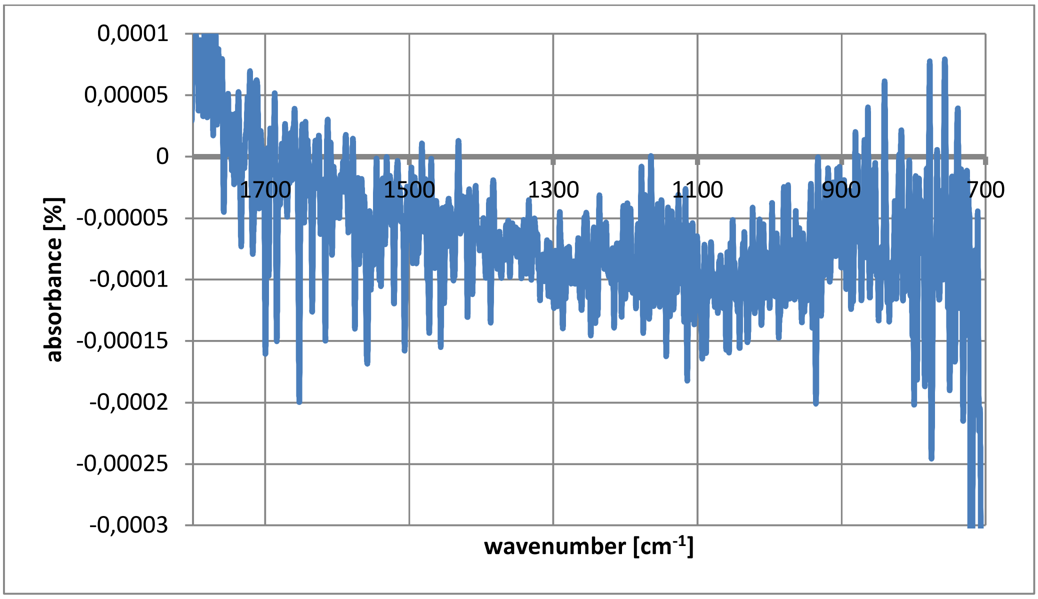

Figure 38: "empty" spectrum

4.2.2 REPEATABILITY

In order to assess the repeatability of the test and of the oxidation indexes evaluation, six samples of the same bitumen have been tested.

It has been found (Figure 39) that the standard deviation of the spectra is almost always below the 10% of the average absorbance, with higher values occurring only where the absorbance itself it about zero and where the crystal peak is located (§3.2.4.1).

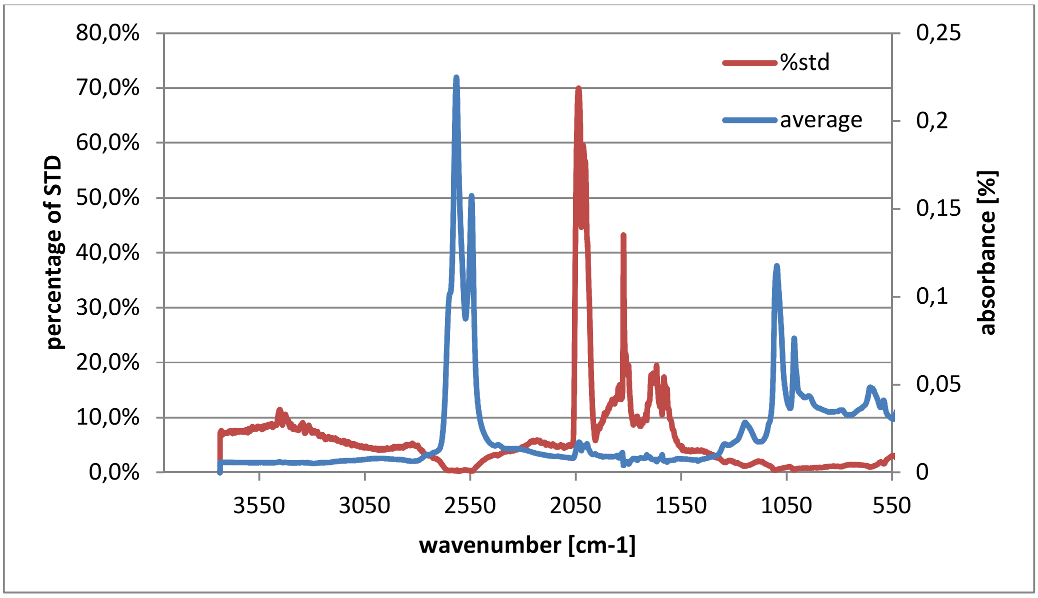

Figure 39: FTIR repeatability

The standard deviation found for the evaluated index is even lower: 2.06% for the Sulfoxide Index and 1.27% for the Carbonyl Index.

4.2.3 OXIDATION IN THE OVEN

In order to test a sample in the DSR the bitumen needs to be heated in the oven (see §2.5.1). To assess that this high temperature step (80-90° higher than the softening point) does not change the chemical structure of the binder two FTIR tests have been run: one before the heating, one after it.

No important changes have been found and the two spectra are almost completely overlapping (Figure 40).

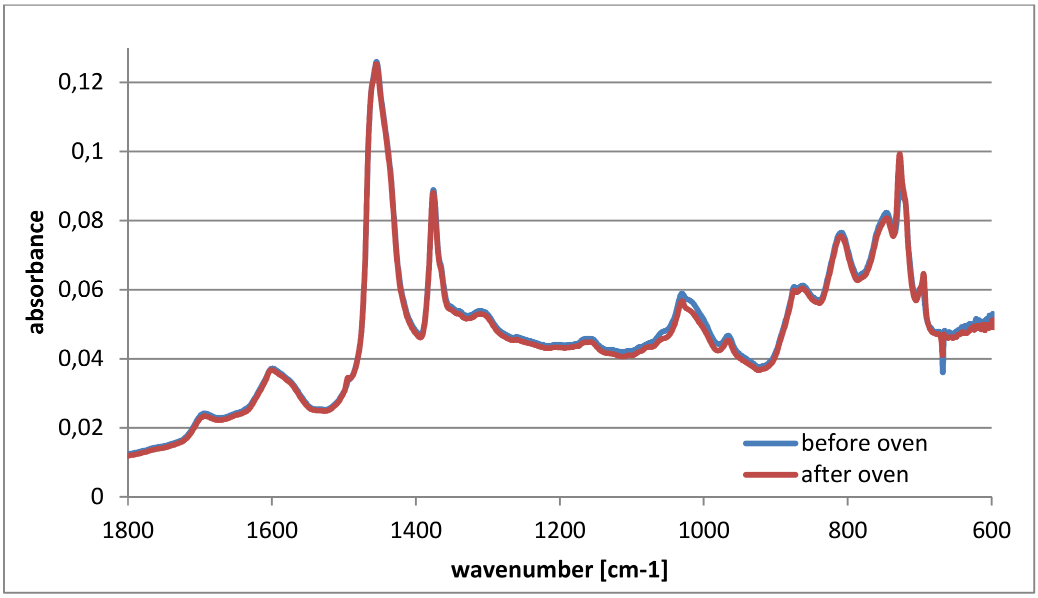

Figure 40: fingerprint spectra

CHAPTER 5: AGING OF WARM ASPHALT

5.1 INTRODUCTION

Warm Mix Asphalt (WMA) technologies have been developed during the last two decades as a solution for environmental issues in the paving process: the conventional Hot Mix Asphalt (HMA) is a source of pollution because of the high temperatures (160°C to 180°C) needed for its production and the consequent huge amount of energy spent. By implementing WMA technologies, mixing and compaction temperatures can be decreased by 40°-50°C, thus reducing fuel consumption and greenhouse emissions.

To lower the mixing temperature a decrease in the viscosity of the mix is needed and can be gained in different ways: using foam bitumen, using emulsions or modifying the binder with additives, either organic or inorganic. Lower asphalt temperatures lead also to other advantages: longer hauling distances, better working conditions (less harmful fume emissions and lower spreading temperature), extended paving season and quick turnover to traffic, decrease of the binder aging during production(Rubio, et al., 2011) (Silva, et al., 2010). However, some drawbacks are to be pointed out: lack of data concerning the long-term performance, higher production costs, for some WMA types greater rutting potential and moisture susceptibility, coating and bonding problems.

5.2 OBJECTIVE AND SCOPE

The aim of this part of the study is to find a test procedure reflecting the binder aging in warm asphalt at the lower temperatures used in the production process. The standard procedure in EN 12607-1 was developed for HMA and requires an aging temperature of 163°C, which is not reached in the case of warm asphalt. Three additives have been studied with laboratory tests: a Fischer-Tropsch wax and two patented chemical additives. Of the latters, one has also been aged *in situ*.

In order to assess the rheological changes caused by aging, the complex moduli and the phase angles of unaged, aged, unmodified and modified blends have been measured. To prove that the laboratory aging mimic the field conditions, the properties of recovered bitumen have also been inquired and compered to the laboratory aged binder results.

5.3 LITERATURE REVIEW AND STATE OF THE ART

Warm Mix Asphalt can be obtained by different methods (Rubio, et al., 2011):

- *Foaming process:* water is mixed with the hot bitumen and thus transformed into steam. This generates a large volume of bitumen foam which reduces the mix viscosity for a limited time. The water can be added to the binder directly (water-based techniques) or by adding synthetic zeolite with water trapped in the crystalline lattice (water-containing technologies) (Rubio, et al., 2011)

- *Emulsions:* produced adding chemical packages to a mix of water and bitumen. When mixed with hot aggregates the water flashes off as steam (Silva, et al., 2010)
- *Organic additives:* waxes added to the binder do both decrease the viscosity at high temperature (above the melting point of the wax, about 110°) and increase the stiffness of the binder as the mixture cools down by creating a crystalline lattice of uniformly distributed particles (Rubio, et al., 2011) (Kheradmand, et al., 2013). Three kind of organic additives can be identified: Fischer-Tropsch waxes (method for the synthesis of hydrocarbons and other aliphatic compounds from synthesis gas); fatty acid amide (manufactured synthetically by causing amines to react with fatty acids); Montan waxes (lignite wax consisting mainly of fossil fatty acid esters).
- *Chemical additives*: to reduce the friction in asphalt: chemical patented additives, containing emulsification agents, surfactants, polymers and additives to improve coating, mixture workability and compaction as well as adhesion promoters (antistripping agents) (Mo, et al., 2012). These additives can be used to produce emulsions or directly mixed with bitumen before batching it into the asphalt mix.

The additives used in the present study belong to the last two families.

5.3.1 SYNTHETIC F-T PARAFFIN WAX

This additive is a long chain of aliphatic hydrocarbons produced from the gasification of coal though the Fischer-Tropsch method. The melting point is at about 85°-115°C and the wax is completely soluble in bitumen for temperatures higher than 115°C. For temperatures above the melting point the wax reduces the binder viscosity while for lower temperatures it creates a crystalline lattice that help increasing the bitumen resistance to deformation.

As numerous studies have proved, with respect to the binder source this additive increases the complex modulus at medium-sweep temperature, $G^*/\sin\delta$, the Zero Shear Viscosity, the softening point and the maximum force of ductility, while reducing the non-recoverable compliance, the phase angle, the penetration number and the Fraass breaking point (Jamshidi, et al., 2012).

It has also been shown that the degree of change in the rheological and chemical properties of the modified binder depends on the wax content, the bitumen type and chemical structure.

Qin, et al. (Qin, et al., 2014) found that time–temperature superposition fails at temperatures above 30 °C and suggested that the formation of network or semi-solid like structure is responsible for this breakdown.

Concerning the oxidation, resistance to oxidation properties have been observed both analysing rheological results (Banerjee, et al., 2012) and FTIR results (Jamshidi, et al., 2012). The modified binder extracted from short-term-aged and long-term-aged WMA, in fact, shows less aging in terms of normalized viscosity, $G^*/\sin\delta$, $G^*\sin\delta$, and binder stiffness, compared to binder extracted from HMA samples thanks to the reduced volatilization and oxidation caused by the lower construction temperatures.

Within the drawbacks of this kind of additives there are reduced resistance on low-temperature and increased fatigue potential, both due to the increased stiffness (Jamshidi, et al., 2012).

5.3.2 CHEMICAL ADDITIVES

It has been found that this kind of additive does not modify the failure temperature and have little effect on the infrared absorbance spectra for unaged samples (Xiao, et al., 2012). It was also found that WMA produced with chemical additives has significantly lower aging factor compared to control HMA, and this linked to the higher rutting depth at the early stage of pavement serviceability. Additionally, the result indicated that the production temperature and amount of additive used to produce WMA did not considerably contributed to the complex modulus, fatigue life, tensile strength and TSR of WMA mixture (Goh, et al., 2013)

5.4 EXPERIMENTAL

5.4.1 MATERIALS

The base binder used is a bitumen 50/70 delivered for the research package PLANET. Three different additives have been used: one organic wax (FR-WAX) and two synthetic additives (FR-PACK and PA-PACK). In the table below the producers’ direction for blending and mixing are shown:

Product	Dosage of additive (w/w) to bitumen	Mix temperature
FR-PACK	0.4%	130
FR-WAX	3%	130
PA-PACK	1%	130

Table 3: dosage of the used additives.

Modified binders have been prepared by heating 250 g of bitumen for 40 minutes at 130°C, until liquid. Then the pre-weighted amounts of additives have been added and the blends have been stirred for 5 minutes with a mechanical stirrer. The modified bitumen has been placed in the oven at 130°C for other 10 minutes and then stirred manually to obtain good homogeneity.

Only the modified binder FR-PACK was used in a test field. On this example the aging in the field was compared with the binder aging in the laboratory. It has been extracted and recovered according to the EN 12697-1 and 12697-3.

5.4.2 AGING PROCEDURE

To simulate the aging in the mixing plant the binders have been aged according to EN 12607-1 with the Rolling Thin Film Oven Test (RTFOT):

- Virgin binder: the aging has been run for 75 minutes at 163° (standard procedure)
- Modified binders: the aging has been run for 75 minutes at a reduced temperature of 130°C, which is the mixing temperature used for these types of warm asphalt.

After the aging procedure, the aged binders of the RTFOT glasses have been combined in a single container, heated again at 130° for 10 minutes and homogenised with a glass rod.

Then, to simulate the *in situ* aging of the binder during use of the road the Pressure Aging Vessel test (EN 14769) has been run: the samples are aged at 100° at a pressure of 2.10 MPa for 20 hours. After the test, the aged binder was combined and homogenized again at 130° (148° for the unmodified bitumen) for 20 minutes.

In the Table 4 the sample labels are shown:

Additive	unaged	after RTFOT	after PAV
No additive	A0	A0-r	A0-p
FR-PACK	AC	AC-r	AC-p
FR-WAX	AS	AS-r	AS-p
PA-PACK	AG	AG-r	AG-p

Table 4: labelling of the test samples.

