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Green biomaterials and advanced technologies for road pavements

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ABSTRACT

The main objective aims at developing methodologies and new biomaterials for the sustainability assessment of "green bituminous mixtures". "Green bituminous mixtures" is used in the context as a general term for all types of bituminous mixtures in which specific materials or technologies are used with the aim of reducing the environmental impact and of reducing health risks of workers. *In the present research new bioadditives were developed and tested to improve the adhesion between bitumen and stones, to modify the rheological characteristic of the bitumen as well as rejuvenating properties of the bitumen.*

Chapter 1

1.1 Introduction

1.1.1 Principles of Sustainability

Taken at the recommendation of UNCED, the Concept of the Russian Federation in 1996 "sustainable development" is understood as "improving the quality of life of people" and must be ensured within the limits of the economic capacity of the biosphere, the excess of which leads to the destruction of the natural mechanism of the biotic regulation of the environment and its global changes [1].

1.1.2 Sustainable pavements

Sustainable development, based on the harmonization of economic, environmental and social aspects, has become a major problem for infrastructure managers. From an economic point of view, the construction and maintenance of pavements around the world takes several hundred billion dollars. To help the road agencies, researchers for sustainable management of pavements have studied all of the above aspects [2]. The Ministry of transport of any country is committed to using technology to help create a more sustainable transport system that meets today's needs and at the same time protects the environment for future generations. To increase the service life of road surfaces on bridges and artificial structures, it is necessary to develop, introduce into practice road construction of modified bitumen of improved quality and new materials based on them, capable of providing higher strength and durability of road surfaces [3].

1.1.3 Different types of additives

Recently, the number of cars is on the rise and the load on the roadbed is accordingly increasing. The traditional bitumen binder can no longer provide the required roadway characteristics. In asphalt concrete, bitumen is both a binder and

a waterproofing material. In this case, the performance of the bitumen binder largely depends on its strength at elevated temperatures (heat resistance) and elasticity at negative temperatures (frost resistance) [4]. Additives have been added to improve bitumen performance at extreme temperatures. The additives include typical materials such as: bitumen modifiers [5]; bitumen adhesive additives[6]; stabilizers for SMAS (Crushed Mastic Asphalt Mix)[7]; modifiers for asphalt concrete mix[8]; structural additives for asphalt concrete mix[9].The additives are introduced either into bitumen or directly into the asphalt concrete mixture. In this case, a certain type of additive can be introduced into two different processes: both in bitumen and in asphalt concrete mixture. One way to improve the properties of asphalt concrete is to modify its binder. One of the most common modifiers is polymers [10]. Highly flexible polymers (synthetic rubbers), which give bitumen flexibility at low temperatures, have excellent adhesion and high resistance to abrupt temperature changes (with transition through 0 ° C). Ethylene copolymers (EVA) can improve the properties of bitumen by changing its rheological properties. Changes in rheological properties lead to higher softening temperatures, higher stiffness at high temperatures and, consequently, higher resistance to permanent deformation.

1.2 Problem statement

1.2.1 Sustainable materials for paving

Paving technology is receiving increasing attention in most countries of the world, as all transport infrastructure depends on maintaining roads in good condition. In this regard, post-recycling and vegetable-based materials can be considered as environmentally friendly road pavement materials aimed at reducing the environmental impact and health risks for workers. The use of recycled products known to us (construction, transport waste), polymers (SBS, PmB) in the production of traditional hot mix asphalt (HMA) does not bring the desired result. As the production takes place at a temperature of 150-180°C, this results in energy savings and increased emissions into the atmosphere.

1.2.2 Bio-based recycling asphalt additives

The creation of a reliable, efficient road network today and in the long term should be based on quality design, reasonable savings in financial and material resources, and guarantees of environmental protection. These challenges can be met by environmentally friendly additives derived both from chemical origin and from plant sources.

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Chapter 2

Materials

Application of oil bitumen as a binding material opened up wide opportunities for improvement of road constructions, provided strength, durability, high transport and operational qualities of road surfaces. However, the variety of oil, methods and products of their processing, in addition to the use of different technologies to produce bitumen without taking into account the nature of oil has led to a sharp deterioration in the quality of bitumen and, consequently, reduced service life of road surfaces. It is generally accepted that the characteristics of bitumen are strongly influenced by the way bitumen is produced and processed, and by the characteristics of bituminous crude oil. Therefore, bitumen characterization is a necessary step to ensure a stable system, especially for bitumen modifications. The objective of this review is to gather information on bitumen, from the early stages of processing of crude oil to the latest developments, namely the results of bitumen modification.

2.1 Crude oil overview

Oil is rightly called the blood of modern economy, and the twentieth century is the century of oil and the "hydrocarbon man". In the twentieth century, the oil industry has won key positions and gained crucial importance for economic development, - which in the twenty-first century is a powerful industry of any state [1]. The oil industry in Kazakhstan is one of the main sectors of the economy of Kazakhstan. It ensures investment inflow into the country and replenishes the budget. The first Kazakh oil was produced in November 1899 at Karashungul field in Atyrau region [2]. Production of crude oil in Kazakhstan in December 2018 was fixed at 1547.159 barrels per day. This represents an increase compared to 2017 of 1,466,822 barrels per day in December. Production data are updated annually, averaging 436,806 barrels per day. December 1960 to 2018, with 59 observations. The data reached a record high of 1,547.159 barrels per day in 2018 and a record low of 107.100 barrels per day in 1960. Production data remain active in CEIC and are reported by the Organization of Petroleum Exporting Countries (Fig. 2.1) [3].

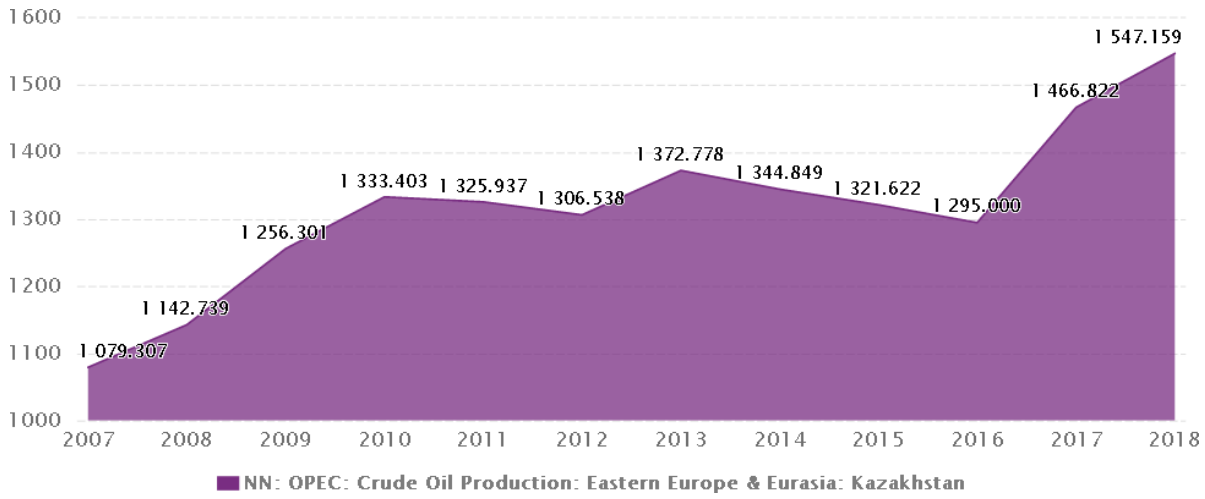

Figure 2.1 Oil Production in Kazakhstan from 2007 to 2018

2.1.1 Crude oil characteristics

Crude oil is a liquid mixture of hydrocarbons of wide physical and chemical composition, which contains mechanical impurities and serves as the main raw material for the production of liquid energy carriers (gasoline, kerosene, diesel fuel, fuel oil), lubricating oils, bitumen and coke. The chemical elements that make up the oil and their ratio characterize the elemental composition. The main composition of oil - carbon (83-87%) - is contained in compounds with hydrogen (12-14%) in the form of complex molecules. These elements represent the main groups of hydrocarbons in oil:

- Alcans CnH2n+2 (methane or paraffin);

- Cycloalkanes (naphthenic or cyclones) are monocyclic CnH2n and polycyclic CnH2n-p (p=2, 4, 6, 8, 10);

- Arena (aromatic)-monocyclic CnH2n-6 and polycyclic CnH2n-p (p=12, 14.18, 20, 24, 30, 36).

The elemental composition of crude oil includes not only organic compounds, but many others (in small quantities), such as hetero-organic resins, asphaltenes, asphaltenes, carbenes, carboids [4].
The most important characteristics of crude oil are [5]: density, sulfur content, fractional composition as well as viscosity and water content, chloride salts and mechanical impurities (Table 2.1).

Table 2.1. Crude Oil's characteristics of properties

Properties	Principles and Definition
density	Depends on the content of heavy hydrocarbons such as paraffins and resins. It uses both relative density expressed in g/cm3 and density expressed in units of the American Petroleum Institute - API, measured in degrees. Relative density = compound mass/water mass API = (141.5/relative density) - 131.5,
Sulfur content	Sulfur compounds in oil are usually harmful impurities. They are toxic, have an unpleasant odor and contribute to the deposition of resins. In water-containing compounds, they also cause intense corrosion of the metal. Especially in this aspect, hydrogen sulphide and mercaptans are dangerous. They have a high corrosive capacity and destroy non-ferrous metals and iron.
Fractional composition	Fractionation is the division of a complex mixture of components into simpler mixtures or individual components. Fractions boiling up to 350°C are called light distillates. Fractions boiling above 350 °C are residues after the selection of light distillates and is called fuel oil.
Content of water	During production and processing, oil is mixed with water twice: when leaving the well at high speed, and during the desalting process, i.e. fresh water flushing to remove chloride salts. In oil and oil products, water can be contained as a simple suspension, thus it is easily stored as a stable emulsion. At this point, it is then necessary to resort to special methods of dewatering.
Mechanical content impurity	Mechanical impurities consist of particles of sand, clay and other hard rocks which settle on the water surface contributing to the formation of an oil emulsion. The mass fraction of mechanical impurities from 0.005% and below is estimated as an absence of impurities.
viscosity	The viscosity is determined by the structure of the hydrocarbons that make up the oil, i.e. their nature and ratio. This characterizes the possibility of spraying and pumping oil and oil products: the lower the viscosity of a liquid, the easier it is to transport it through pipelines for processing.

However, the main analysis for obtaining specific information on the yield of crude oil is the distillation test. The diagram (Fig.2.2) shows how crude oil on an industrial scale is divided into different fractions.