5.4.3 TEST METHODS

Along with the conventional softening point test, the rheological properties of the binders have been measured using the DSR in the oscillation mode, at 10°, 20°, 30°, 40°, 50°, 60° and different frequencies, to get enough data for a master curve. For every material, two geometries have been used:

- 8mm geometry, for 10° to 40°C
- 25mm geometry, for 30° to 60°C

The infrared spectra of the binders have been obtained using the ATR-FTIR in the absorbance mode to determine the aging indexes (see §3.2.4.2).

5.5 RESULTS

5.5.1 SOFTENING POINT[10]

The chart below (Figure 41) shows the values of the ring and ball softening point. In the unaged state, two of the modified binders have a softening point lower than the virgin bitumen, while the wax modified sample showed a considerable higher value.

The introduction of the wax, in fact, creates a crystal lattice that makes the material more viscous at temperature below the melting point of the wax itself and, as a consequence, more resistant to permanent deformation.

The softening point of the binders modified with the chemical additives is similar to the non-modified binder in the virgin state. The slight decrease of 3°C in the softening point of the two chemical modified binders FR-PACK and PA-PACK is marginal and should not affect greatly their *in situ* performances.

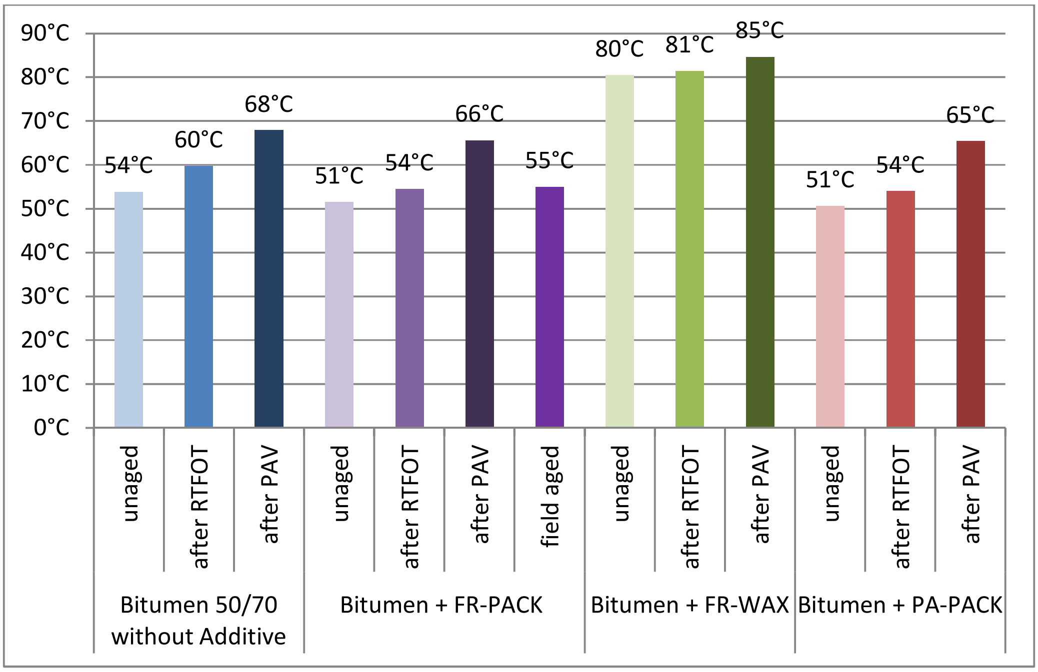

Figure 41: Results of softening points ring and ball before and after aging

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[10] The softening points below 80° were obtained in water bath while the ones above 80° were obtained in glycerol bath, according to the European standard EN 1427-2007 (CEN, 2007)

The influence of the reduced working temperature is clearly visible when comparing the softening points before and after the RTFOT: the warm asphalt binders, in fact, show smaller increments than the unmodified one (3° to 1°C vs 6°C). This proves that the lower aging temperatures have a positive effect on the short term oxidation.

On the contrary, long term aging seems to affect equally unmodified bitumen and bitumen modified with chemical additives: the softening point, in fact, is increased by 14°C with respect to the value in the unaged state for all of the three materials. The wax modified bitumen is an exception as already the value before aging is 80°C, which is 26°C higher compared to the non-modified bitumen. On the other hand, the increase after aging with RTFOT or PAV is much smaller (1 and 4°C).

The sample from the test field shows a similar softening point as the laboratory sample after RTFOT aging.

5.5.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

In the charts below the spectra for the different binder are shown. The unaged binders' spectra are overlapping in the fingerprint region (Figure 42), but the peaks due to the chemical additive addition[11].

After RTFOT aging, the virgin binder has increased the carbonyl and sulfoxide peak more than the modified binders (Figure 43), while this difference decreases after the PAV aging (Figure 44).

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[11] See APPENDIX A: CHEMICAL ADDITIVES SPECTRA.

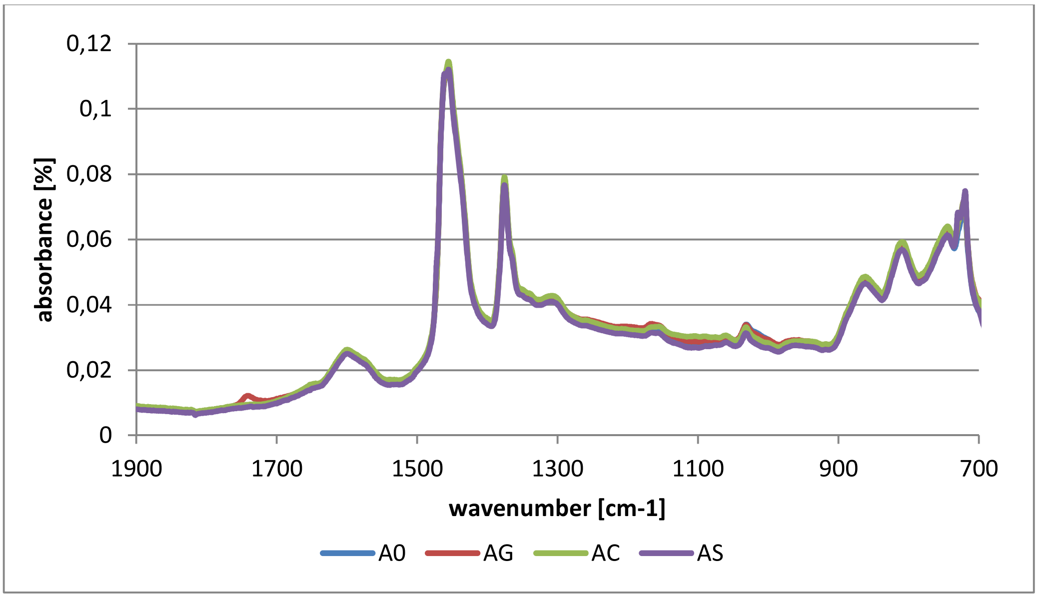

Figure 42: warm asphalt. Unaged binders' fingerprint spectra

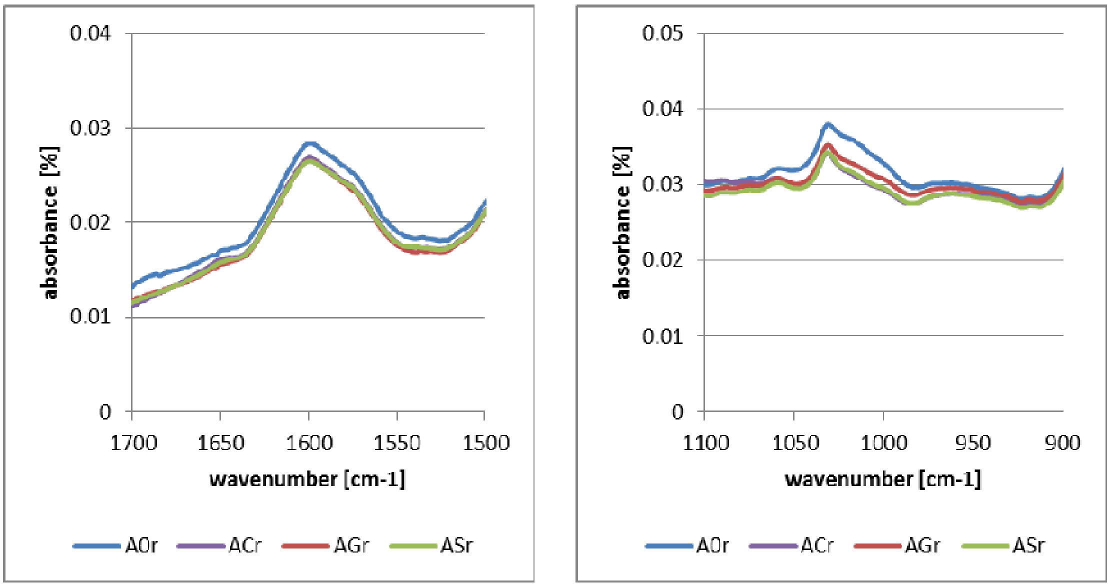

Figure 43: warm asphalt. RTFOT binders' Carbonyl peaks (left) and Sulfoxide peaks (right)

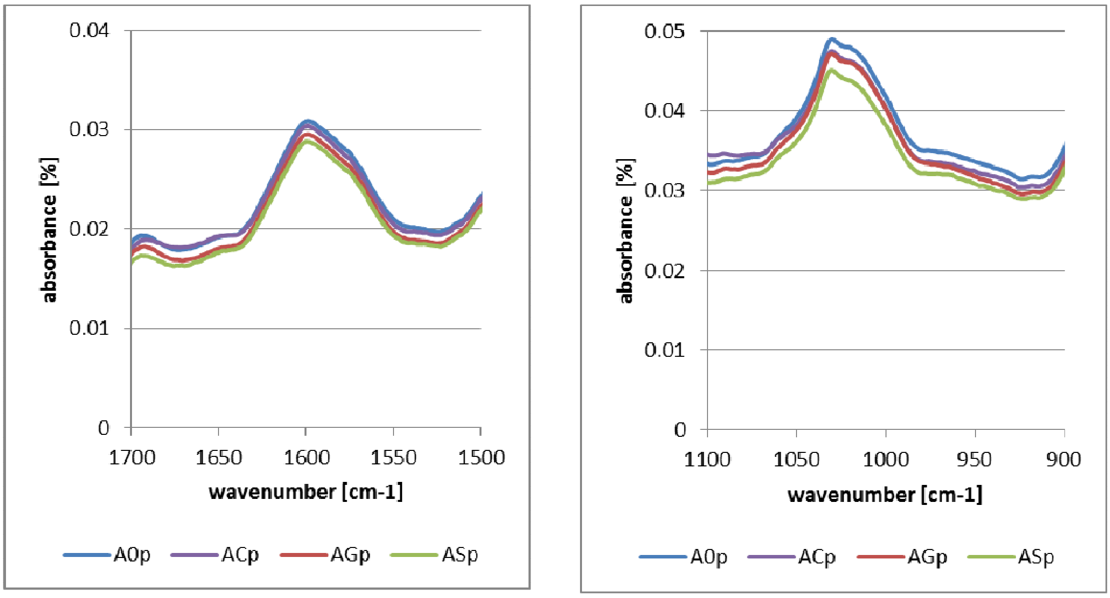

Figure 44: warm asphalt. PAV binders' Carbonyl peaks (left) and Sulfoxide peaks (right)

Then, from the FTIR spectra the Carbonyl and Sulfoxide Indexes have been evaluated (Table 5). As it is shown in the charts below (Figure 45 and Figure 46), the reduction of the working temperature leads to a consistent reduction of the CI in the RTFOT binders. Also the SI is reduced with respect to the virgin binder, but the improvement is less pronounced.

		Carbonyl Index	Sulfoxide Index
A0	unaged	0	0.035713
	after RTFOT	0.002858	0.044308
	after PAV	0.023049	0.078156
AC	unaged	0	0.02144
	after RTFOT	0.000102	0.028311
	after PAV	0.020216	0.074905
AG	unaged	0	0.027008
	after RTFOT	0.000608	0.03292
	after PAV	0.019054	0.076121
AS	unaged	0	0.020277
	after RTFOT	5.04E-05	0.030472
	after PAV	0.020038	0.071312

Table 5: warm asphalt. Carbonyl and Sulfoxide Indexes.

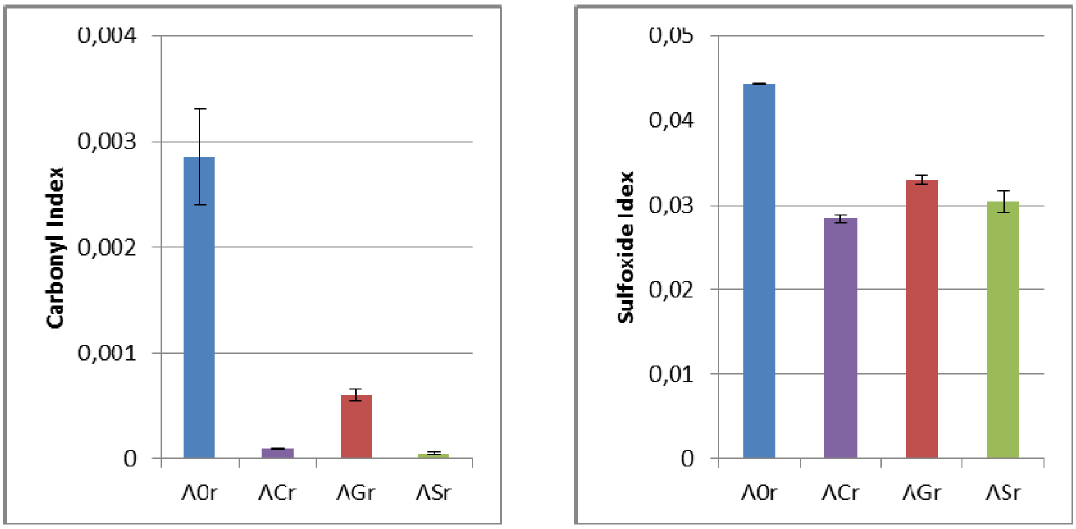

Figure 45: warm asphalt. RTFOT binders' Oxidation Indexes

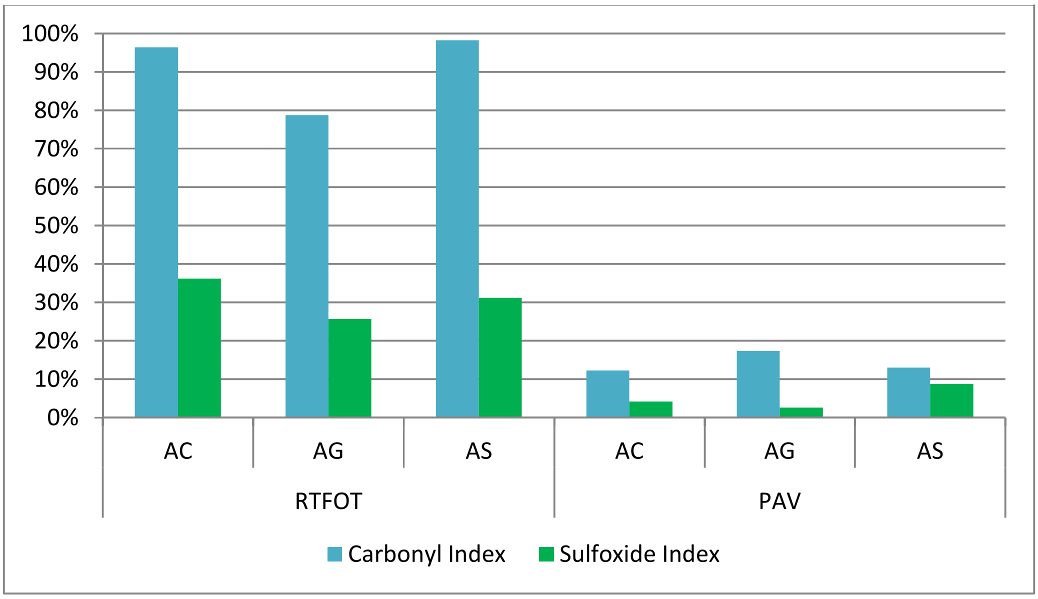

Figure 46: Warm asphalt, reduction of the indexes with respect to the unmodified binder

Concerning the PAV aged binders, the additives seem to have almost no effect in preventing the long period aging (Figure 47). Moreover, when the Carbonyl and Sulfoxide Indexes are compared with their value after the RTFOT (Figure 48) you can see that the increments in the CI are about the same for all of the binders and the Sulfoxide ones are even higher for the modified binder than for the virgin one.

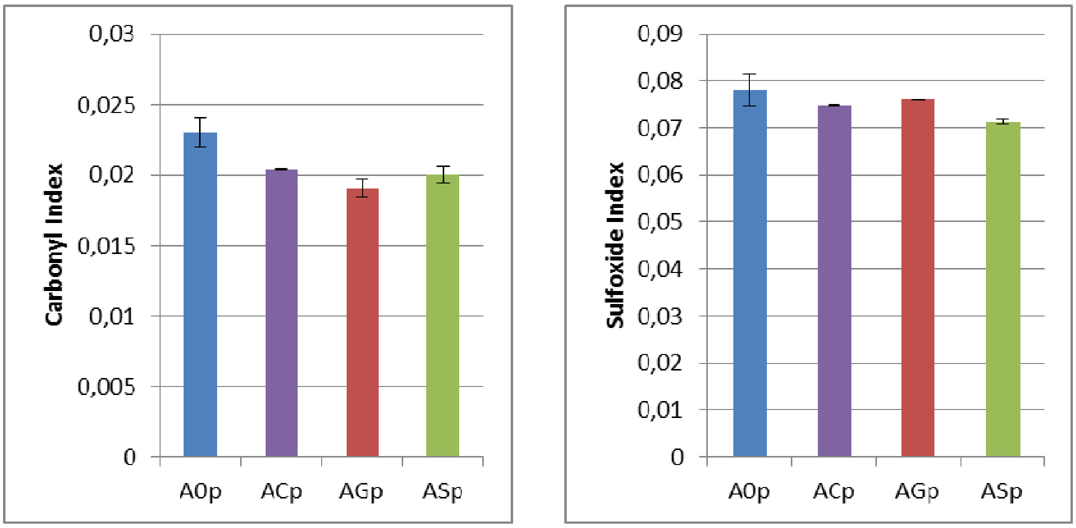

Figure 47: warm asphalt. PAV binders' Oxidation Indexes.

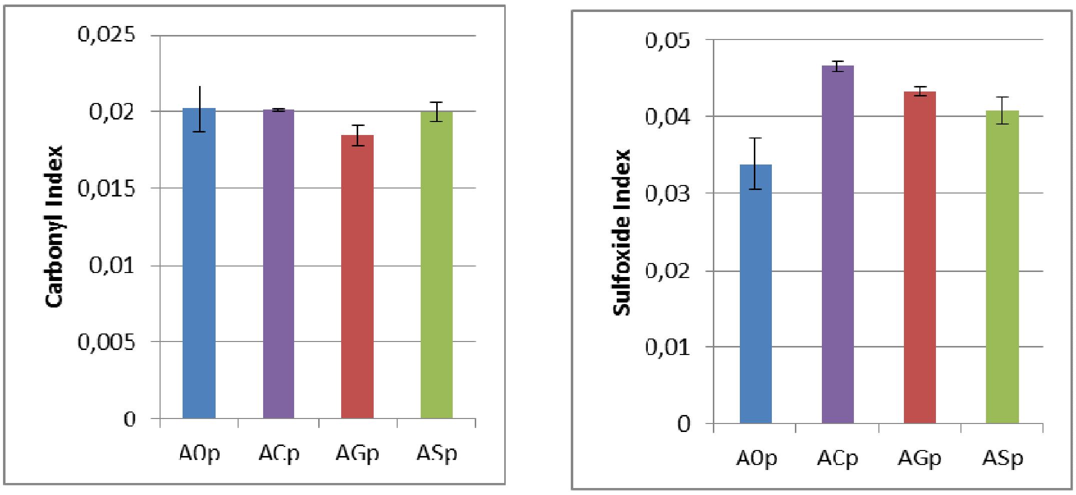

Figure 48Carbonyl (left) and Sulfoxide (right) increment with respect to the RTFOT aged binders.

5.5.3 DYNAMIC SHEAR RHEOMETER

The rheological behaviour found with the R&B tests is confirmed by the DSR test.

Comparing the master curve for the different aging conditions, it can be seen that the hardening occurs for every kind of binder. Nevertheless, the hardening due to the RTFOT is less pronounced in the modified binder than in the virgin one and is almost inconsistent in the FR-WAX modified bitumen.

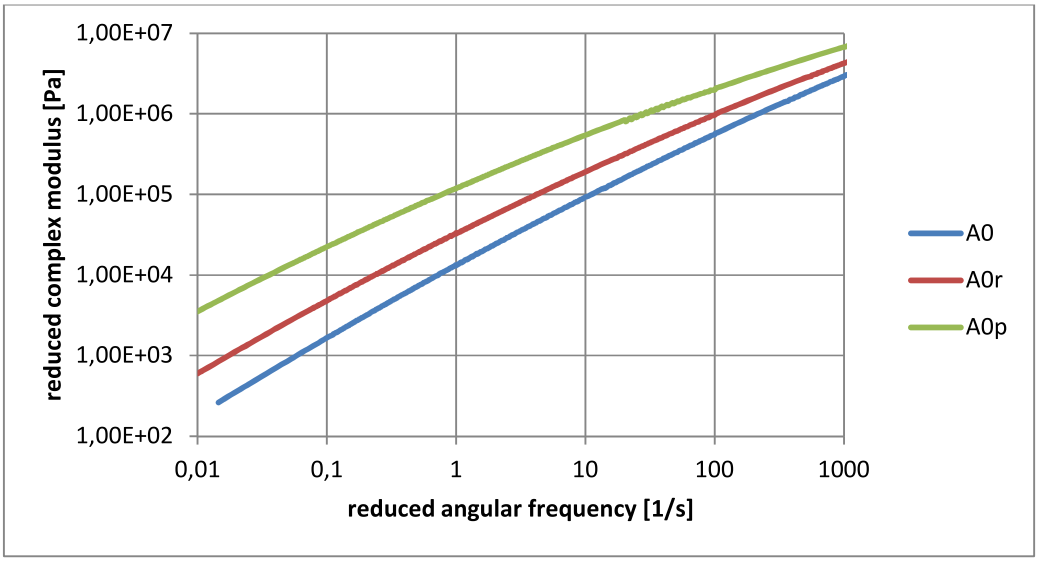

Figure 49: warm asphalt. Virgin binder’s master curve.

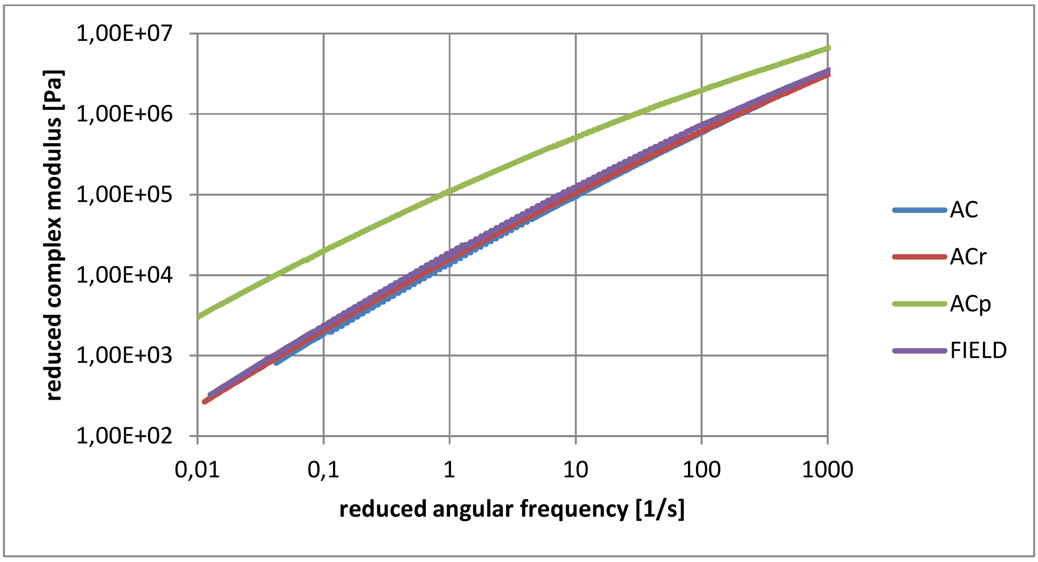

Figure 50: warm asphalt. FR-PACK modified binder’s master curve.

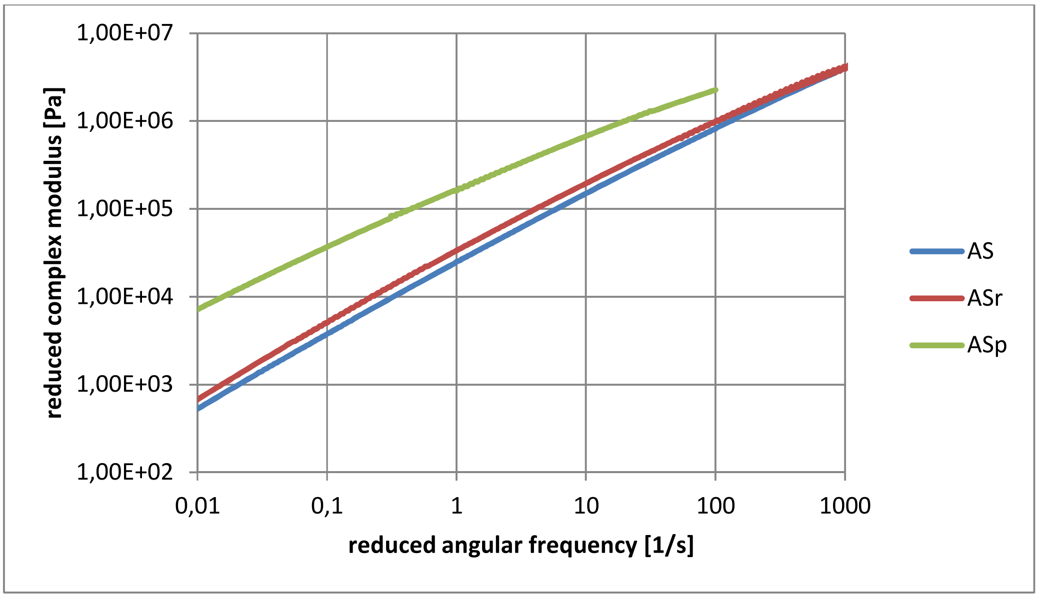

Figure 51: warm asphalt. FR-WAX modified binder’s master curve.

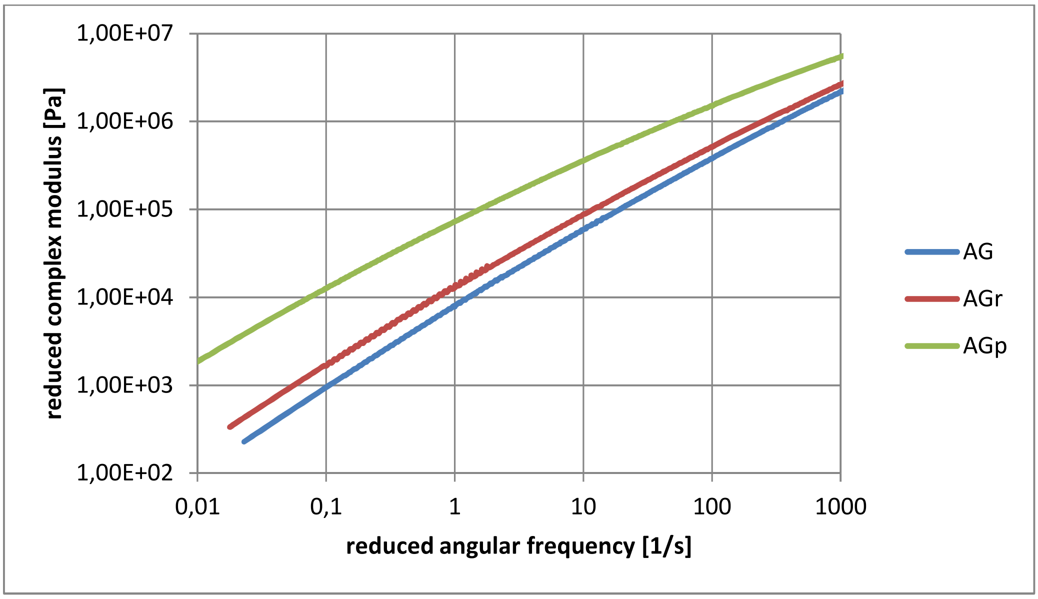

Figure 52: warm asphalt. PA-PACK modified binder’s master curve.

In order to show how the materials behave at different temperatures, the complex modulus and the phase angle have been plotted against temperature itself at a specific frequency (5.15 rad/s). Both for the unaged and aged conditions the performances of the binders are slightly improved (higher complex modulus and lower phase angle) by the modification with the wax, while are slightly decreased by the two chemical packages (Figure 53 and Figure 54).