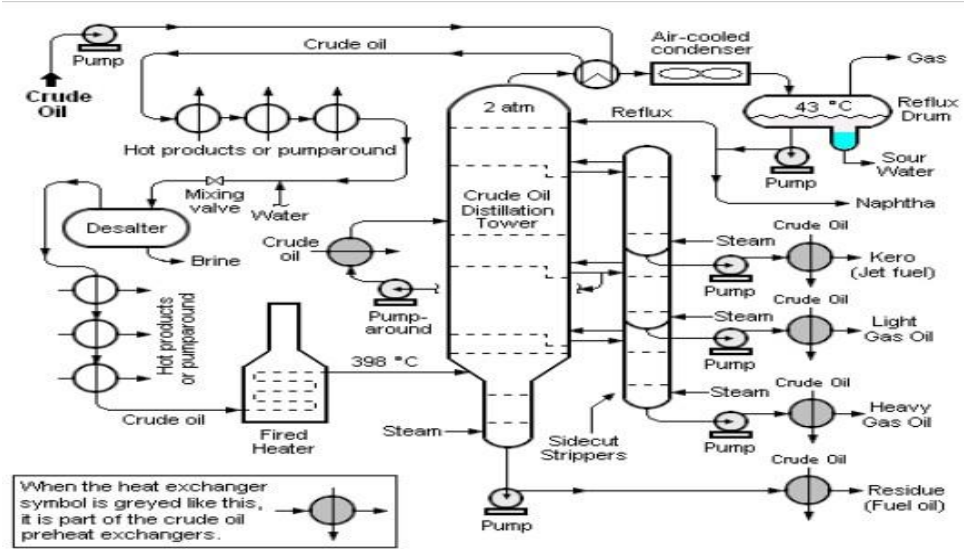

Figure 2.2 Schematic plan of crude oil distillation procedure [6].

This process flow diagram is typical of a crude oil distillation unit. The Crude Oil Distillation Unit (CDU) is the first process unit at almost all refineries. The CDU distills the incoming crude oil into various fractions with different boiling ranges, each of which is then processed in other refineries. CDU is often referred to as an atmospheric distillation unit because it operates at pressures slightly above atmospheric conditions. The incoming crude oil is preheated by exchanging heat with some hot, distilled fractions and other flows. It is then desalted to remove inorganic salts (primarily sodium chloride). After desalting, the crude oil is additionally heated by exchanging heat with some hot, distilled fractions and other flows. It is then heated in a fuel-fired furnace (heater with heating) to a temperature of about 398 °C and sent to the bottom of the distillation unit. Cooling and condensation of the upper part of the distillation column is provided partly by heat exchange with incoming crude oil and partly by air or water condenser. The additional heat is removed from the distillation column by means of a pumping system as shown in the diagram. As shown in the block diagram, the upper fraction of the distillate column is naphtha. The fractions removed from the side of the distillation column at various points between the top and bottom of the column are called side fractions. Each of the side cut-outs (i.e. kerosene, light gasoil and heavy gasoil) is cooled by heat transfer with incoming crude oil. All fractions (i.e. upper naphtha, side compartments and lower residue) are sent to intermediate storage tanks before further processing. In this paper, we consider different fractions for distillation, particularly the bituminous fraction.

2.2 Bitumen

Bitumen is a solid or resin-like product with a density of 0.95-1.5 g/cm^3, which is a mixture of hydrocarbons and their nitrogen, oxygen, sulfur and metal-containing derivatives. It perfectly resists the impact of various chemical reagents, is insoluble in water, resistant to various types of radiation and prolonged thermal impact. Bitumen has no melting point. The transition from solid to liquid state is characterized by a softening temperature, which is determined by the "ring and ball" method. Bitumen hardness can be determined by measuring penetration, while plasticity can be determined by tensile strength (ductility) [7].

Bitumen can be natural - in the natural process of oxidative polymerization of oil, asphalt-rocks in the form of porous rocks impregnated with bitumen, and oil are formed. Natural bitumen can also be in the form of residue after distillation of fuel oil [8]. The chemical composition of bitumen is complex - it contains about 200 different organic substances, and in general they belong to different colloidal-disperse systems, which makes the full chemical characteristics of bitumen very challenging to understand. The different solubilities of the components of bitumen in organic solvents has provided information on its group composition and properties of substances in these groups. A common method of fractioning bitumen is deposition of insoluble lower alkanes part (asphaltenes) and the division of the soluble fraction (maltens) by the method of liquid chromotography into hydrocarbons and resins [9]. Nomenclature of groups of components of bitumen according to Markusson: carboids (part of bitumen, not soluble in what solvents); carbens (soluble in sulfur carbon, but not soluble in quad-chloride carbon); asphaltenes (obtained after separation from bitumen carbens and carboids deposition of individual paraffin hydrocarbons); maltens. According to VNIINP-SoyuzDorNII [10], bitumen is divided into asphaltenes, resins and oils (the sum of oils and resins is called maltens. Oils in bitumen reduce the temperature of its softening, and hardening. They also increase its fluidity and volatility. Oils consist of paraffin, paraffin-naften, naphthenic and aromatic compounds [11]. Bitumen contains 45-65% oils on average.

It is known that oil asphaltenes are a complex multi-component mixture, the fractioning of which can reveal the presence of a subcomponent with significantly different physical and chemical characteristics. A comprehensive study of asphaltenes and their individual fractions with different solubilities allowed to prove the existence of molecular structures of both types - "continent" and "archipelago" (Fig. 2.3) [12]. According to the "continental" model, supported by various researchers at different times, asphaltene molecules include a condensed center of an average 6-7 aromatic rings and several side aliphatic chains with rare

heteroatom inclusions. The alternative model "archipelago" consists of polycyclic "islands" with 5-7 aromatic rings on the average, connected with each other by short aliphatic chains, possibly containing functional groups (mainly thioether) [13].

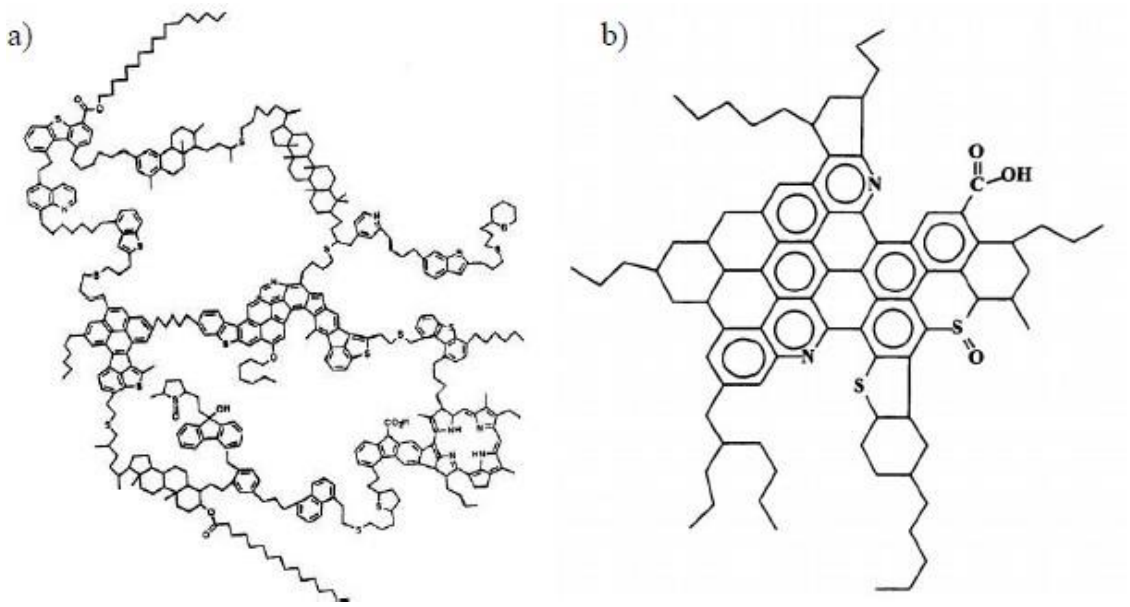

Figure 2.3 Hypothetical structure of asphaltenes: a) Archipelago structure b) Continent structure [12.13]

Asphaltenes are high-molecular weight components of bitumen. Their molecules include hexagonal aromatic and naphthenic rings, hexagonal heterocycles with paraffin chains of various degrees of branching [14]. The molecular weight of asphaltenes varies within the limits of 1700-7500 a.m. Elemental composition (in weight %) of carbon is 80-84; hydrogen - 7.5-8.3; sulphur - 4.6-8.3; oxygen - up to 6; nitrogen - 0.4-1. The content of heteroatoms in asphaltenes is higher than in oils and resins isolated from the same bitumen [15]. The resins differ from asphaltenes in their lower condensation, lower molecular weight and higher hydrogen content. The main structural elements of resin molecules are condensed cyclic systems containing aromatic, cyclo-paraffin, heterocyclic rings, which are connected with each other by relatively short aliphatic bridges. They contain besides carbon (79-87 %), hydrogen (8,5-9,5 %), oxygen (1-10%), sulphur (up to 2%), many other elements including metals (Fe, Ni, V, Cr, Mg, Co, etc.) [16, 17]. Carbon skeleton of resin molecules is a polycyclic system consisting mainly of condensed aromatic rings with aliphatic side chains. The number of carbon atoms in compounds

making up resins is between 80-100. In comparison with asphaltenes, resins have a large number and length of aliphatic side chains [18].

2.3 Different bitumen sources

2.3.1 Natural bitumen

Natural bitumen - organic - binding agent of dark brown or black color. In terms of structure, natural bitumen is close to oil, but contains more oxygen and asphalt acids. This explains their high adhesion to stone materials.

2.3.2 Oxidized bitumen

Oxidized bitumen is obtained in periodic and continuous machines. The principle of getting oxidized bitumen is based on sealing reactions at elevated temperatures in the presence of air, leading to an increase in the concentration of asphaltenes, contributing to an increase in the softening temperature of bitumen, and resins that improve the adhesive and elastic properties of the product.

2.4 Asphalt

Asphalt is a universal chemically resistant material that adapts to almost any climatic conditions, consisting of a mixture of carbon. Asphalt, also called mineral resin, is obtained from natural sources, from by-products of oil industry processing. The composition of the asphalt is divided according to whether it is natural or artificially produced. Natural asphalt is mined in the Dead Sea in Israel, Lake Peach Lake in Trinidad, Alberta Province in Canada. There are also small deposits in Cuba, the United States and Iran. Artificial asphalt consists of the main component and additional ones. The main component is bitumen, but not natural asphalt, which is created artificially. Small, viscous oil, modified bitumen is used.

2.4.1 Asphalt rocks

Limestones and sandstones impregnated with natural asphalt bitumen in their deposits are called asphalt rocks or asphalt stone. The content of asphalt bitumen in asphalt rocks depends on their porosity and fracturing and is always quite uneven. The bitumen content of asphalt rocks varies widely. The bitumen content is already 3-5% industrial. The best asphalt rocks contain from 7 to 15%, as an exception in the deposits there are areas and richer.

2.4.2 Tar

Tar is an externally resinous substance formed after processing of oil products. It has a viscous structure and a distinct black color. The proportion of tar is between 8 and 45% of the mass of oil. The precursor of this substance is oil products, so tar is very similar to oil fractions in composition. Mandatory components are:

- oil resins, consisting of complex hydrocarbons which confer goodron viscosity and viscosity (2-38%);
- asphaltenes are solid substances that increase temperature resistance (3-17%);
- asphaltic acids and their resinous anhydrides, which are polynaphthnic acids (45-95%);
- high content of metal impurities present in oil (V-0,046%; Ni-0,014%).

Tar and bitumen are actively used in construction and in production of various materials. They are similar in appearance, composition and some properties, and are therefore often confused with each other. A brief description can be seen in Table 2.4.

Table 2.4 Distinctions of tar characteristics from bitumen [19]

Characteristics	Bitumen	Tar
Nature	Organic substance of natural or artificial origin	Residue produced by distillation from oil at atmospheric pressure under vacuum of fractions boiling 450-6000^{0}C
Appearance	Runs in solid form and as a viscous liquid.	Usually exists only as a viscous liquid.
Density (ρ-g/cm^3)	0,95-1,50	0,95-1,03
MeltingTemperature (T-^{0}C)	160-200	12-55

2.5 Bitumen modifiers

Increasing traffic and difficult climatic conditions have meant that traditional binders used for the preparation of asphalt concrete mixes can no longer provide the necessary durability of the roadway. Over the past decades, many studies have been conducted to improve the quality of pavements. As a result, it has been concluded that it is not necessary to abandon traditional bitumen, but its characteristics have to be corrected by introducing special additives - modifiers. The process of modifying bitumen is a process aimed at improving its properties by combining bitumen with special polymer additives. Introduction of a suitable

polymer to obtain modified bitumen allows the substance to possess improved properties, namely, increased heat or frost resistance, increased resistance to stress, better elasticity, durability. The most common types of bitumen modifiers are classified as physical modifiers (i.e, polymers) or chemical modifiers (i.e., organometallic compounds, sulfur compounds). Modified bitumen is that which is improved by using additives of certain substances (polymers, rubber crumb, sulfur, adhesive additives, etc.). Polymer-bitumen binders (PBB) are bitumen improved with polymer additives. Bitumen with a rubber additive is called a bitumen-rubber binder (BKB), while bitumen with a rubber crumb additive is called a rubber-bitumen binder (RBB) [20-23].

2.5.1 Polymer modified bitumen

The main goal of introducing the polymer into bitumen is to reduce the temperature sensitivity of the binder, i.e. to increase its hardness in summer and reduce it in winter, as well as to give the binder elasticity - the ability to reversibly deform over the entire range of operating temperatures. If this goal is achieved, asphalt concrete with polymer bitumen has increased shear stability, low-temperature crack resistance and fatigue life. A prerequisite for achieving polymer bitumen is the compatibility of both components, i.e. the ability of the polymer to swell or dissolve in the bitumen dispersion medium. It is important to combine the polymer with bitumen, the choice of which is determined by the properties of the materials used. The main methods of obtaining polymer bitumen: 1) mixing the polymer (in the form of powder or granules) with bitumen at 150 - 200 ° C and intensive mixing; 2) injection of polymer solution (in various hydrocarbon solvents) into heated bitumen (bitumen temperature depends on the type of solvent). To obtain the polymer bitumen, devices of various types are used namely - blade agitators, colloidal mills, hydrodynamic mixers [24-30].

Initially, the improved properties of polymer-bitumen compositions tried to explain the formation of chemical bonds between bitumen and polymers. Chemical research methods in this case were powerless, as the very complex composition of bitumen and polymers makes these methods ineffective. However, since the infrared spectroscopy method became available for most polymer-bitumen compositions, it has been shown that there are no growths in the mixture. According to most authors, polymers do not chemically interact with bitumen, but dissolve in low concentrations, or disperse in it to strengthen its structure. As the concentration increases, the polymer particles increase in size, due to aggregation as they cluster together and form a loose mesh structure [31]. The most commonly used polymeric materials in road construction are elastomers, thermoplastics and

thermoplastic elastomers (TEP). Elastomers are polymers that have highly elastic properties in their range of application. Introduction of elastomers into road binder elastomers leads to elasticity in bitumen, thus increasing the deformation properties of asphalt concrete in a wide range of operating temperatures, but does not increase the softening temperature. Thermoplastics are polymers that can soften many times when heated and harden when cooled. They modify bitumen, creating in it a rigid spatial grid which resists deformation, increases elasticity, cohesion and adhesion properties and also reduces binder fragility at negative temperatures. This class of polymers is not elastic and crack resistant enough at low or negative temperatures. Thermoplastic elastomers are granular or powdered amorphous polymers of a linear or branched structure whose molecules contain monomeric links or blocks of butadiene and styrene, randomly or statistically arranged in a chain [32]. There is a tendency on the world bitumen market to increase the share of PMB use. The commercial use of modified bitumen is increasing, with the highest rate in developing countries. The world market value of modified bitumen (PmB) was estimated at 7.67 billion dollars. The global market for modified bitumen was estimated at $7.67 billion in 2014. At the same time, the market was projected to grow over the next seven years due to growing demand from various application sectors, including road construction, roofing and adhesives. In 2016, the global market was estimated at $9.5 billion. In 2016, the global market was estimated at USD 9.5 billion, and CAGR industry growth was expected to be more than 4% on or before 2024. North America accounts for more than a quarter of the entire IMB market share. The Asia Pacific region has one of the fastest growing markets for modified bitumen. In China and India, the demand for housing is increasing, leading to large new construction projects. This factor drives the PMB market in Asia and the Pacific. It is difficult for companies operating in the European PCB market to support the market due to the huge competition from major players. However, ``Shell, continues to grow and invest in its bituminous business in this region, which is secured by two of the largest plants located in the Netherlands and Germany [33].

2.6 Adhesion promoter for bitumen

Adhesion is explained by the formation of a double electric field on the separation surface of the bitumen film and stone material. Adhesion of bitumen depends on the polarity of the components (asphaltenes and maltens) and is characterized by the electrical conductivity of solutions of these substances in non-polar solvents. As the molecular weight of asphaltenes in the bitumen increases, the adhesion properties improve, the water resistance coefficient increases and the heat

resistance coefficient of asphalt concrete mixtures decreases. Adhesion of bitumen to stone materials is also characterized by surface tension at the interface and represents the work required to separate bitumen from stone material. The presence of paraffin wax in bitumen reduces adhesion and should therefore be limited to 5% [10]. Adhesion of bitumen of different grades is usually the same, and cohesion (intermolecular forces of interaction in the volume of bitumen) increases during hardening of bitumen, and the fracture of the bituminous-mineral compound becomes adhesive rather than cohesive [34]. A strictly substantiated method for determining adhesion has not yet been developed due to the high complexity of real interactions. Therefore to compare the adhesion of bitumen, we use the past method, which entails keeping bituminous-mineral mixture in boiling water and a visual evaluation of the degree of coverage of bitumen mineral particles [35]. Adhesive additives are widely used in the production of asphalt concrete as a modifier that improves the properties of oil bitumen and increases the efficiency of its adhesion to stone materials of different fractions and origin. This positively affects the quality of the asphalt concrete mixture and the final composite - asphalt concrete [36-37].

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Chapter 3
Experimental Techniques

The objective of this paper is to determine traditional (physical and mechanical properties, adhesion) and modern properties (by the Superpave method, necklace formation) of PmB and asphalt concrete. The aim is to determine the optimum polymer dosage option for bituminous binders.

3.1 Traditional characteristics

3.1.1 Main indicators of physical and mechanical properties of bitumen

Oil viscous road bitumen is produced in accordance with the requirements of CT RK 1373-2013 according to technological regulations approved in the established order.
Depending on the depth of penetration of the needle at 25 °C bitumen is prepared as follows: BND 130/200, BND 100/130, BND 70/100, BND 50/70, BND 35/50 [1]. According to physical and mechanical indicators, bitumen must meet the requirements and standards specified in Table 3.1.

Table 3.1 Physical and mechanical properties of the bituminous binder

Indicatorname	**Unit measurements**	**Normforbitumenbrand**			**Experimental method**
		BND 130/200	**BND 100/130**	**BND 70/100**	
1Depth of needle penetration, at temperature 25 °C 0°C, no less	x0,1mm	 131-200 40	 101-130 30	 71-100 22	CT RK1226[2]
2 Softening point on the ring and the ball, not lowerthan	°C	40	43	45	CT RK1227[3]
3 Tensile at temperature, no less: 25 °C, 0 °C	Cm	 - 6,0	 90 4,0	 75 3,8	CT RK1374[4]
4 The viscosity is dynamic at 60 ° C, no less	Па·с	80	120	145	CT RK1211[5]
5 Fragility Temperature Fraas, not higher.	°C	-24	-22	-20	CT RK1229[6]

The modified bitumen is made according to requirements of CT RK 2534-2014 under the technological documentation confirmed in the established order.

According to physico-chemical and operational indicators, modified bitumen must meet the requirements of Table 2 [7].

Table 2 Physical and mechanical indicators PmB

Indicator name	Norm for BMP brands				
	70/100		100/130		130/150
	I	II	I	II	
1. Needle penetration depth x0.1 mm, at 25 °C.	71-100		101-130		131-150
2. Softening point (R&B), °C, not lower than 2.	60	58	55	52	52
3. Ductility at 25 ° C, cm,no less.	25	28	30	32	35
4. Fraass Breaking Point, ° C, no higher.	-18 -20	-20 -22	-20 -22	-22 -24	-25 -26

The indicators shown in the table can be defined as follows:

Needle penetration depth - Consistency expressed by the distance measured in tenths of a millimetre that a standard needle passes under certain conditions - temperature, load and duration of its application. To determine the depth of penetration of the needle, a penetrometer of any design can be used, provided that the needle and the basic parameters of this device (size and weight of the needle holder, the mass of additional cargo) meet the requirements of NS 1440.

Softening point (R&B) - The temperature at which bitumen in a ring of specified dimensions softens under test conditions and moves under the influence of a steel ball, touching the bottom plate.

Ductility – This is the ability of bitumen to stretch to its maximum length before breaking at constant speed and temperature. The essence of the method is to determine the maximum length of bitumen in terms of tensile strength before rupture at a constant speed and at a given temperature. Tensile tests are performed at 0 ^{0}C and 25 ^{0}C and a constant tensile speed of 50 mm/min.

Fraass Breaking Point – This is the temperature in degrees Celsius at which the bituminous film of a certain thickness breaks under the specified load conditions.