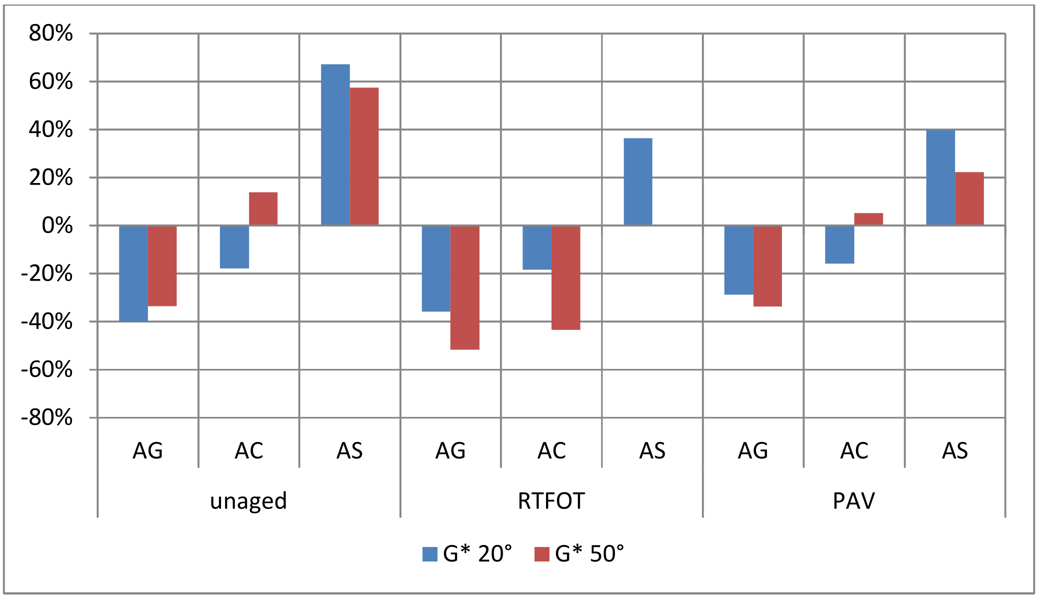

Figure 53: warm asphalt. Variation of the complex modulus with respect to the unmodified binder.

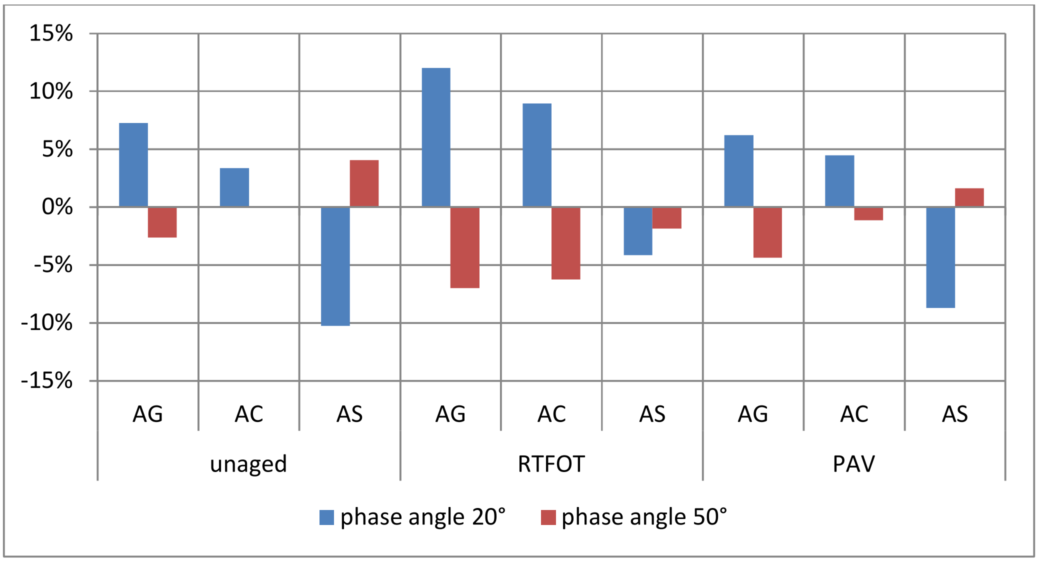

Figure 54: warm asphalt. Variation of the phase angle with respect to the unmodified binder

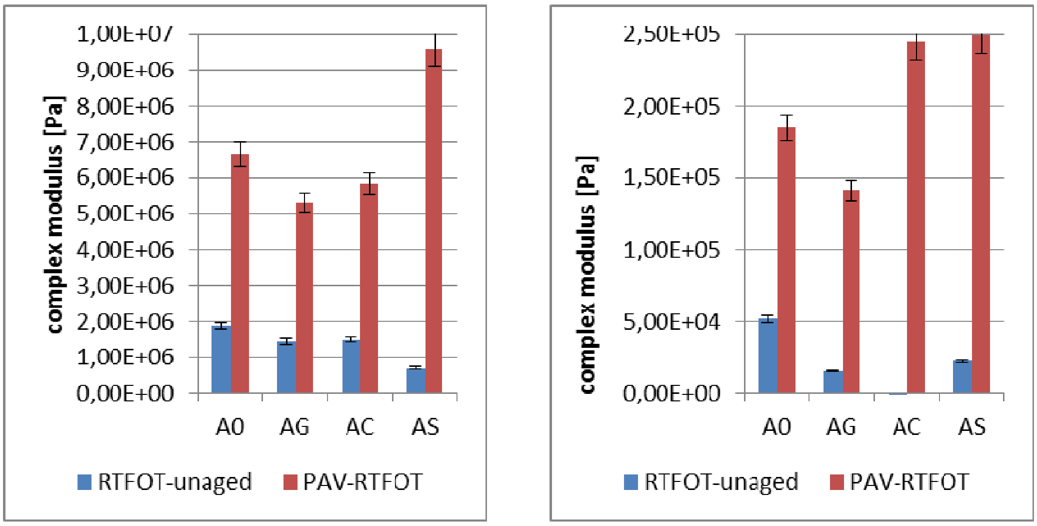

Figure 55: warm asphalt. Variation of the Complex modulus at 20° (left) and 50° (right).

Comparing the changes in the complex modulus and phase angle before and after the two aging steps, some characteristic pattern can be seen: the aging hardening due to the RTFOT is less pronounced in the modified binder than in the virgin one (Figure 55), while the phase angle after the PAV aging is increasing more in the modified ones than in the virgin one (Figure 56).

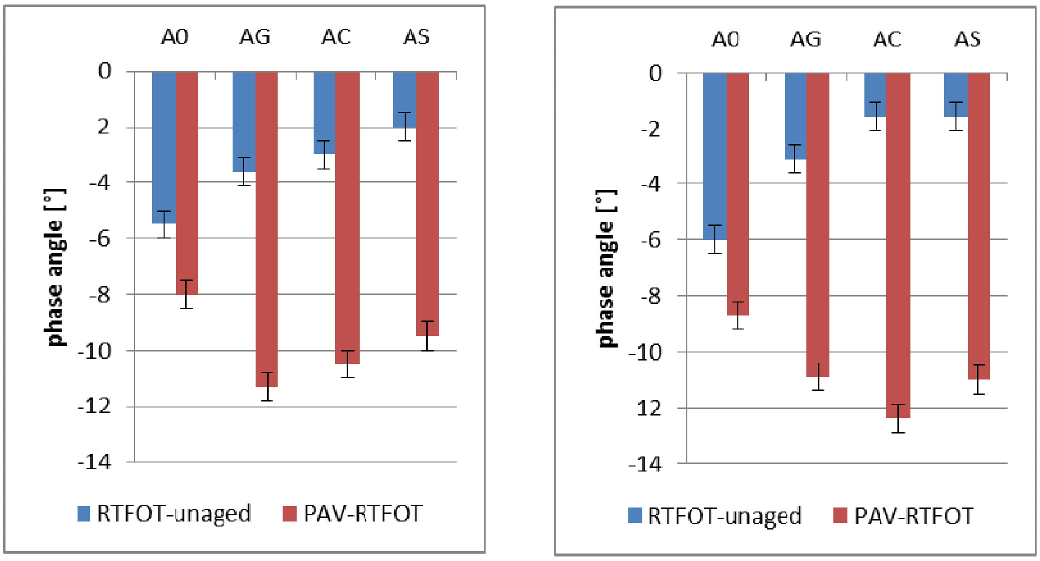

Figure 56: warm asphalt. Variation of the phase angle at 20° (left) and 50° (right).

5.5.4 FIELD AGED BINDER

From a rheological point of view, the behaviour binder recovered from the test field is reproduced well by the RTFOT aged binder (Figure 50). On the other hand, the results of the infrared analysis lead a different conclusion: the oxidation of the field binder is almost as high as the oxidation of the PAV aged binder (Figure 57). However, the oxidation after PAV seems to have little influence on the rheological behaviour of the binder.

The difference in the results of the rheological analysis and chemical analysis, moreover, shows that a direct correlation between the two analyses is not always possible and advisable.

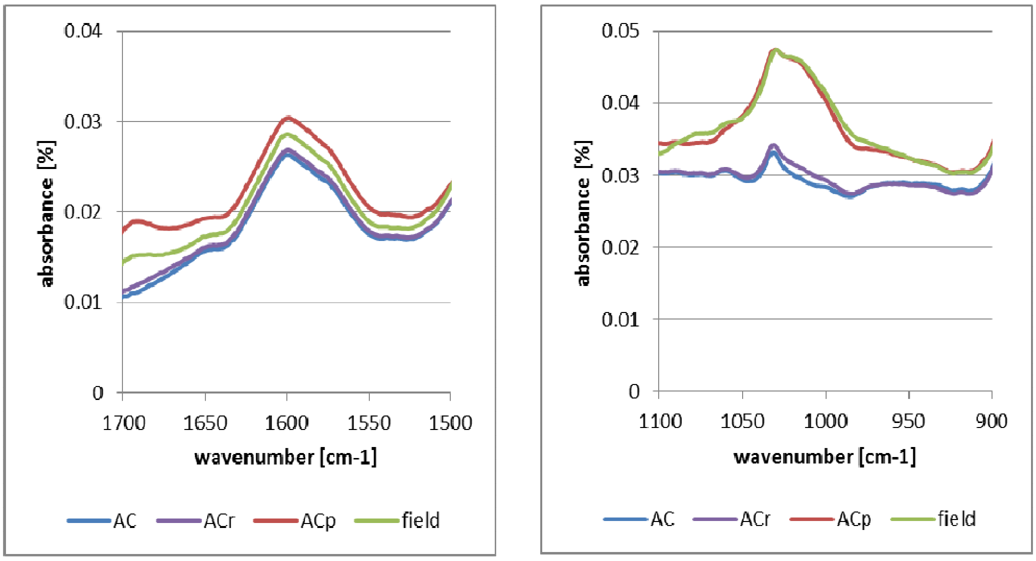

Figure 57: warm asphalt. FR-PACK binders' carbonyl peaks (left) and sulfoxide peaks (right).

5.6 CONCLUSIONS

In this work the influence of the working temperature reduction on short and long term aging has been investigated. The rheological properties have been evaluated using the softening point and the DSR, while the chemical ones have been evaluated by infrared spectroscopy. Besides, the results concerning one laboratory-aged blend have been compared with the results of the same blend from the test field.

Based on the analysis presented in the previous paragraphs, the following conclusions can be drawn about the laboratory-aged bitumen:

- The lower RTFOT aging temperature for warm asphalt binders representing the mixing temperature shows a significant decrease in the aging behaviour in terms of softening point and complex modulus (DSR), which correspond perfect with the results from the recovered field sample. From the rheological point of view, the short term aging is reduced when the WMA technique is applied. When long term aged, instead, the difference between WMAs and HMA tends to disappear.
- The long term aging after PAV is similar for modified and non-modified binders. Due to the recent construction date no field sample was available to be compared to the lab results. The rheological data about the wax-modified bitumen show and increased resistance to deformation at medium to low temperature, which is not influenced by the aging of the material.
- The infrared spectra analysis reveals that the short term oxidation is largely reduced and that the effect of this reduction is still present in the long term aged materials.

From the comparison of the laboratory aged samples and the field ones the following conclusions can be drawn:

- The RTFOT is representative of the rheological behaviour of a short aged material but not of its oxidation state.
- A direct correlation between the rheological and the chemical results it is not always possible and the oxidation state might not have a strong influence on the rheological behaviour of a binder.

CHAPTER 6: EFFECTS OF AGING ON POLYMERS IN POLYMER-MODIFIED BITUMEN

6.1 INTRODUCTION

Since the 1970s synthetic polymers have been added to conventional bituminous binders to improve mechanical and rheological properties of the latters and thus answering the increasing design requirements of the pavements. Polymer Modified Bitumen (PmBs) are mainly used for highly trafficked roads or for innovative pavements, like draining or noise-reducing surface layers, thanks to their increased resistance to rutting, low temperature cracking, stripping and aging(Mouillet, et al., 2008).

Most of the used additives belong to the elastomeric family and, within this group, the styrene block copolymers have shown the best potential to blend with bitumen(Airey, 2003). Their structure consists of Styrene Butadiene Styrene (SBS) tri-block chains, whose strength the elastic poly-butadiene middle part and the two poly-styrene end parts, which allow good fixation in the bitumen matrix.. The polystyrene end blocks are responsible for the strength of the polymer, while the polybutadiene blocks are responsible of its elasticity (Sengoz, et al., 2008).

However, also the polymers suffer from aging and degradation both during mixing and during the service life due to the double bonds of the poly-butadiene part, which are sensitive to oxidation, which result in cleavage of the polymer. The issue is to understand the extent of this phenomenon and its effects on the PmBs properties on the short and long period.

Three different polymer modified bitumen have been studied with laboratory tests: the RTFOT was performed to simulate the short term aging, while the long term one was simulated by the PAV test.

6.2 OBJECTIVE AND SCOPE

The aim of this part of the study is to analyse the effects of the polymer degradation in polymer modified bitumen and to find a correlation between chemical and rheological properties.

The polymer degradation and the chemical changes in bitumen have been analysed by Infrared Spectroscopy and Gas Permeation Chromatography, which allowed identifying the products of aging, while in order to assess the rheological changes complex moduli and phase angles have been measured. The tests have been run for every aging condition

6.3 LITERATURE REVIEW AND STATE OF THE ART

Polymer modified bitumen is a modified bitumen obtained incorporating the polymer in the bitumen using mechanical mixing or chemical reactions. The properties of the final blend of polymer and bitumen depend on the characteristics of the original materials, but also on the polymer content and on the manufacturing process (Lu, et al., 19997).

The polymers used to additive the bitumen can be divided in two families (Bulatovic , et al., 2012):

- Thermoplastic polymers: they have a glass transition temperature higher than the bitumen and are used to improve the resistance of the latter to high temperatures
- Elastomeric polymers (or rubbers): they have a glass transition temperature lower than the bitumen and are used to improve the resistance of the latter to low temperatures

SBS copolymers combine both elastomeric and thermoplastic properties and are therefore know as thermoplastic rubbers(Airey, 2003). This dual behaviour, together with his relatively low cost, has made SBS the most used polymer in bitumen modification (Wu, et al., 2009) and nowadays a great variety of different SBS polymers is available, with different molecular architecture and block lengths (Canto, et al., 2006).

Considerable research has been undertaken in the investigation of the aging effects on SBS modified binders. Airey (Airey, 2003), studying the rheological changes in laboratory aged modified bitumen, found that they have different behaviour depending on the polymer content: the low polymer content binders show stiffening comparable to the one of normal bitumen, while ones with the high content show a shift toward more elastic behaviour. The same results were found by Senegoz and Isikyakar (Sengoz, et al., 2008) analysing the bitumen with fluorescent microscopy.