Dynamic viscosity η – This is the ratio of applied shear stress to liquid shear rate. The term "dynamic viscosity" can also be used to refer to the relationship between shear stress and shear rate, which have a sinusoidal time relationship. Viscosity η, Pa-s, is calculated by the formula:

$$\eta = C \cdot t \qquad (1)$$

where: C - constant viscometer, Pa; t - arithmetic mean of the expiry time, s.

3.1.2 PmB adhesion

The quality of the adhesion is assessed visually by the degree of preservation of the film of the bituminous binder on grains of crushed stone after its boiling in distilled water [8].

For the test, six grains of gravel with sizes not less than 10 mm are selected and dried in a drying cabinet at temperatures (105 - 110) °C. Each grain of crushed stone is tied with a thin wire (diameter not exceeding 0.5 mm) and heated in a drying cabinet. The heating temperature of rubble must be when using viscous bitumen (130 -150) ° C. After 1 hour, the heated grains are alternately immersed for 15 seconds in the used heated bitumen binder, and then removed and hung on a tripod to drain off excess bitumen. Tests are carried out not earlier than 1 hour after draining. Each grain hanging on a tripod is lowered one by one into the middle of a glass beaker filled with distilled water which is placed on a hot plate. The grains are lowered in such a way that they don't touch the bottom or the walls of the cup and are kept in boiling water when using viscous bitumen for 30 minutes. Grains of rubble are taken out of the glass and immersed in a glass with cold distilled water for 1-3 minutes to cool and fix the remaining on the surface of the rubble film of bitumen. The remaining crushed stone is removed from the water and placed on filter paper. The surface of the crushed stone grains is inspected and the quality of adhesion of the bituminous binder with the crushed stone is assessed according to the degree of safety of the binder film in accordance with Table 3.

Table 3 assessment of adhesion quality of bitumen binder to crushed stone

Feature of the bitumen blot on the crushed stone surface	**Clutchquality assessment**
The binder blot is completely stored on the surface, and its thickness can be reduced in some places.	Excellent (fivepoints)
The binder film is completely retained on the surface, but partially separated from the sharp corners and ribs.	Good (fourpoints)
Binder blot over 50% retained on the crushed stone surface	Satisfactory (threepoints)
A binder blot of less than 50% is retained on the crushed stone surface. Individual droplets of bitumen are observed on the exposed surface.	Bad (twopoints)

3.1.3 Basic indicators of physical and mechanical properties of asphalt concrete

Physical and mechanical properties of asphalt and polymerasphaltic concrete were determined in accordance with CT RK 1225 [9] and CT RK 1223[10]. In this paper, the composition of asphalt concrete for type B I mark was selected. In terms of physical and mechanical indicators, the asphalt concrete must meet the requirements and standards specified in Table 4.

Table 4 Physical and mechanical indicators of asphalt concrete

№	The name of indicators	ND on test methods	Norm on ND CT PK 1225
1.	Water saturation, % by volume	CT RK1218. Part 13	1,0 - 4,0
2.	Compressive strength at temperature 20°C, MPa	CT RK1218. Part 15	Not less than2,5
3.	Compressive strength at temperature 50°C, MPa	CT RK 1218 Part 15	Not less than1,3
4.	Compressive strength at temperature 0°C, MPa	CT RK 1218 Part 15	Not more than13
5.	Water resistant	CT RK 1218 Part 21	Not less than0,85
6.	Sliding stability by: - to the internal friction coefficient; - shear clutch at temperature 50 °C, MPa	CT RK 1218 Part 18	not less than 0,83 not less than 0,38
7	Crack resistance on the cracking strength at a temperature of 0 ° C	CT RK 1218 Part 16	From 3,5 before 6,5

The indicators shown in the table can be defined as follows:
Water Saturation - The essence of this method is to determine the amount of water absorbed by the sample at a given saturation mode. The saturation of the sample (W, %) is calculated by the formula:

for mixtures
$$W = \frac{g_5 - g}{g_2 - g_1} 100, \qquad (2)$$

fortified soil $$W = \frac{g_5 - g}{g - g_1} 100 \quad (3)$$

where g- is the mass of a sample suspended in the air, g;
g_1 - weight of the sample weighed in water, g;
g_2 - Mass of the sample aged for 30 min in water and weighed in air, g;

g_5 - mass of a water-saturated, airborne sample, g.
Compressive strength limit at 0, 20 and 50^{0}C- The essence of this method is to determine the load required to destroy the sample under given conditions. Compressive strength limit (Rc, MPa), calculated by the formula:

$$R_c = \frac{P}{F} 10^{-2} \quad (4)$$

where P- is a destructive load, H;
F- is the first cross-sectional area of the specimen, Cm^2;
10^{-2} - Conversion coefficient in MPa.
Water-resistance - The essence of this method is to determine the ratio of compressive strength of samples after 15 days of exposure to water to the initial strength of parallel samples.
Based on the tests results to the accuracy of the second decimal place, water resistance (w.r) is calculated after prolonged water saturation by the formula;

$$K_{w.r} = \frac{R_c^{w.r}}{R_c^{20}} \quad (5)$$

Where $R_c^{w.r}$ - the limit of compression strength at temperature (20±2) °C of samples after saturation with water for 15 days, MPa;
R_c^{20} - the limit of compressive strength at a temperature of (20±2) °C of samples before saturation with water, MPa.
Shear stability - The essence of this method consists in determining the maximum loads and corresponding limit deformations of standard cylindrical specimens at two stress-strain states. For each specimen tested for uniaxial compression and compression by the Marshall Scheme, the work (A, J) spent on failure is calculated by formula:

$$A = \frac{Pl}{2} \quad (6)$$

where P- is a destructive load, kN;
l - ultimate deformation, mm.
The coefficient of internal friction of asphalt concrete (tgϕ) is calculated by formula

$$tg\varphi = \frac{3(A_m - A_c)}{3A_m - 2A_c} \qquad (7)$$

where A_m, A_s is the average work of deforming asphalt concrete specimens when tested according to the Marshall Scheme and in uniaxial compression, Dzh is the average work of deforming asphalt concrete specimens when tested according to the Marshall Scheme and in uniaxial compression.
Shear clutches (S_c, MPa) are calculated by the formula:

$$S_c = \frac{1}{6}(3 - 2\tan\varphi)R_c \qquad (8)$$

where R_c -is the ultimate in uniaxial compression stress, MPa.
Crack resistance - The essence of this method is to determine the load required to split the sample into a formation. Limit of tensile strength at splitting (S_t MPa), is calculated by the formula

$$S_t = \frac{P}{hd}10^{-2} \qquad (9)$$

where P- is a destructive load, H;
h- is the height of the specimen cm,
d - diameter of the sample, cm;
10^{-2}- Conversion coefficient in MPa.

3.2 Modern characteristics of PMB and asphalt concrete

3.2.1 Main indicators of the Superpave bitumen binder.

Superpave stands for Superior Performance Pavements, a method used for designing asphalt concrete mixes for high performance road surfaces. Superpave accurately determines the physical-mechanical properties and behavior of asphalt concrete under operating conditions:

- crack resistance;
- moisture resistance;
- susceptibility to rutting;
- modulus of elasticity under the influence of different temperatures was estimated.

Any asphalt concrete mixture consists of mineral materials: bitumen, sand, crushed stone and gravel. The durability of the final mixture largely depends on the quality of the binding bitumen. Superpave Technology assumes the exact selection of bitumen not on obsolete norms, but on a specially created PG Grade scale. The PG classification allows the determination of a bitumen binder suitable for a specific road section. The quality of the PG grade bitumen binder is determined on the basis of the results of rheological tests, which are carried out at the maximum design temperature (in place of the determination of the softening point according to R&B) and the minimum design temperature (in place of the determination of the brittleness temperature according to Fraass).

3.2.2 Method for determining the stiffness and creep of a bituminous binder at negative temperatures using a bending bar rheometer (BBR)

This test method entails the determination of the flexural-creep stiffness or compliance and m-value of asphalt binders by means of a bending beam rheometer. It is applicable to materials having flexural-creep stiffness values in the range of 20 MPa to 1 GPa (creep compliance values in the range of 50 nPa–1 to 1 nPa–1) and can be used with unaged or aged materials. The test apparatus may be operated within the temperature range from –36°C to 0°C.

The device for conducting the test can function in the temperature range from-36°C to 0°C [11]. The diagram of the instrument is shown in the Fig. 1.

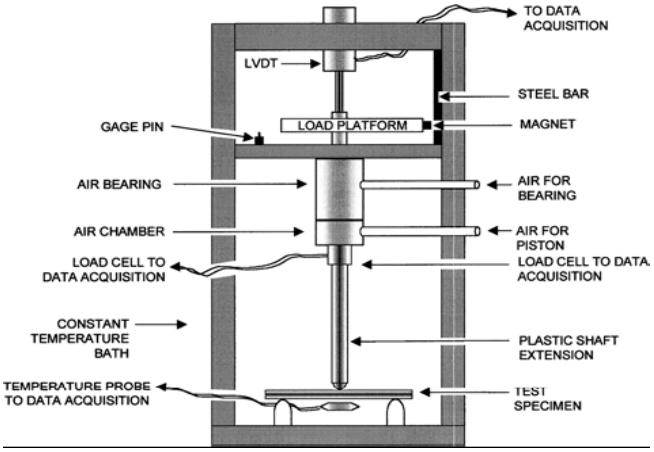

Figure 3.1 - Schematic of Test Device

The rise time for the test load should be less than 0.5 s. The rise time is the time required for the load to rise from the 35 ± 10 mN contact load to the 980 ± 50 mN test load. During the rise time, the system should dampen the test load to 980 ± 50 mN. Between 0.5 and 5.0 s, the test load should be within ± 50 mN of the average test load, and thereafter should be within ± 10 mN of the average test load. Details of the loading pattern are shown in Fig. 3. 2.