Cortizo et al(Cortizo, et al., 2004) studied the chemical changes that occur with aging and found out that products of the polymer degradation can combine with some bitumen components (like C=C double bonds) increasing polarity and molecular size of the latters. They also found that the differences in the architecture or molecular weight of different kinds of SBS are responsible of important differences in the interaction between bitumen and polymer or degradation products. Mouillet et al (Mouillet, et al., 2008) found that SBS modified bitumen becomes more homogenous when aged, because of polymer degradation and consequent better compatibility between smaller polymer chains and bigger molecules of the oxidized bitumen. On the contrary, Wu et al (Wu, et al., 2009) found that the changes that occur during aging lead to an incompatible system in the blend, thus impairing the function of SBS modifiers. They also proved that after aging the mechanical and rheological behaviour of PmB tends to be like the one of un-modified bitumen.

Studying the differences between laboratory and field aged PmBs, Liu et al (Liu, et al., 2014) found that the first have more asphaltenes than the latter and that the aging time to correctly reproduce field aging are different for chemical and rheological properties.

6.4 EXPERIMENTAL

6.4.1 MATERIALS

Three modified bituminous binders have been used. The samples were part of a wider project concerning fracture toughness evaluation (Bueno, et al., 2014) on polymer-modified binders. The materials were provided by the manufacturer, thus binder formulation and modification as well as polymer type and content are unknown.

The three binders were artificially aged with the RTFOT and the PAV techniques.

Binder type	Characteristics	Labels
PmB 50/70-53	Polymer modified bitumen	F4
PmB 25/55-65	Polymer and wax modified bitumen	F6
PmB 90/150-60	Polymer modified bitumen	F15

Table 6: labels for the Polymer modified Bitumens

6.4.2 TEST METHODS

The rheological properties of the binders have been measured using the DSR in the oscillation mode, at 0°C, 10°C, 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C and different frequencies, to get enough data for master curves and black diagrams (§2.3.3). For every material, two geometries have been used:

- 8mm geometry, for 0° to 40°C

– 25mm geometry, for 40° to 80°C

The infrared spectra of the binders have been obtained using the ATR-FTIR in the absorbance mode to determine the aging indexes (see §3.2.4.2) and the changes in the polymers’ peaks. Eventually, the GPC has been used to assess the chemical degradation of polymers (see §3.3.2 and §3.3.3). Only the retention times of the peaks and their broadness have been considered. The molecular weights of the bitumen blends were not evaluated.

6.5 RESULTS

6.5.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

The infrared spectra reveal the presence of the polymers in the blend: the styrene peak is showing up at 697 cm^{-1} (C-H aromatic bonds) and the butadiene peak at 964 cm^{-1} (C-H vinyl bonds).

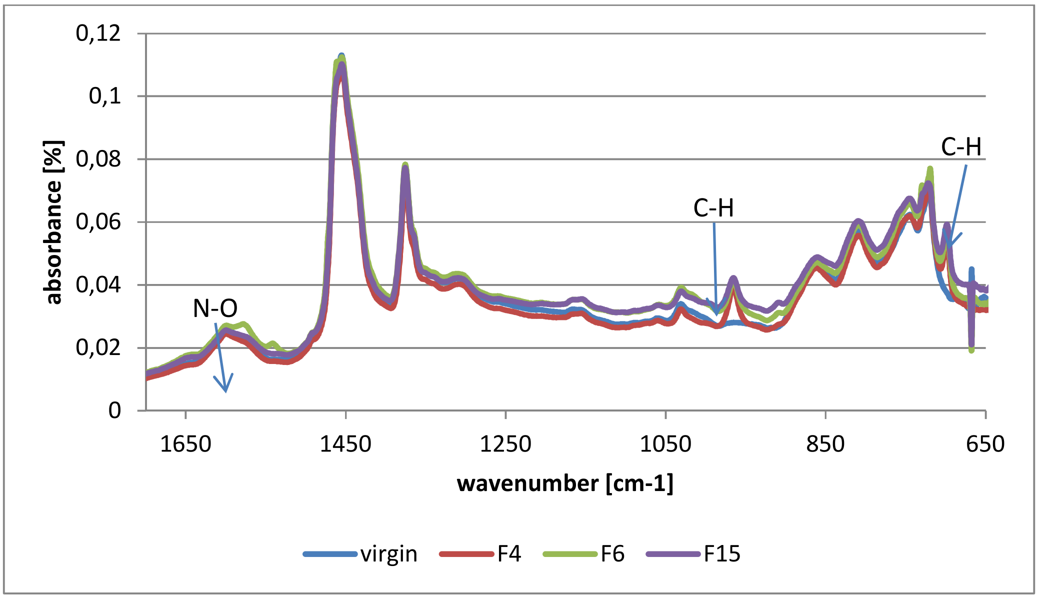

Figure 58: PmBs. Infrared spectra of unaged binders.

The main chemical modification detected by the infrared analysis is the oxidation of the bitumen components. After the RTFOT the Carbonyl Index shows the same grade of oxidation for all three materials, while the Sulfoxide Index is higher for the F6 and F15. After the PAV, on the contrary, the Sulfoxide Index is almost the same for all three materials, while according to the Carbonyl Index the F4 the more oxidised.

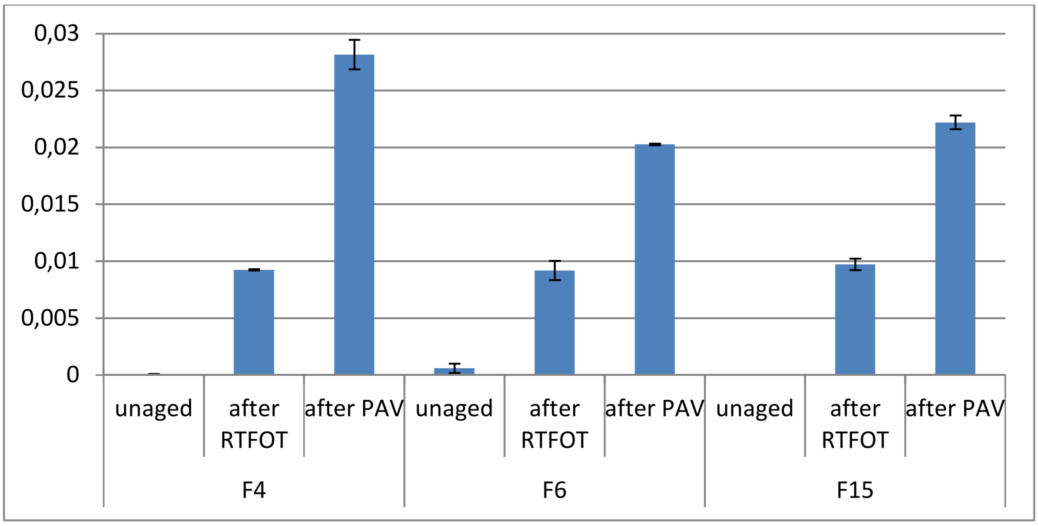

Figure 59: PmBs. Carbonyl Index.

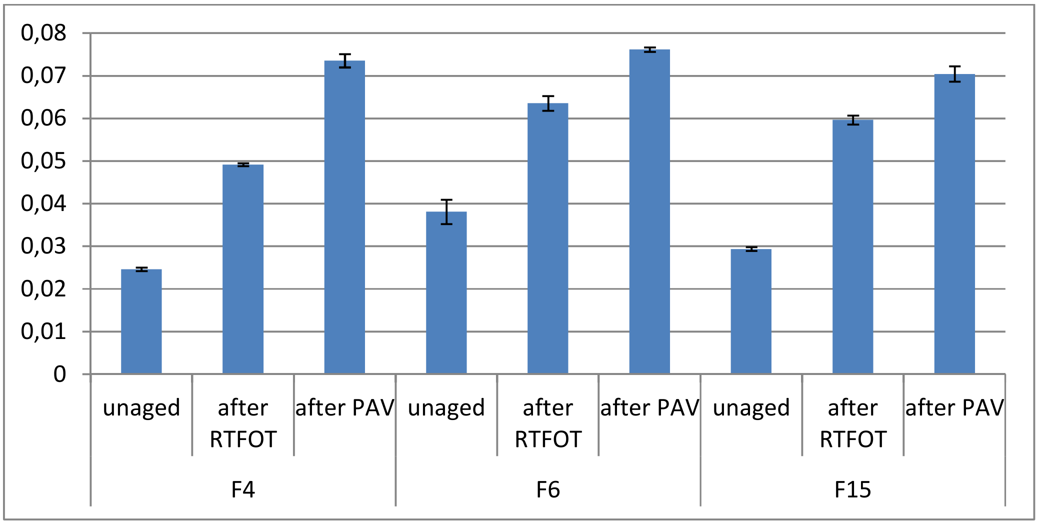

Figure 60: PmBs. Sulfoxide Index.

For the purposes of this study two ageing indexes related with the polymers have been defined:

$$Butadiene\ Index\ (CI) = \frac{A_{964}}{A_{CH_2}+A_{CH_3}}$$
$$Styrene\ Index\ (StI) = \frac{A_{697}}{A_{CH_2}+A_{CH_3}} \qquad (22)$$

where A_{964} is the area centred on the butadiene peak, at about 964 cm^{-1}.

A_{697} is the area centred on the styrene peak, at about 697 cm^{-1}.

The degradation of the polymers could be detected analysing the Butadiene Index only in sample F4: in this binder the index is clearly decreasing after the aging procedures, while in the other two bitumens its value is almost stable or slightly increasing.

The Styrene Index appears to be stable for the F4 and increasing with aging in F6 and F15. This behaviour might be due to the degradation of other components of the binder, whose products have a peak partially overlapping with the styrene one.

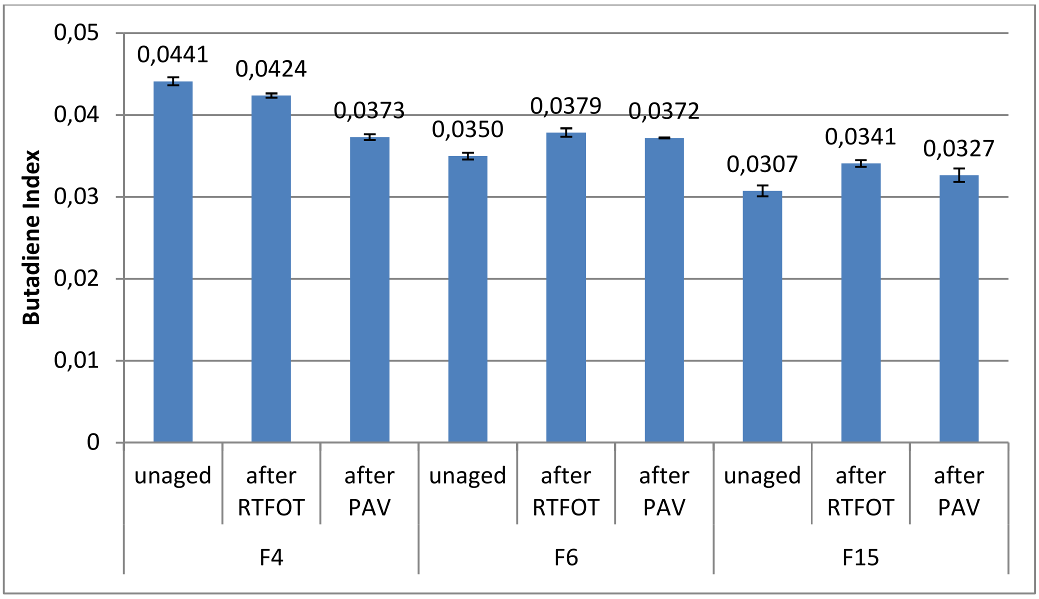

Figure 61: PmBs. Butadiene Index.

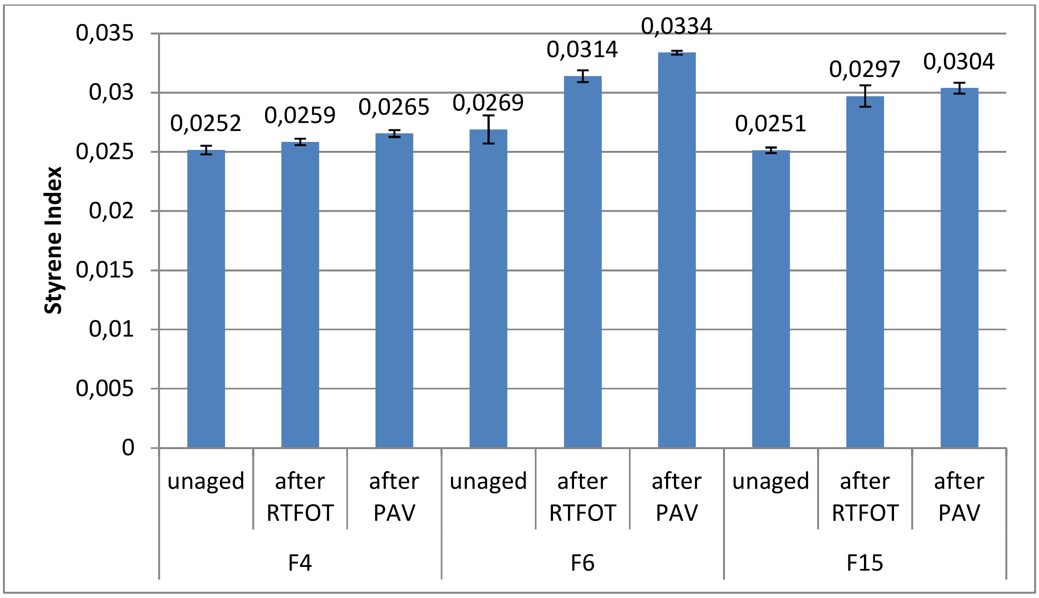

Figure 62: PmBs. Styrene Index.

6.5.2 DYNAMIC SHEAR RHEOMETER

In order to show the viscoelastic properties of PmBs the so called “Black Diagram” has been used: in it, the complex modulus is plotted against the phase angle, irrespective of experimental temperature and frequency(Djonlagic, et al., 1996). For PmBs, in fact, the TTS principle is not always valid and often the master curve cannot be defined (Airey, 2002): in this study, for instance, it was possible to define the master curve only for the F4 modified bitumen.

The control PmB (Figure 63) shows the typical behaviour of bitumen modified with a low percentage of polymers (Airey, 2003): for G* higher than 10^5 the behaviour is influenced mostly by the bitumen and between 10^5 and 10^4 a plateau can be found, while for lower values of complex modulus the phase angle increase again. Upon aging, this bitumen becomes more elastic and does not change the shape of the curve, showing behaviour similar to the one of the penetration grade binders: probably, the degradation of the polymer is not as influent as the degradation of the bitumen itself.