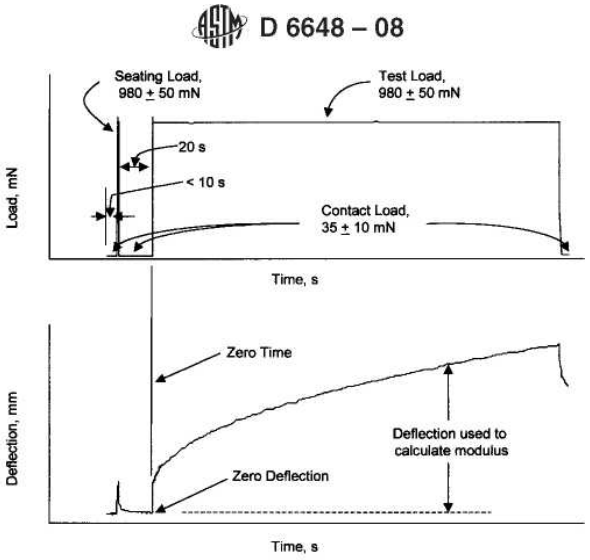

Figure 3.2 Definition of Loading Pattern

The results of the deflection of the bar and the corresponding loading time form an array of data to calculate the bitumen stiffness as a function of the loading time. Bitumen stiffness, S(t), MPa, is calculated using formula 10:

$$S(t) = \frac{PL^3}{4bh^3\delta(t)} \qquad (10)$$

where δ (t)- is the deflection of a bar at a time t s, mm
S(t) - rigidity at time t s, MPa
L - beam span length (distance between supports), mm
h - beam height, mm
b - beam width, mm
P is the applied load, H

3.2.3 Method for determining the properties of bituminous binders using a dynamic shear rheometer (DSR)

This test method covers the determination of the dynamic shear modulus and phase angle of asphalt binder when tested in dynamic (oscillatory) shear using parallel plate test geometry. It is applicable to asphalt binders having dynamic shear modulus values in the range from 100 Pa to 10 MPa. This range in modulus is typically obtained between 6 and 88°C at an angular frequency of 10 rad/s. This test method is intended for determining the linear viscoelastic properties of asphalt binders as required for specification testing and is not intended as a comprehensive procedure for the full characterization of the viscoelastic properties of asphalt binder [12]. Samples which are 1 mm thick and 25 mm thick or 2 mm thick and 8 mm thick are formed between parallel metal plates. During the experiments, one of the parallel plates vibrates relative to the other at pre-selected frequencies and rotational strain amplitudes (strain control) (or torque amplitude (stress control)). The required stress or strain amplitude depends on the value of the complex shear modulus of the asphalt binder being tested. The required amplitudes have been chosen to ensure that the measurements are in the area of linear behavior. Test specimens with thicknesses of 1 mm by 25 mm in diameter or 2 mm by 8 mm in diameter are formed between parallel metal plates. During testing, one of the parallel plates is oscillated with respect to the other at pre-selected frequencies and rotational deformation amplitudes (strain control) (or torque amplitudes (stress control)). The required stress or strain amplitude depends on the value of the complex shear modulus of the asphalt binder being tested. The required amplitudes have been selected to ensure that the measurements are within the region of linear behavior. The schematic image is shown in picture 3.3.

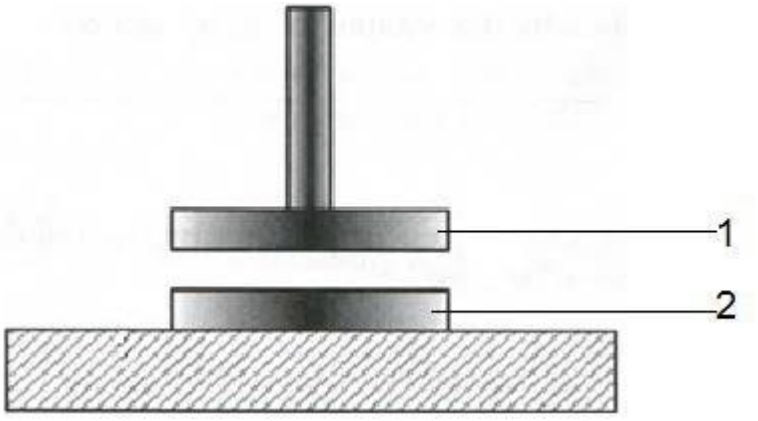

Figure 3.3 Test system diagram. 1- Upper plate (sliding), 2-Bottom plate (fixed)

The results of the tests are processed using data automatically determined by the automatic data acquisition and recording system, a complex shear module (G*) and a phase angle (δ).

$$G^* = \left(\frac{2 \cdot h}{\pi \cdot r^4}\right) \cdot \left(\frac{\tau}{\theta}\right) \qquad (11)$$

where G* is a complex shift module
τ - torque
Ɵ - maximum angular offset
h - thickness of the test specimen
r - plate radius.

3.3 Rutting resistance

Testing for resistance to rutting of asphalt and polymerasphaltic concrete was carried out on the "Hamburg Wheel" installation (Figure 20) in accordance with the requirement of CT RK EN 12697-22-2012[13]. This test was developed to assess the rutting resistance of asphalt concrete under laboratory conditions that simulate the effects of vehicles on the road surface. The machine consists of a press frame made of a strong aluminium alloy and a PID-controlled temperature chamber (Fig.3.4)

Figure 3.4 Installation of the Hamburg Wheel

Samples of asphalt concrete and polymer-asphaltic concrete in the form of a rectangular plate with dimensions of 10.0x30.5x30.5 cm after their compaction in a roller compactor were subjected to rutting resistance. Test specimens were placed on a working plate, which made reciprocating movements (stroke size in one

direction 230 mm) on linear guides at a given speed. The loaded rubber wheel was rolled over the top of the specimen and resulted in a gauge, the process of formation of which was measured using strain gauge deformation measurement. Tests were conducted at a temperature of + 60 ° C, the number of wheel passes - 10 000, with a test time of 6 hours 30 minutes.

The equipment monitors the test process and stores all test data using a built-in interface combined with the software. At the end of the test, the software allows the calculation of the gauge and the printing of the test report (Fig.3.5).

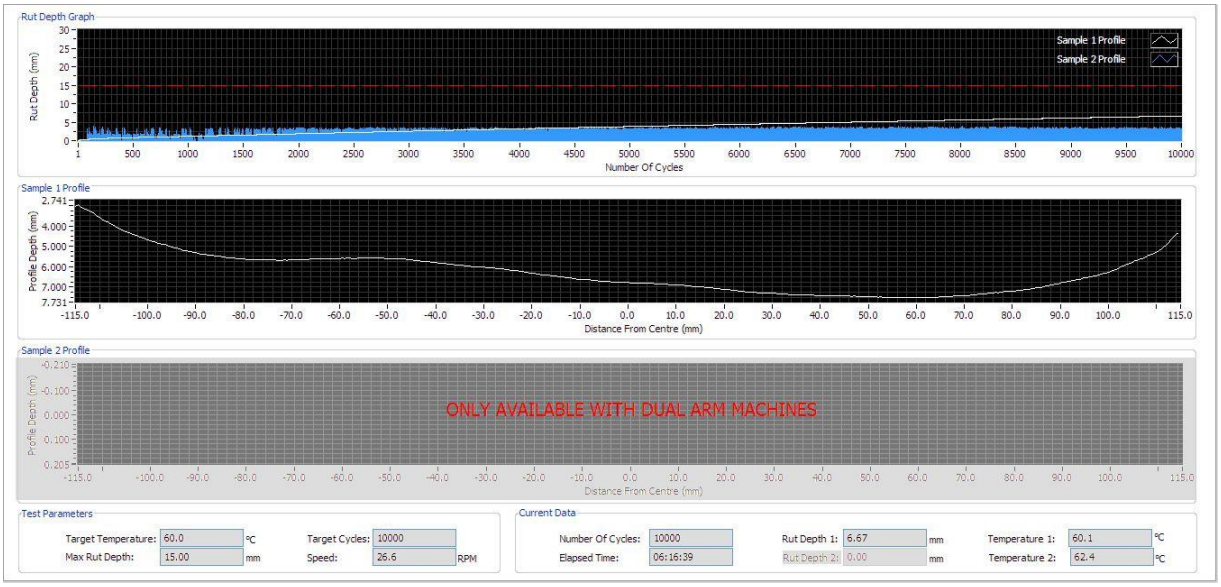

Figure 3.5 Routing of asphalt concrete on bitumen BND 100/130.

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Chapter 4

applied sciences

MDPI

Article

Mechanical Resilience of Modified Bitumen at Different Cooling Rates: A Rheological and Atomic Force Microscopy Investigation

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Abstract: Due to the wide variation in geographic and climatic conditions, the search for high-performance bituminous materials is becoming more and more urgent to increase the useful life of pavements and reduce the enormous cost of road maintenance. Extensive research has been done by testing various bitumen modifiers, although most of them are petroleum-derived additives, such as polymers, rubbers and plastic, which in turn do not prevent oxidative aging of the binder. Thus, as an alternative to the most common polymeric rheological modifiers, selected binder additives falling in the categories of organosilane (P2KA), polyphosphoric acid (PPA) and food grade phospholipids (LCS) were homogeneously mixed to a base bitumen. The goal was to analyse the micro-morphology of the bitumens (neat and modified) subjected to different cooling rates and to find the corresponding correlations in the mechanical response domain. Therefore, microstructural investigations carried out by Atomic Force Microscopy (AFM) and fundamental rheological tests based on oscillatory dynamic rheology, were used to evaluate the effect of additives on the bitumen structure and compared with pristine binder as a reference. The tested bitumen additives have been shown to elicit different mechanical behaviours by varying the cooling rate. By comparing rheological data, analysed in the framework of the "weak gel" model, and AFM images, it was found that both P2KA and PPA altered the material structure in a different manner whereas LCS revealed superior performances, acting as "mechanical buffer" in the whole explored range of cooling rates.

Keywords: modified bitumen; Atomic Force Microscopy; Dynamic Oscillatory Rheology; complex modulus; "weak gel" model

1. Introduction

In today's road construction technology, the demand for bitumen characterised by high mechanical properties becomes increasingly insistent, even if it represents only a minor component of asphalt (5–8% by weight of binder) [1].

Bitumen, which is a complex solid or semisolid colloidal dispersion of asphaltenes into a continuous oily phase constituted by saturated paraffins, aromatics and resins [2–4], is a viscoelastic material whose mechanical response is both time and temperature dependent [5]. However, because of the wide variation in geographical and climatic conditions, a careful selection of bituminous materials is required to increase the useful life of the pavement and reduce the huge cost of road maintenance. For instance, for a good road performance, it would be highly desirable that the deformation properties of bitumen remain unchanged under the effect of different cooling rates, and mitigate the susceptibility of asphalt concrete to several drawbacks such as thermal cracking and thermal stress accumulation [6]. Indeed, depending on the geographical areas, the bitumen used in hot-mix asphalt concretes for road construction may suffer severe thermal shocks during placement of the asphalt top layer onto pavements, characterised by a wide range of surface temperatures [7,8]. Therefore, to facilitate the evaluation of cooling rate sensitivity in controlled lab-scale conditions, the temperature of both pristine bitumen and bitumen modified with three additives was varied from 105 °C to 25 °C using cooling rates of 1, 5 and 10 °C/min, respectively. Being aware that the selected cooling rates might not exactly reproduce the realistic pavement conditions met in a field study, the purpose of this analysis was to gain a preliminary understanding of the impact that additives distinct from the most common polymers [9–11] may have on the bitumen rheological response to changes in the cooling rate. Therefore, a rheological investigation was performed to compare the mechanical behaviour manifested by a base bitumen modified with three additives, namely, organosilane (P2KA), polyphosphoric acid (PPA) and food grade phospholipids (LCS), whose properties as rheological/adhesion bitumen modifiers have been widely investigated [12–15]. Specifically, oscillatory rheological tests were carried out to monitor the dependence of complex mechanical modulus on the type of additive at various cooling rates. According to the present research project, we seek the most efficient additive that would make the mechanical modulus of the correspondent modified bitumen less temperature-sensitive in the explored cooling ramp range. A parallel structural investigation by using Atomic Force Microscopy (AFM) has been also undertaken at 25 °C to monitor changes in the micro-morphology of both virgin and modified bitumens once subjected to different cooling rates. Indeed, previous AFM investigations were found successful in studying the bitumen microstructure at nanoscale level, including its surface morphology dependence on various physico-chemical parameters [16–18]. Therefore, the results illustrated in the present study and obtained from a combination of oscillatory rheology and AFM measurements have been found very useful in the identification of the best additive able to leave the bituminous structure nearly unaffected by the action of different cooling rates applied in range of 1–10 °C/min.

2. Materials and Methods

2.1. Materials

The asphalt binder was kindly supplied by Loprete Costruzioni Stradali (Terranova Sappo Minulio, Calabria, Italy) and was used as base bitumen. It was produced in Italy and the crude oil was from Saudi Arabia. The neat bitumen was modified by adding commercial additives, namely, (a) phospholipids in the form of light yellow powder (hereafter LCS) provided by Somercom srl (Catania, Italy); (b) organosilane P2KA provided by KimiCal s.r.l. (Rende, Italy) and (c) polyphosphoric acid (PPA) provided by Sigma Aldrich (Milano, Italy).

2.2. Sample Preparations and Setup of Cooling Ramps

The additives were mixed separately to hot bitumen (140–160 °C) at fixed content of 2% wt/wt [12–14] by using a mechanical stirrer (IKA RW20, Königswinter, Germany). First, 100 g of bitumen was heated up to 140–160 °C until it flowed fully, then a given amount of additive was added to the melted bitumen under a high-speed shear mixer at 500–700 rpm. Furthermore, the mixtures were stirred again at 140–160 °C for 30 min. After mixing, three different cooling ramp rates were applied to bitumen

samples modified with P2KA, PPA and LCS, respectively. Parallel temperature ramp tests were carried out on unmodified bitumen as a reference system. The experimental conditions were isothermal annealing for 10 min at 160 °C then cooling at 1, 5 and 10 °C/min until room temperature was reached.

2.3. SARA Determination

The Iatroscan MK 5 Thin Layer Chromatography (TLC) was used for the chemical characterisation of bitumen by separating it into four fractions: Saturates, Aromatics, Resins and Asphaltenes (SARA) [19]. During the measurement, the separation took place on the surface of silica-coated rods. The detection of the amount of different groups was according to the flame ionisation. The sample was dissolved in peroxide-free tetrahydrofurane solvent to reach a 2% (*w*/*v*) solution. Saturated components of the sample were developed in *n*-heptane solvent while the aromatics were developed in a 4:1 mixture of toluene and *n*-heptane. Afterwards, the rods had to be dipped into a third tank, which was a 95 to 5% mixture of dichloromethane and methanol. That organic medium proved suitable to develop the resin fraction whereas the asphaltene fraction was left on the lower end of the rods. Details of bitumen composition are listed in Table 1.

Table 1. Group composition of the tested neat bitumen.

SAMPLE	SARA Fraction in Weight % (±0.1)
Saturated	4.2
Aromatics	51.6
Resins	21.3
Asphaltenes	22.9

2.4. Empirical Characterisation

Penetration tests for bitumens were performed according to the standard procedure (ASTM D946) [20]. The bitumen consistency was evaluated by measuring the penetration depth (531/2-T101, Tecnotest, Castelfranco, Treviso, Italy) of a stainless steel needle of standard dimensions under determinate charge conditions (100 g), time (5 s) and temperature (25 °C).

2.5. AFM Microstructure Analysis

Atomic Force Microscopy equipment (Multimode VIII with a Nanoscope V controller, Bruker, Karlsruhe, Germany) was used to analyse the samples. The AFM was used in tapping mode, where the cantilever oscillates up and down close to its resonance frequency so that the tip contacts the sample surface intermittently. When the tip is brought close to the surface, the vibration of the cantilever is influenced by the tip–sample interaction. In particular, shifts in the phase angle of vibration of the cantilever are due to the energy dissipation in the tip–sample ensemble. The phase shift provides information on surface properties such as stiffness, viscoelasticity and adhesion. For measurements, Antimony-doped silicon probes (TAP150A, Bruker) with resonance frequency 150 kHz and nominal tip radius of curvature 10 nm were used. All the measurements were performed at room temperature. Phase images were acquired simultaneously with the topographic mode. Materials with different viscoelasticity were clearly distinguishable. The softer domains appeared dark while the stiffer ones appeared bright in the phase images (see Figure 1A–H).

2.6. Isothermal Rheological Tests after Different Cooling Ramps

After each cooling ramp, samples were subjected to oscillatory rheological tests at constant temperature t = 25 °C, controlled by a Peltier element (±0.1 °C), using a dynamic stress-controlled rheometer (SR5, Rheometric Scientific, Piscataway, NJ, USA) equipped with a parallel plate geometry (gap 2.0 ± 0.1 mm, diameter 25 mm). The linear viscoelastic regime of both neat and modified bitumens was checked through the determination of the complex shear modulus G*(ω) in the regime

of small-amplitude oscillatory shear [21,22]. G*(ω) can be considered the sample's total resistance to deformation when repeatedly sheared. For viscoelastic materials, G*(ω) is split into a real and an imaginary part, respectively, [23]:

$$G^*(\omega) = G^t(\omega) + i\,G''(\omega) \quad (1)$$

The frequency-dependent functions $G^t(\omega)$ and $G''(\omega)$ define the in-phase (storage) and the out-of-phase (loss) moduli, respectively, i being the imaginary unit of the complex number. $G^t(\omega)$ is a measure of the reversible, elastic energy, while $G''(\omega)$ represents the irreversible viscous dissipation of the mechanical energy [24]. Both the storage and loss moduli are related to each other through the phase angle δ defined by:

$$\tan\delta = G''(\omega)/G^t(\omega) \quad (2)$$

Aimed at investigating the material structure, frequency sweep tests were performed at 25 °C and proper stress values were applied to guarantee linear viscoelastic conditions.

3. Results and Discussion

Bitumen was characterised by the SARA method and four different groups were individuated: Saturates, Aromatics, Resins and Asphaltenes (SARA). We recall here that according to the current accepted colloidal model for bitumen, asphaltene molecules rich in resins as peptizing agents self-assembly into micellar-like structures dispersed into the continuous phase composed mainly by the saturated and aromatic oil fractions (maltene) [25–27]. The SARA content of the pristine bitumen was determined (see Section 2) and the results are shown in Table 1.

3.1. AFM Results

Both neat and modified bitumens have been studied in micro-scale at room temperature (RT) after being subjected to different cooling rates. Figure 1 collects AFM phase images acquired after the tested specimens had been slowly cooled at 1 °C/min from 105 °C to RT (Figure 1A,C,E,G) and compared to an analogous series of images from the same samples subjected to a faster cooling ramp at 10 °C/min (Figure 1B,D,F,H). A first effect of cooling rate can be observed on the unmodified bitumen where coarse and isolated aggregates (which form the catana-phase [16,28]), with irregular or ellipsoid shaped domains dispersed into maltene matrix, are replaced by smaller oblong shaped structures with a rippled interior (1A vs. 1B). The occurrence of those discrete domains has been attributed to the crystallisation process of the paraffin wax fraction [16–18,29] where the formation of small crystalline nuclei may be kinetically favoured with respect to the particle growth process if bitumen undergoes too fast cooling rates [30]. A more dramatic micro-morphology change can be observed when the organosilane additive (P2KA) is added to the base bitumen (1C vs. 1D). After a slow cooling ramp temperature (1 °C/min, 1C), a rough surface morphology has been imaged at RT, constituted by irregular often-interlocking domains. As the sample is cooled at a faster rate (10 °C/min, 1D), the phase-contrast images reveal several small submicrometer crystalline structures resembling the 'ant-like' spots observed by Ramm et al. [31], considered as metastable aggregates subjected to a kinetic rather than thermodynamic control.

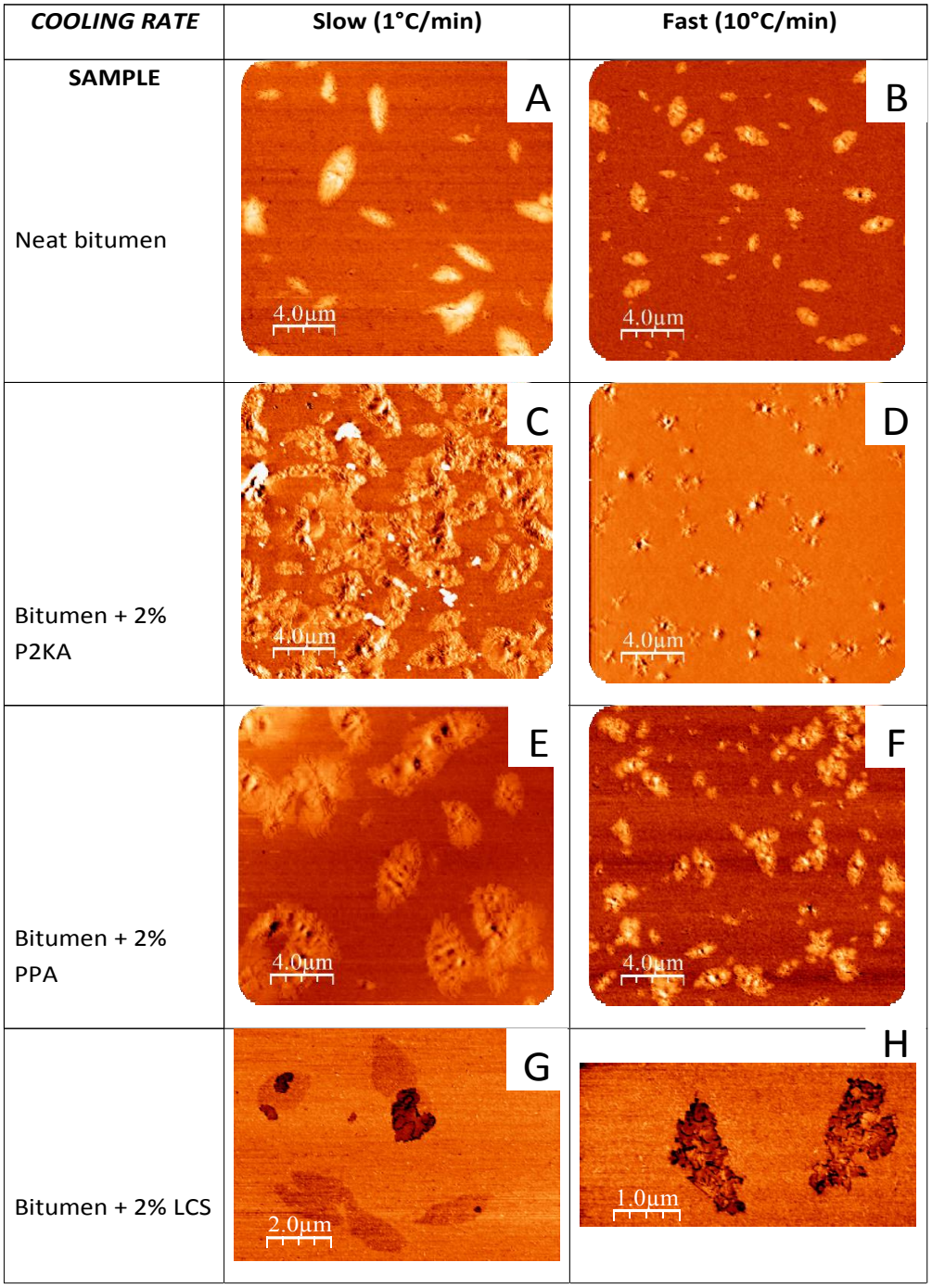

Figure 1. Atomic Force Microscopy (AFM) phase images at room temperature (RT) of both neat bitumen and bitumens modified by addition of 2% P2KA, PPA and LCS, respectively. The microphotographs were acquired after different thermal treatments: slowly cooled at 1 °C/min to RT (**A**,**C**,**E**,**G**) and quickly cooled at 10 °C/min to RT (**B**,**D**,**F**,**H**).