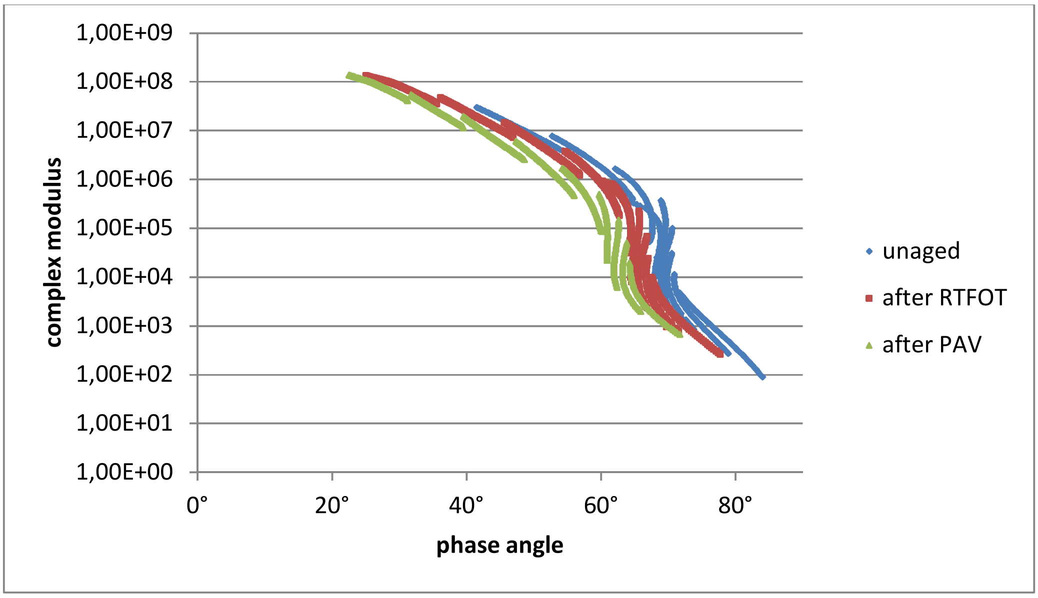

Figure 63: PmBs. Black Diagram of F4.

The bitumen modified with the non-waxy polymer (Figure 64) is more elastic then the reference one for every aging condition and shows higher influence of the polymer degradation: for G* lower than 10^4 the aging increments the viscosity of the material, probably because of the degradation of the polymer.

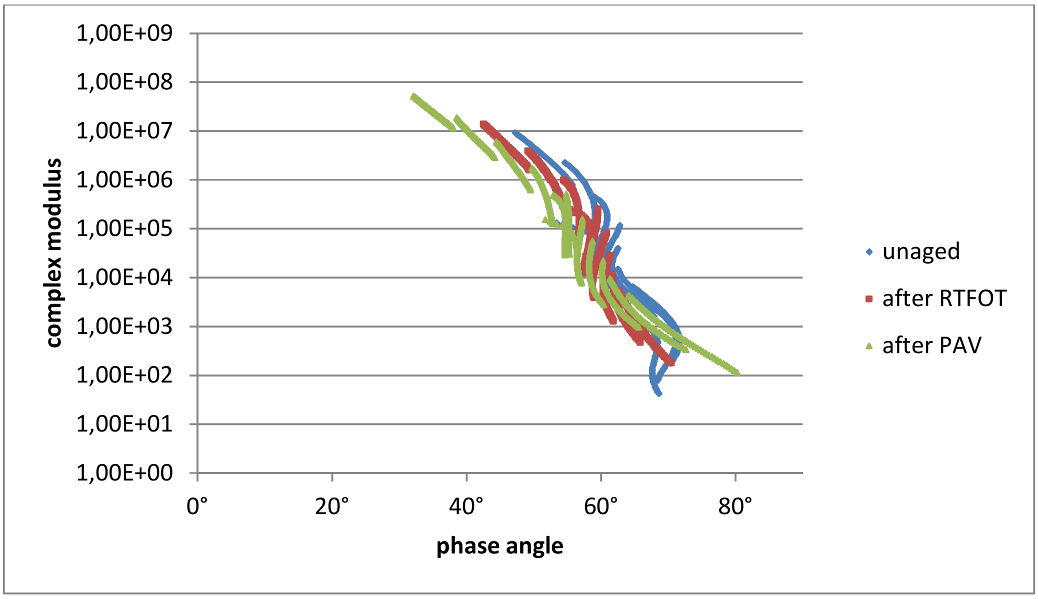

Figure 64: PmBs. Black Diagram of F15.

Eventually, the bitumen modified with the waxy polymer is the most elastic of the three materials. In unaged conditions it shows the typical behaviour of high polymer content bitumen (Airey, 2003): for G* higher than 10^5 the behaviour is influenced mostly by the bitumen and between 10^5 and 10^4 a plateau can be found, while for lower values of complex modulus the phase angle decrease.

The deterioration of the polymer during the aging tests is clear in this material: after the RTFOT for low values of complex modulus the behaviour of the material changes dramatically and gets closer to the behaviour of the other materials (and of penetration grade bitumen). The PAV aging emphasizes this effect and makes the bitumen almost linear.

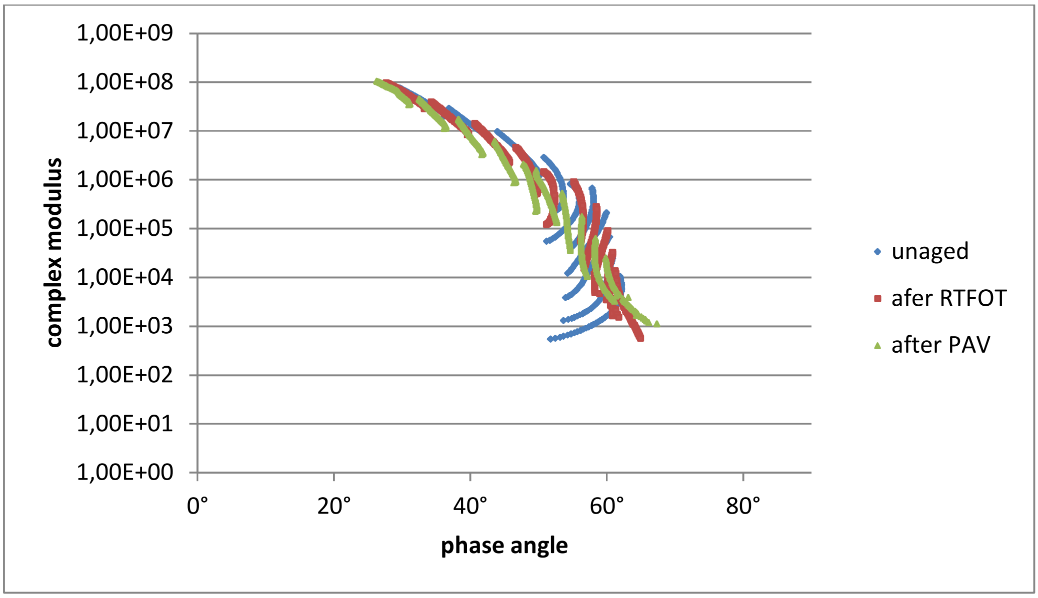

Figure 65: PmBs. Black Diagram of F6.

Comparing the charts for unaged binders and the same materials after the PAV test, the effects of aging can be seen quite easily: the behaviour becomes more uniform, with almost no differences between F6 and F15 while the plateau disappear almost completely in all three materials.

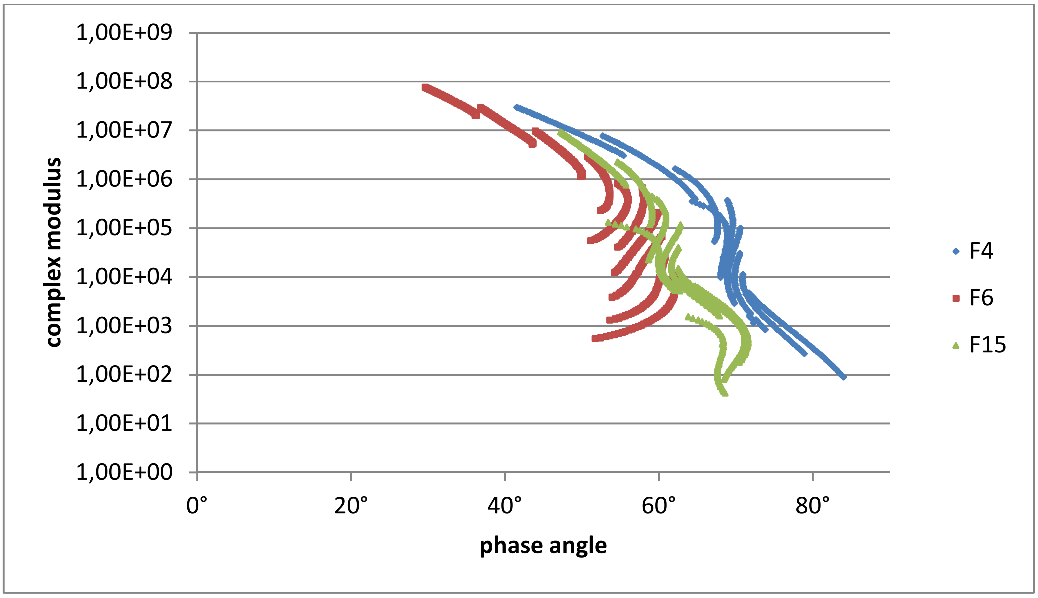

Figure 66: PmBs. Black Diagram of unaged binders.

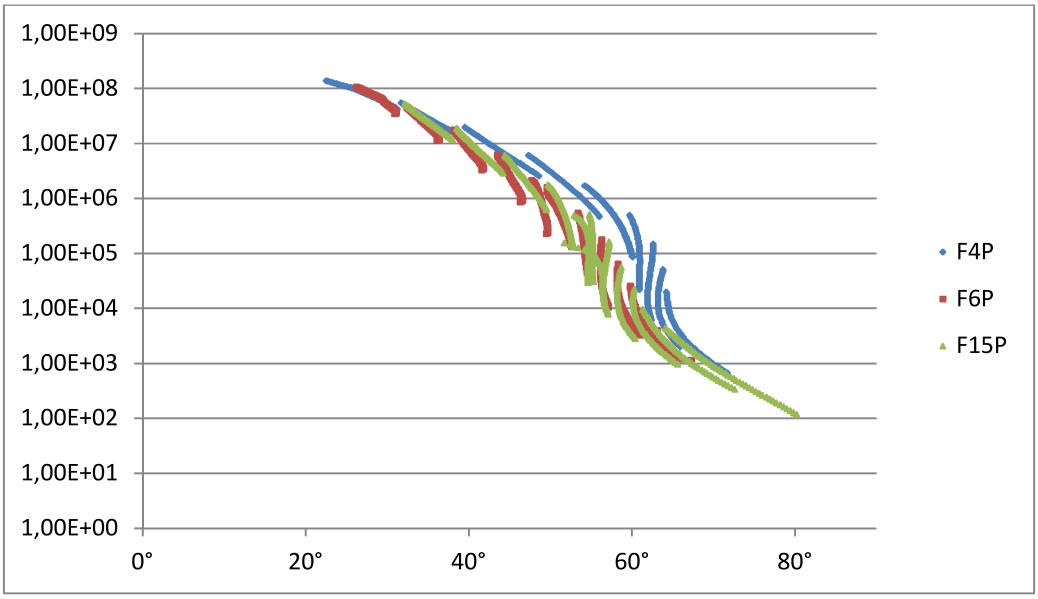

Figure 67: PmBs. Black Diagram of PAV aged binders.

Although from the black diagram the aging process seems to affect the F6 more than the other two materials, the ratios between unaged and aged complex modulus for a specific frequency (5.15rad/s) shows different results: after the PAV test the stiffness in F6 is increased of about 2%, while for F15 the increment is higher than 3% and for F4 higher that 4%.

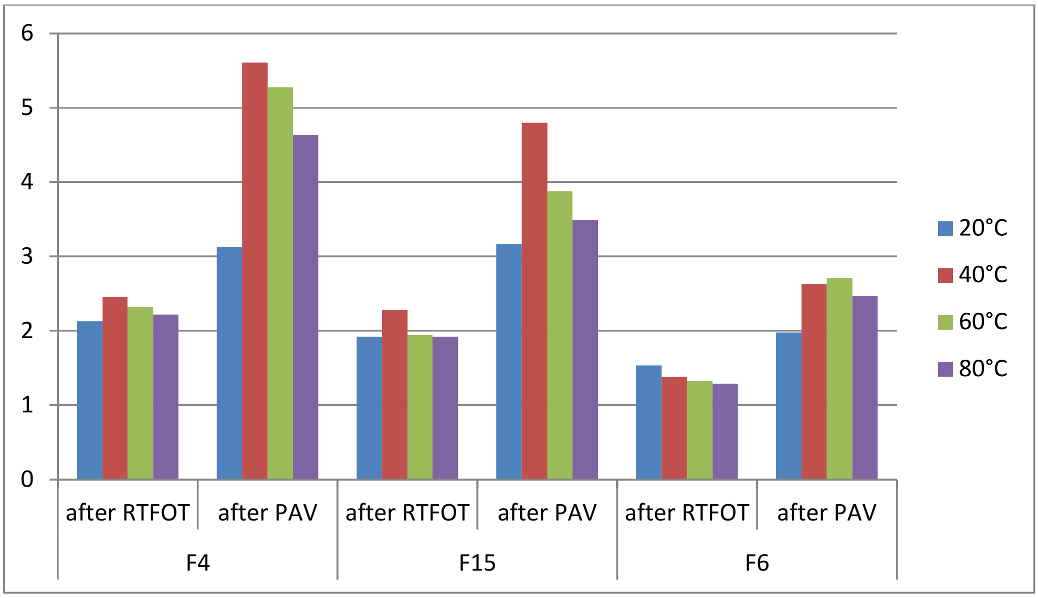

Figure 68: PmBs. Complex modulus ratio at 5.15rad/s.

6.5.3 GEL PERMEATION CHROMATOGRAPHY

The constituents of bitumen have different molecular weights with reference to the polymers in the PmB and can therefore be separated be GPC. In this study, which investigated aging characteristics of polymers in PmB samples, Three different PmB-samples have been analysed in different aging states (unaged, after RTOT and PAV) to see to which degree the polymer has been changed or destroyed.