Addition of polyphosphoric acid (PPA) gives rise to surface structuring very similar to pristine bitumen. Indeed, after a slow cooling rate, large pseudo-spherical or lenticular domains have been imaged (1E) characterised by catana-phase with transverse stripes of high and low surface height surrounded by peri-phase regions; likewise, it has been observed in analogous AFM studies [18,32]. However, after subjecting the bitumen to rapid cooling treatments, smaller crystallites with irregular or ellipsoidal shapes are formed, yet retaining the same inner rippled microstructure (1F).

A completely different scenario has been found for bitumen modified with 2 wt % of phospholipids (LCS). Indeed, irregular domains with low phase contrast coexist with fractal-like and more defined particles with similar average dimensions. Those micro-morphological features have been found unaffected by the different cooling ramps applied to LCS-modified bitumen, as can be easily verified by comparing the AFM phase images acquired after slow cooling (1G) and fast cooling (1H) rates, respectively. During the investigation of LCS samples, the contact between the tip and the sample was unstable, due to the large attractive forces caused by the probable presence of LCS even on the sample surface, and this led to difficulties in imaging large areas. The measurements were, then, performed on small areas in order to visualise the single domain's size.

It is worth noting that the apparent aggregates' invariance detected at microstructural level regardless of the chosen ramp is reflected also by a correspondent mechanical resilience manifested by LCS-modified bitumen, as will be described in more details in the next paragraph.

3.2. Oscillatory Shear Experiments

The viscoelastic properties of bitumens were analysed by oscillatory experiments (frequency-sweeps and temperature sweeps) at 25 °C. Preliminary stress-sweep tests were also performed by applying small strain amplitudes in order to define linear viscoelastic conditions. The frequency dependence of the experimental complex modulus |G*| measured at 25 °C for both unmodified and modified bitumens is illustrated in Figure 2 in correspondence to different thermal cooling gradients of, respectively, 1 °C/min (A), 5 °C/min (B) and 10 °C/min (C).

Clear evidence can first be observed at low rates (1°/min) and fast (10°/min), showing substantial differences of |G*| among the various samples, attributable to the presence of the additives (see Figure 2A,C). An exception can be found for P2KA and PPA modified bitumens, characterised by |G*| data, which are almost overlapped for 1 °C/min (Figure 2A). However, the effect of the additives seems to be cancelled out at the intermediate cooling rate of 5 °C/min, where the respective rheological behaviours are hardly distinguishable from those of neat bitumen (see Figure 2B). As observed from AFM images, the development of amorphous/crystalline polydomains in the bitumens is controlled by nucleation and growth rates of disperse catana/peri-phase induced by different cooling rates, which in turn are affected also by the presence of additives. It should be expected that upon rapid cooling small aggregates would engender the formation of a network stabilised by physical interactions with a consequent increase of complex modulus |G*|. To understand whether the added compounds are somewhat engaged in the formation of noncovalent interactions between asphaltene aggregates able to stabilise or even destabilise supramolecular networks upon cooling, the rheological data have been analysed in the framework of the colloidal gel model.

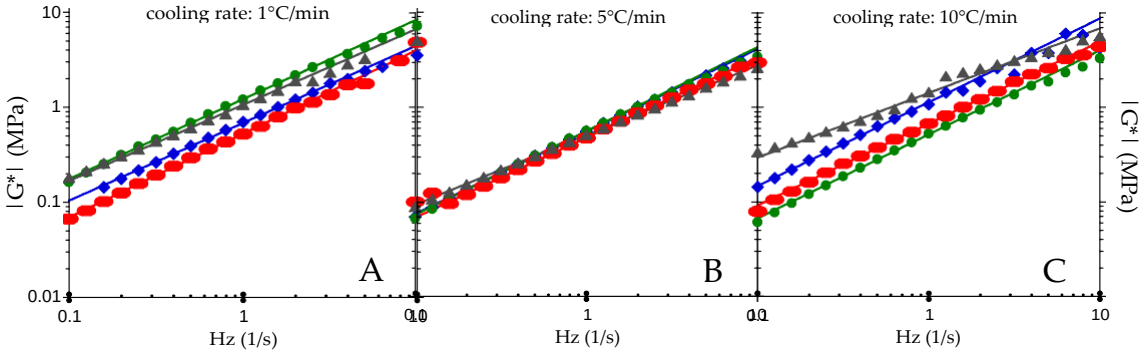

Figure 2. Complex modulus |G*| vs frequency determined at 25 °C for neat bitumen (diamonds), and bitumens modified by addition of 2% P2KA (circles), LCS (squares) and PPA (triangles), respectively, after the specimens were subjected to different thermal treatment: (**A**) 1 °C/min, (**B**) 5 °C/min and (**C**) 10 °C/min. Solid lines represent the best non-linear fits according to the power law of Equation (3), whose fitting parameters z and A have been listed in Tables 2 and 3, respectively.

According to the theory of Bohlin [33] and Winter [34], which has been applied to several colloidal complex systems [35–37] and widely reported in literature as the "weak-gel model" [38], a weak-gel material is defined as a complex system characterised by a cooperative arrangement of flow units connected by weak physical interactions that cooperatively ensure the stability of the structure. Thus, the weak-gel model provides a direct link between the microstructure of the material and its rheological properties. The most important parameter is the "coordination number", z, which is the number of flow units interacting with each other to give the observed flow response. It was shown in reference [33] that, above the Newtonian region, there exists a regime characterised by the following flow equation:

$$|G^*(\omega)| = \sqrt{G't(\omega)^2 + G''(\omega)^2} = A\omega^{\frac{1}{z}} \quad (3)$$

where A is a proper constant related to the overall stiffness or resistance to deformation of the material within the linear viscoelastic region at an angular frequency of 1 rad/s. Clearly, a log–log plots of |G*| vs. frequency should yield a straight line with slope $1/z$ and intercept A.

In Tables 2 and 3, the parameters z and A, calculated from non-linear fitting of viscoelastic data to Equation (1), are listed for all investigated samples subjected to different cooling rates. Three systems out of four, namely, neat bitumen and bitumens modified with P2KA and LCS, share a similar z variability in the narrow range 1.12–1.22, confirming the presence of interacting asphaltenes that form lightly entangled networks. On the contrary, PPA shows a slightly higher flow coordination number, especially in the range 5–10 °C/min, evidencing its network-promoting effect, according to previous investigations [39,40]. In any case, the calculated z values indicate that the coordination numbers are slightly affected by the thermal history as evidenced by the upper plot in Figure 3. A more useful parameter is represented by the constant prefactor of Equation (1) characterising the "interaction strength" of the three-dimensional structure of a gel, which is very sensitive to the cooling rates. Interestingly, an initial decrement of A is observed for all the tested specimens in correspondence of the increment 1 °C/min → 5 °C/min in the cooling rate. Upon further increase to 10 °C/min, both neat and PPA-modified bitumen show an upturn in A whereas P2KA and LCS give rise to a minor change of A (see the lower plot in Figure 3). What is worthy to remark here is that addition of LCS to bitumen provides the smallest A-variation within the explored range of cooling rates and this indicates that overall LCS is able to mitigate the effects provoked by a wide range of thermal gradients. The addition of LCS, whose adhesion efficiency has been recently ascertained [41], precludes the growth of nuclei formed during the nucleation stage, thus making the bulk bitumen structure almost unperturbed by drastic temperature variations.

Table 2. Dependence of the coordination number z on the cooling rate, calculated as a fitting parameter in Equation (1) adapted to experimental oscillatory rheological data, |G*| vs. frequency, for neat bitumen and bitumens modified with additives.

Cooling Rate (°C/min)	**1**	**5**	**10**
Sample	z	z	z
Bitumen	1.22 ± 0.01	1.15 ± 0.01	1.13 ± 0.03
Bitumen + P2KA 2%	1.19 ± 0.01	1.13 ± 0.01	1.12 ± 0.01
Bitumen + LCS 2%	1.13 ± 0.01	1.18 ± 0.01	1.15 ± 0.01
Bitumen + PPA 2%	1.25 ± 0.02	1.36 ± 0.01	1.46 ± 0.06

Table 3. Dependence of the "interaction strength" *A* on the cooling rate, calculated as a fitting parameter in Equation (1) adapted to experimental oscillatory rheological data, |G*| vs. frequency, for neat bitumen and bitumens modified with additives.