In the reference binder (F4) the polymer peak has its maximum about 12.9 min and it lasts for about 0.4 min. After the RTFOT the peak has almost disappeared and, after the PAV, it is completely gone. On the same time, the aging procedure oxidizes also the bitumen: the bitumen peak is slightly reduced and the area of the medium retention time (14 to 16 min) molecules is largely increased. (Figure 69)

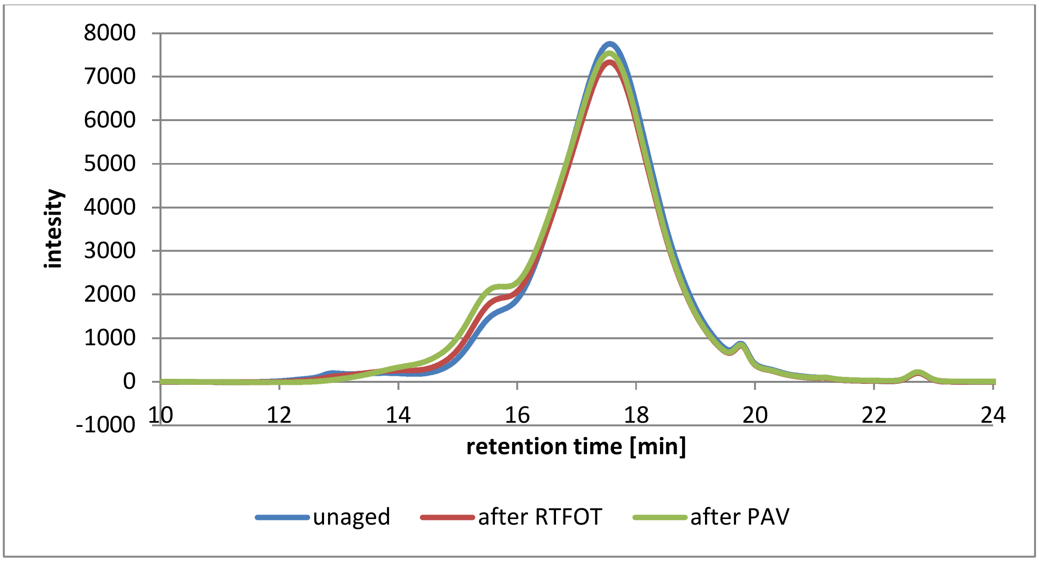

Figure 69: PmBs. UV chromatogram of F4 samples.

Both F15 (Figure 70) and F6 (Figure 71) modified binders have two peaks due to the polymers: the first one has its maximum about 12.4 min and it lasts for about 0.6 min, while the second one has its maximum about 13.1 min and it lasts for about 0.5 min. After the RTFOT both peaks are largely reduced but can still be distinguished. After the PAV the first peak is completely gone and the second one has been absorbed by the area of the degraded bitumen molecules. As for the reference binder, also the bitumen suffers some damage and the products of this damage can be found in the area of medium retention time.

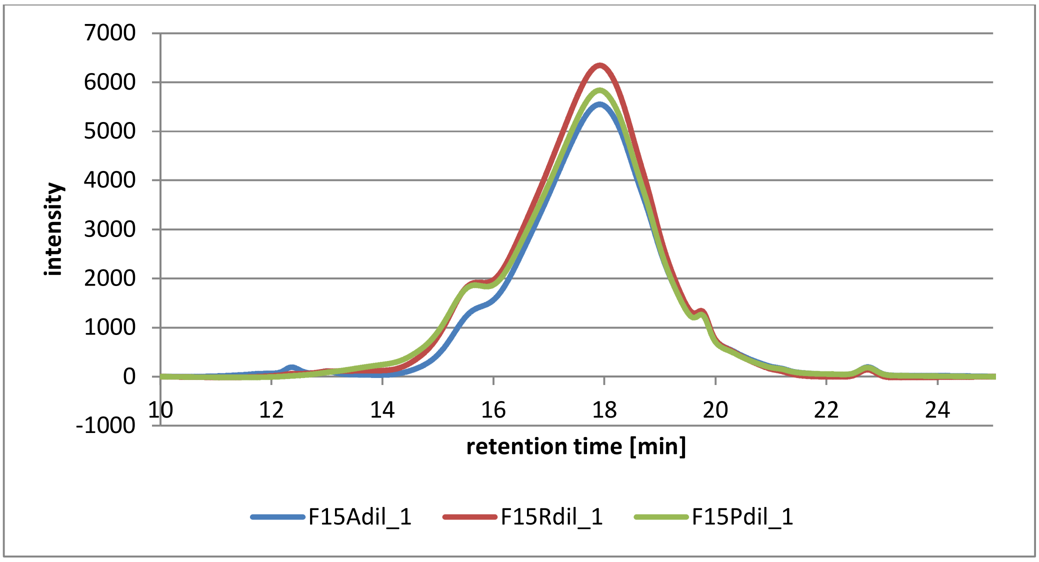

Figure 70: PmBs. UV chromatogram of F15 samples.

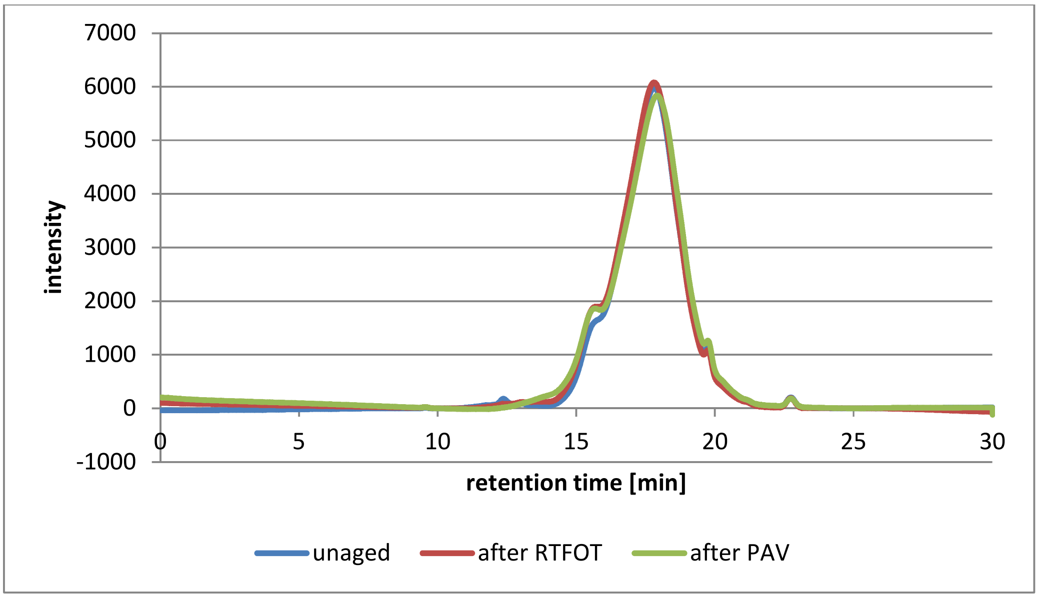

Figure 71: PmBs. UV chromatogram of F6 samples.

To investigate the chemical changes more eaesily the GPC curve has been separated in four different areas, whose separation points were based on the retention time of the valleys of the peaks:

- First polymer peak area (A_1): 12min to 13.22min for F4, 12min to 12.82min for F6 and F15.
- Second polymer peak area (A_2): 12.82min to 13.4min for F6 and F15.
- Medium retention time area (A_m): 14.3 min to 16 min for F4, 13.4min to 16min for F6 and F15.
- Bitumen peak area (A_b): 16 min to 19.55 min for F4, 16 min to 19.6 min for F6 and F15.

Then four Ageing Indexes (AI) have been defined as the ratios between the previously defined areas and the total area above the baseline, between 12min and 22min:

- AI_1: from the chart below it can be seen that roughly half of the degradation occurs in the short period aging and that after the long period one the polymer is almost completely degraded.

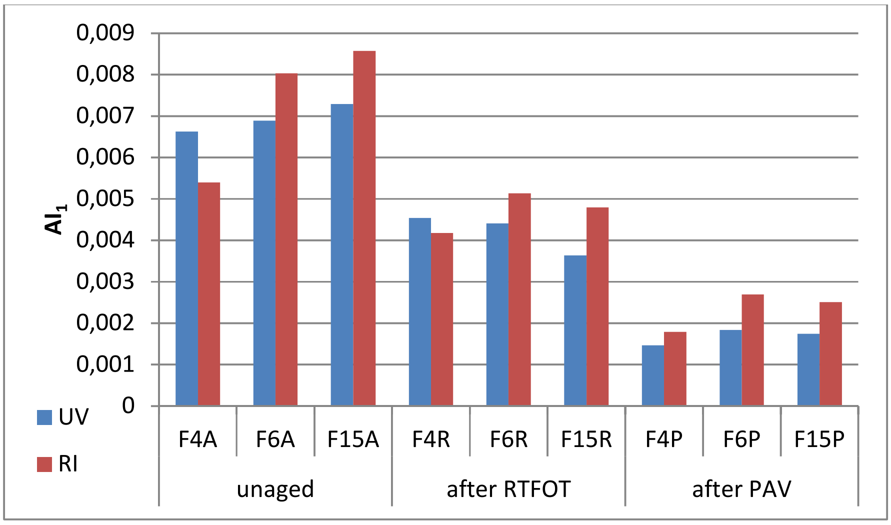

Figure 72: PmBs. AI_1.

- AI_2: the products of the degradation of the first peak and of the bitumen peak are partially located in this area. The stable value of the index is probably due to that, even though it cannot be excluded that this kind of polymer could resist to aging degradation.
- AI_m: the products of the degradation of the first peak and of the bitumen peak are mainly located in this area. Thus, the index is slightly increasing during the aging process.

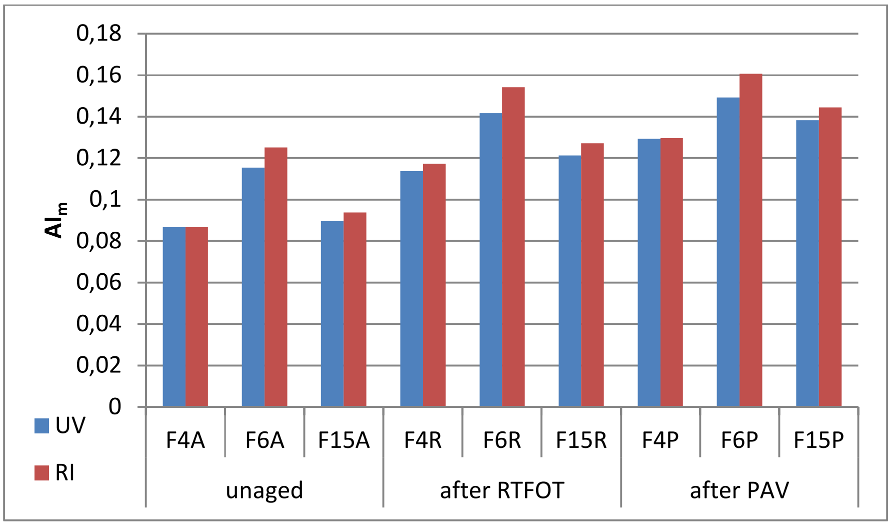

Figure 73: PmBs. AI_m.

- AI_b: this index is slightly reduced by the aging, because during this process the maltens components are substituted by heavier asphaltenes and because of the loss of volatile components.

The presence of wax in one of the binders could not be detected by this kind of analysis.

6.6 CONCLUSIONS

In this part of the study the aging of polymer modified bitumen has been investigated. The polymers’ degradation have been evaluated using infrared spectroscopy (FTIR) and size-exclusion chromatography (GPC), while the rheological properties of unaged and aged binders have been evaluated using the DSR.

Based on the analysis presented in the previous paragraphs, the following conclusions can be drawn about the degradation of the polymers:

- The standard aging procedures cause the degradation of polymers in PmBs. The chemical analysis (GPC) shows that roughly the 70% if the polymers’ volume is degraded to smaller compounds after the long term aging. From a rheological point of view (DSR), the behaviour of aged PmBs is similar to the one of non-modified aged binders, likely because of the demolition of the polymers due to the aging.
- Half of the loss of polymers’ volume in the binders is due to the short term aging and for two out of three binders the rheological behaviour changes after the RTFOT from the one typical f PmBs to the one typical of pen-grade binders. This suggests that PmBs with low polymer content might not have better real life performances than non-modified binders.
- The FTIR spectroscopy is not able to show the degradation of the three analysed polymers: This is because only a small percentage of the C-C double bonds of the polymers are destroyed. But the cut of one double bond is already enough to show a significant change in the rheological behaviour of the PmB. This can not be detected by FTIR, because it is showing the sum of all C-C double bonds.

CHAPTER 7: AGING OF REPEATED RECYCLED ASPHALT

7.1 INTRODUCTION

Since the late Seventies asphalt pavements have been reclaimed and recycled, in order to reduce both the amount of waste material to dispose of and the use of expensive virgin materials.

Reclaimed Asphalt Pavement (RAP) is a complex material: it is composed of aggregates, filler and oxidised binder. The latter is stiffer than the virgin one and has different performances, so its presence must be taken into account in the mix design.

Repeated recycling is one of the main issues nowadays: the massive use of reclaimed asphalt, indeed, dates back to more than twenty years ago, thus leading to the need of a destination for the by now damaged second generation asphalt. So, as to reduce the waste material, the higher amount of this second generation asphalt must be reclaimed and re-used, along with the minimum amount of virgin materials possible.

In order to understand how the several times recycled binder within the RAP can affect the properties of the final binder, aging till the fourth generation has been reproduced in the laboratory: the original binder has been aged and, after that, mixed again with some virgin bitumen. Then, rheological and chemical properties of the different blends have been evaluated.

7.2 LITERATURE REVIEW AND STATE OF THE ART

When a pavement has expired its service life, the rutted and cracked asphalt must be milled and disposed. In order to reduce the amount of waste material, the reclaimed asphalt is recycled in the new pavement.

The national standards of various countries are limiting the percentage of RAP that is allowed in a mix (Al-Qadi, et al., 2007): in fact, past studies have found that, when it is mixed with virgin materials, the bitumen of the RAP blends with the virgin one (Hussain, et al., 2013) and modifies the properties of the latter according to the amount of RAP in the mix (Bowers, et al., 2014). It has been suggested that when less than 15% of RAP is added to the mix the blend can be considered as stiff as the virgin bitumen, while when more than the 25% of it is added the stiffness of the resulting grade must be evaluated for every specific case (Kandhal, et al., 1997).

In order to improve the environmental and economic benefits of the use of RAP, high rates of the latter should be used. Several studies, both in laboratory and in the field, have shown the feasibility of mixing including up to 80% of RAP. In fact, recycled mixtures seem to behave like conventional high modulus binder (Valdes, et al., 2011), especially when high percentage of fine RAP are added. The same study showed also that aged RAP blends have the same rheological and mechanical properties of aged high modulus binders, thus leading to the possibility of recycling RAP aged binders as if it was conventional binder.

7.3 EXPERIMENTAL

7.3.1 MATERIALS AND AGING PROCEDURE

The base binder used is a bitumen 70/80. The aged binders have been obtained by the following procedure:

- The base bitumen has been mixed with aggregates and aged for four days at 100°C.
- The bitumen has extracted and recovered from the RAP thus obtained.
- The recovered binder has been mixed with a blend of 70/80 (22%) and 160/220 (78%), in order to get the same penetration value of the base binder.
- The blend has been mixed with aggregates and aged as at the 1st point.

The cycle has been stopped at the 2nd point to simulate the RAP at the first recycling. To get the second/third recycling binders the procedure above has been run two/three times.

In the table below (Table 7) the percentages of virgin and aged binder in every blend are shown.

	blend			
binder	virgin mix	1st recycling	2nd recycling	3rd recycling
new	100%	60%	60%	60%
recycled once		40%	24%	24%
recycled twice			16%	9,6%
recycled three times				6,4%

Table 7: percentages of virgin and aged binders in the blends.

7.3.2 TEST METHODS

The rheological properties of the blends have been measured using the DSR in the oscillation mode and every 5°C. For every material, two geometries have been used:

- 8mm geometry, for 0° to 40°C
- 25mm geometry, for 40° to 80°C

The infrared spectra of the blends have been obtained using the ATR-FTIR in the absorbance mode and, then, the oxidation indexes have been evaluated.

7.4 RESULTS

7.4.1 DYNAMIC SHEAR RHEOMETER

In order to show the rheological changes that occurred to the binder during the recycling process, the master curves of virgin and recycled materials are plotted (Figure 74).

While the first recycling process causes a remarkable hardening in the binder, the complex modulus is not increased by the following steps. Hence, the presence of material which has been recycled more than once seems not to have any effects on the rheological properties of the studied blends.

On the other hand, blending softer and stiffer binder to get a specific penetration grade seems not to reproduce the actual rheological behaviour of the original binder.

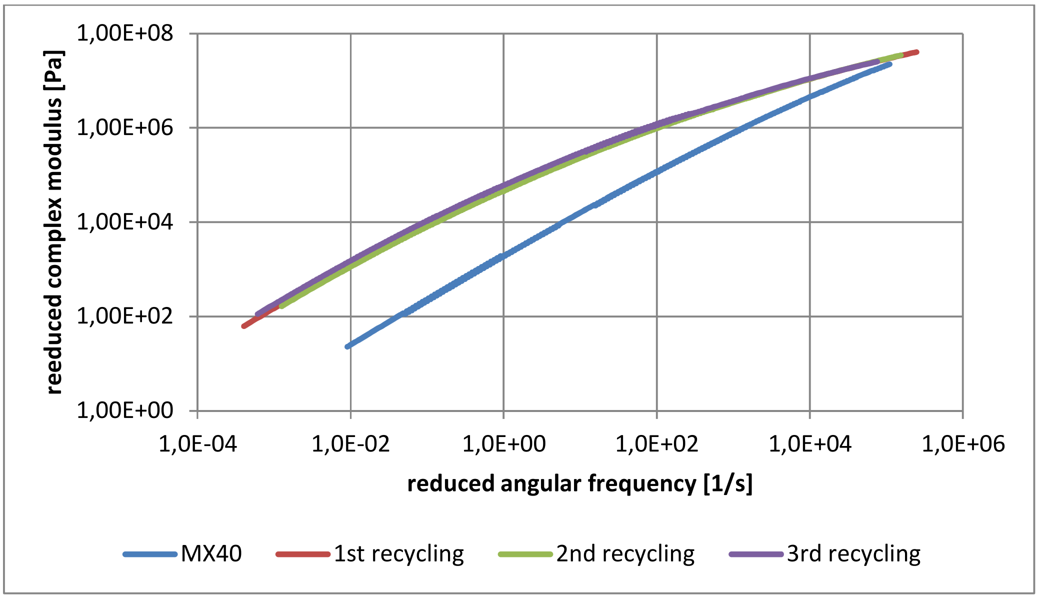

Figure 74: repeated recycling. Master curves.

7.4.2 FOURIER TRANSFORMAT INFRARED SPECTROSCOPY

From the FTIR spectra the Oxidation Indexes have been evaluated. As it is shown in the charts below (Figure 75), the oxidation is not increased by the repeated recycling process: the main changes in the chemical properties are the ones that occur in the first aging step and the presence of several times recycled materials has no influence on them.

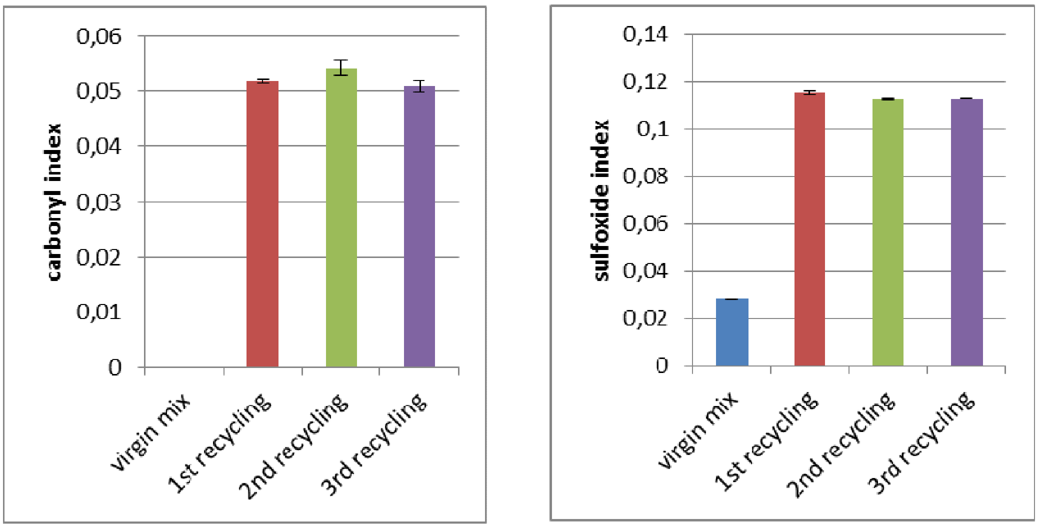

Figure 75: repeated recycling. Carbonyl (left) and Sulfoxide (right) Indexes

7.5 CONCLUSIONS

In this study the influence of repeated recycled RAP on the binder has been investigated, both from a rheological and chemical point of view. The following conclusion can be drawn:

- The amount of oxidation products (expressed as Oxidation Indexes) seems to be not increased by recycling the bitumen more than once. Hence, from a chemical point of view, no drawbacks for the repeated recycling can be pointed out.
- The rheological behaviour of several time recycled blends is almost alike the one of simple RAP. Thus, also from a rheological point of view, no drawbacks for the repeated recycling can be pointed out.
- Comparing the rheological properties of the original binder and of the blends, it can be seen that the latters are stiffer than the former, despite the blending of RAP wit binder softer than the original one. Thus, blending softer and stiffer binders according to the penetration value to get the mechanical properties of a goal binder is not always reproducing the actual rheological properties of the latter.

CONCLUSIONS

In this thesis three cases of bitumen aging have been studied, assessing both rheological and chemical properties. The conclusions for the single study case have been displayed in the previous chapters[12], while here some final conclusions on bitumen aging and testing procedures in general will be drawn:

- Within the aging procedures, the PAV test is the most severe. It is able to reproduce the oxidation phenomena that occur in the test field from both a rheological and a chemical point of view. The RTFOT, on the contrary, is less severe and seems not to be always able to reproduce the chemical changes that occur in the mixing process.
- When the aging of bitumen needs to be assessed, the FTIR analysis has proved to be the most interesting: it allows to easily quantifying the increase of C=O bonds, which is a good indicator for bitumen oxidation.
- When, on the other hand, the bitumen is modified with polymers and the degradation of the latters has to be evaluated, the GPC analysis is the most valuable one. Indeed, it

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[12] See §5.6, §6.6 and §7.5.

allows seeing and measuring the degradation of the polymers’ larger molecules into smaller ones.

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TABELS

FIGURES

APPENDIX A: CHEMICAL ADDITIVES SPECTRA

The charts below show the spectra of the additive used for the warm asphalt production (§5.4.1). The main peak of the first one (Figure 76) is at about 1100 cm^{-1}, corresponding to C-O stretching vibrations (possibly due to the presence of either aliphatic ether or secondary alcohol), while the main peak of the second (Figure 77) is at about 1741 cm^{-1}, corresponding to C=O stretching vibrations (possibly due to the presence of esters).

The presence of an additive (PA-PACK) in the mix can be clearly detected comparing the spectra of the mixes and the one of the rejuvenator itself. As it can be seen in the Figure 78, in the fingerprint region the spectrum shows a main peak in correspondence of 1744 cm^{-1}. At the same wavenumber, the only difference between the mixes is found, with a new peak appearing in the modified mix.

This result proves that, despite the little amount of addictive, this shows off in the mix spectrum, thus allowing, if the kind of addictive is not known, to identify it *a posteriori*.

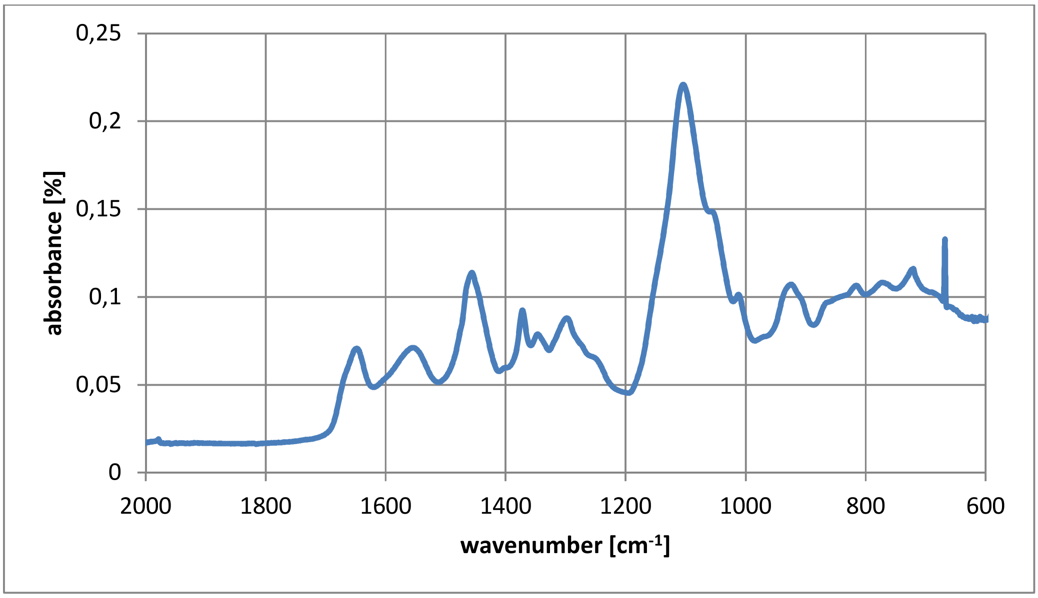

Figure 76: FR-PACK infrared spectrum.

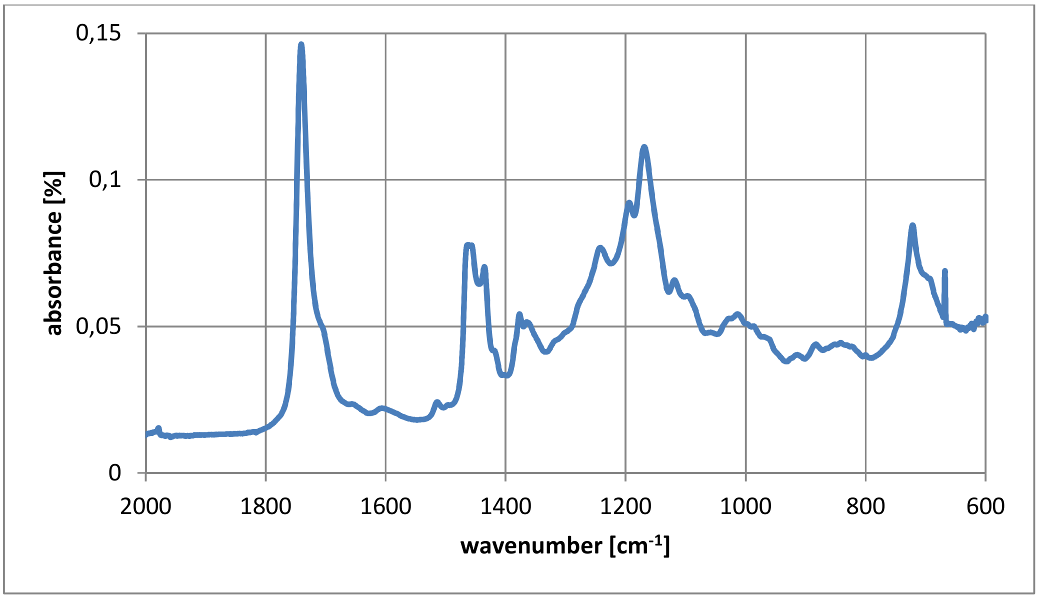

Figure 77: PA-PACK infrared spectrum.

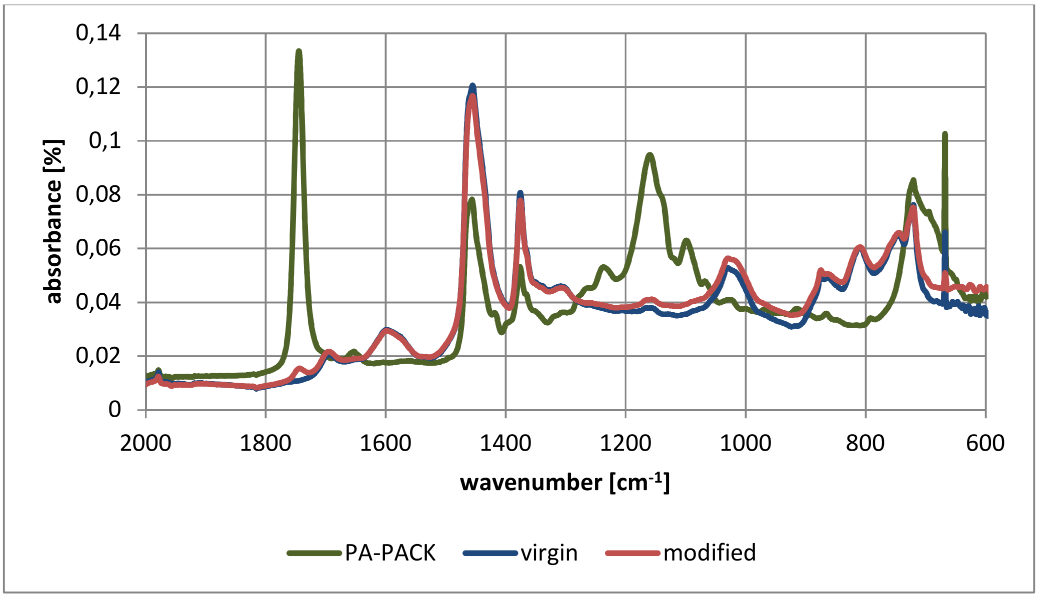

Figure 78: FTIR spectra for additive detection.

APPENDIX A: CHEMICAL ADDITIVES SPECTRA