Cooling Rate (°C/min)	1	5	10
Sample	$A \times 10^{-6}$	$A \times 10^{-6}$	$A \times 10^{-6}$
Bitumen	0.68 ± 0.01	$0.558 \pm 1 \times 10^{-3}$	1.14 ± 0.01
Bitumen + P2KA 2%	1.22 ± 0.01	$0.563 \pm 3 \times 10^{-3}$	$0.518 \pm 2 \times 10^{-3}$
Bitumen + LCS 2%	$0.530 \pm 3 \times 10^{-3}$	$0.479 \pm 2 \times 10^{-3}$	$0.675 \pm 2 \times 10^{-3}$
Bitumen + PPA 2%	1.06 ± 0.01	$0.511 \pm 1 \times 10^{-3}$	1.42 ± 0.03

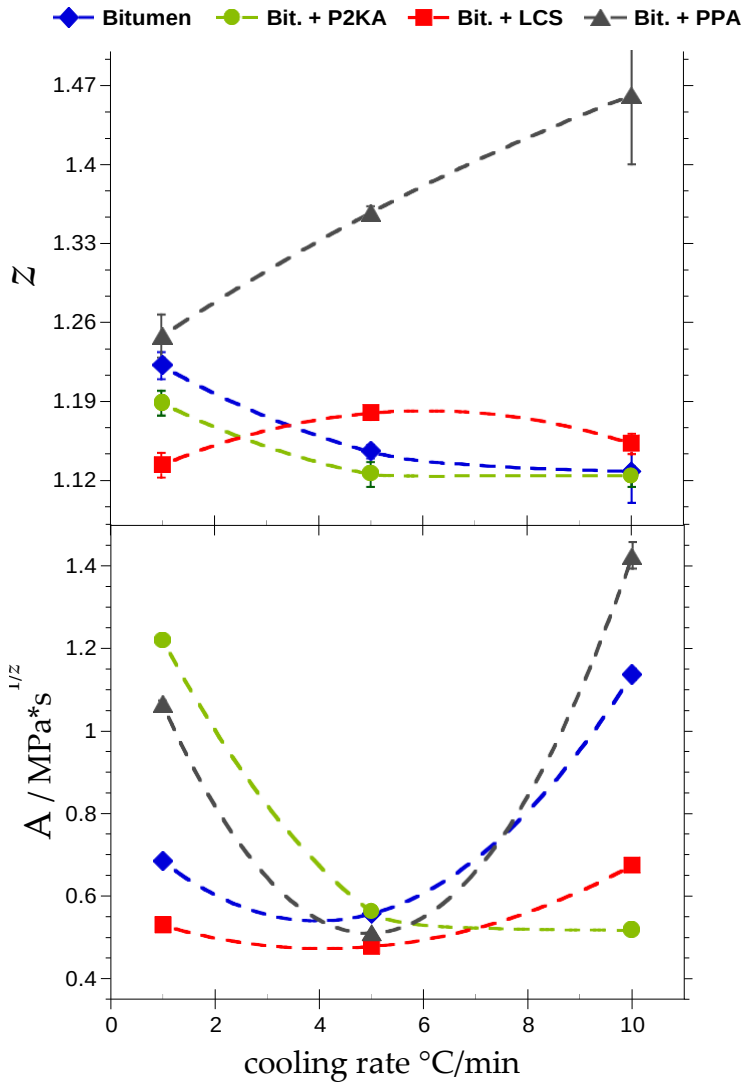

Figure 3. Dependence on the cooling rate of both *z* coordination number (upper plot) and interaction strength A (lower plot) for neat bitumen (diamonds) and bitumens modified by addition of 2% P2KA (circles), LCS (squares) and PPA (triangles), respectively.

4. Conclusions

A comparative investigation of the mechanical responses manifested by bitumen modified with three non-polymeric additives was performed at 25 °C, after the corresponding specimens were subjected to different cooling rates in the range 1–10 °C/min. The selected range of cooling ramps

represented a good compromise between suitable experimental conditions performed at lab-scale and hypothetical cooling events that might occur in realistic environmental conditions.

Aimed at searching for microstructural differences between various types of modified bitumens when they have undergone the action of several thermal ramps, a parallel morphological investigation was also carried out by using Atomic Force Microscopy (AFM). The correspondent rheological response was interpreted under the framework of the "weak gel" model whose analysis revealed the presence of lightly entangled networks with the exception of PPA-modified bitumen. A striking result was recorded from bitumen incorporating a raw mixture of natural phospholipids (2% LCS additive), which was able to leave the asphaltene aggregates fairly unaltered after the hot material was either slowly (1 °C/min) or rapidly (10 °C/min) cooled to the final reference temperature of 25 °C. The complex modulus of the correspondent LCS-modified bitumen was found almost independent of the cooling rate as well. The addition of LCS to bitumen should prove extremely fruitful in increasing the mechanical resistance of bitumen to thermal shocks and provide an attempt to substitute polymer-based rheology modifiers with additives derived from renewable bio-resources.

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Author Contributions: Cesare Oliviero Rossi and Ruggero Angelico conceived and designed the experiments; Maria Penelope De Santo performed the AFM experiments; Saltanat Ashimova prepared the samples and performed the rheological experiments; Pietro Calandra analyzed the data.

Conflicts of Interest: The authors declare no conflict of interest

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Chapter 5

applied sciences

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Article

Effects of Natural Antioxidant Agents on the Bitumen Aging Process: An EPR and Rheological Investigation

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Featured Application: Additives obtained from natural waste materials could effectively reduce the hardening effect of bitumen aging in road pavements by exerting an effective antioxidant protection.

Abstract: Bitumen aging is the major factor contributing to the deterioration of the road pavement. Oxidation and volatilization are generally considered as the most important phenomena affecting aging in asphalt paving mixtures. The present study was carried out to investigate whether various antioxidants provided by natural resources such as phospholipids, ascorbic acid as well as lignin from rice husk, could be used to reduce age hardening in asphalt binders. A selected bituminous material was modified by adding 2% *w*/*w* of the anti-aging natural additives and subjected to accelerated oxidative aging regimes according to the Rolling Thin Film Oven Test (RTFOT) method. The effects of aging were evaluated based on changes in sol-gel transition temperature of modified bitumens measured through Dynamic Shear Rheology (DSR). Moreover, changes of Electron Paramagnetic Resonance (EPR) spectra were monitored on the bituminous fractions asphaltene and maltene separated by solvent extraction upon oxidative aging. The phospholipids-treated binder exhibited the highest resistance to oxidation and the lowest age-hardening effect compared to the other tested anti-oxidants. The combination of EPR and DSR techniques represents a promising method for elucidating the changes in associated complex properties of bitumen fractions promoted by addition of free radical scavengers borrowed by green resources.

Keywords: bitumen; antioxidant agent; rheology; electron paramagnetic resonance

1. Introduction

In asphalt industry, the term *aging* identifies the process of deterioration of bitumen due to the occurrence of oxidation mechanisms and progressive loss of volatile components. This alteration occurs over time and causes a change in the chemical, physical, colloidal and rheological properties of the bitumen itself, affecting the useful life of the road pavement as aging tends to make the binder more fragile and therefore the conglomerate more prone to cracking [1]. The aging process

is strongly linked to the thermal susceptibility of bitumen and evolves depending on two main factors: the original crude oil and the production process. The bitumen oxidation process is extremely complex. Because of the varied and complex molecular composition, it is unthinkable to isolate and identify the individual species obtained as a result of oxidation. However, understanding the mechanisms by which it takes place is of fundamental importance as it represents the main factor responsible for the hardening of road pavements and therefore of irreversible changes in the physical properties of the binder. Despite the impossibility of isolating the single oxidized components, the main functional groups have been identified. These include predominantly ketones and sulfoxides, accompanied by dicarboxylic anhydrides and dicarboxylic acids in much smaller concentrations [2]. As described by Petersen [3], the oxidation mechanism can be divided into two sequential phases. The primary or short-term aging, which occurs in the phase of production of bituminous mixes and during the paving phase of the bituminous conglomerates, and secondary or long-term aging, which manifests with increasing the pavement service life. Besides, the field aging of asphalt pavements must also be considered, and a number of studies have attempted to characterize the aging viscoelastic properties of asphalt mixtures such as dynamic modulus at different aging times and pavement depths, to account for the effects of long-term aging and non-uniform field aging in the pavement depth [4,5]. Primary aging is a process of short temporal duration, compared to the secondary one and is generated during the mixing phase of the binder with the aggregates and the process of spreading and compacting [6]. Inevitably, the main consequences due to primary aging concern the variation of the chemical composition, caused mainly by oxidation processes. Bitumen storage, even for a long time, does not generate important changes in the consistency of the binder due to the limited access of oxygen. During mixing, transport and spreading of the conglomerate, the thin film bitumen is instead exposed to high temperature and atmospheric oxygen; the resulting chemical changes translate into obvious physical changes. In particular, there is a substantial reduction of the aromatic fraction together with the increase in the content of resins and asphaltenes [7,8]. The saturated content remains substantially unchanged due to the relatively low reactivity of the components in question. The changes in the chemical composition determine an increase in the average size of the molecules present (with increase in molecular weight) accompanied by a hardening of the bitumen [9]. The addition of antioxidant compounds to a bituminous aggregate is therefore a good strategy to increase its durability and prevent deterioration.

Many studies have appeared in the specific literature about the addition of various additives to the bitumen, with the aim to evaluate their antiaging performances. Several organic and inorganic compounds have been tested to improve the aging resistance of bitumen and, hence, its durability in the asphalt mix [10–15]. For example, Banerjee et al. [16] tested Sasobit, Rediset, Cecabase, and Evotherm, of which the first additive is a Fischer–Tropsch paraffin and the other antioxidants are synthetic. Further applications can be found in a recent comprehensive review of aging of asphalt paving materials with focus on antioxidant additives [17]. However, a few studies deal with the application of natural additives or byproducts rich in antioxidants as free radical scavengers to protect bituminous materials from oxidation phenomena [18–20]. The antioxidant properties of many raw materials borrowed from renewable natural resources have yet to be tested such as, e.g., the polyunsaturated fatty components of natural phospholipids. The application of cheap and environmentally friendly anti-aging additives to virgin bitumen would enjoy the double advantage of using sustainable and renewable compounds and at same time reducing the carbon footprint of the products of asphalt industries according to the circular economy's recommendations.

The objective of the present work is to investigate whether the addition to bitumen of antioxidant agents obtained by natural resources improves its resistance towards short artificial aging by Rolling Thin Film Oven Test (RTFOT). The research design is accomplished by investigating the effects of the aging process on both the mechanical response of binders by running Dynamic Shear Rheology (DSR) tests, and the free radical content detected by Electron Paramagnetic Resonance (EPR) spectroscopy on asphaltene and maltene bituminous fractions. The experimental approach is sketched in the flowchart

of Figure 1. Bitumen manifests EPR spectra due to organic radicals [21–23] the signal shape of which is susceptible to changes in the oxidative state, and vanadyl ions VO^{2+} [24] associated with porphyrin species, which instead appear to be unaffected by oxidative treatments. Here we will focus our attention on the two most representative components present in the bitumen, namely, asphaltenes and maltenes [25]. The former are macromolecular compounds, comprising polyaromatic nuclei linked by aliphatic chains or rings of various lengths and sometimes by functional groups [26]. A peculiar characteristic of petroleum asphaltenes is the presence of stable free radicals, well detectable by EPR, associated with a non-localized π system of electrons stabilized by resonance. Maltene represents the bitumen fraction soluble in n-pentane, which in turn can be split into saturates, aromatics (also apolar aromatics), and resins (also polar aromatics) [27]. The results of the present work show that it is possible to draw useful anti-aging additives from renewable sources capable to reduce the age-hardening effect and concomitantly protect bitumen against oxidative aging.

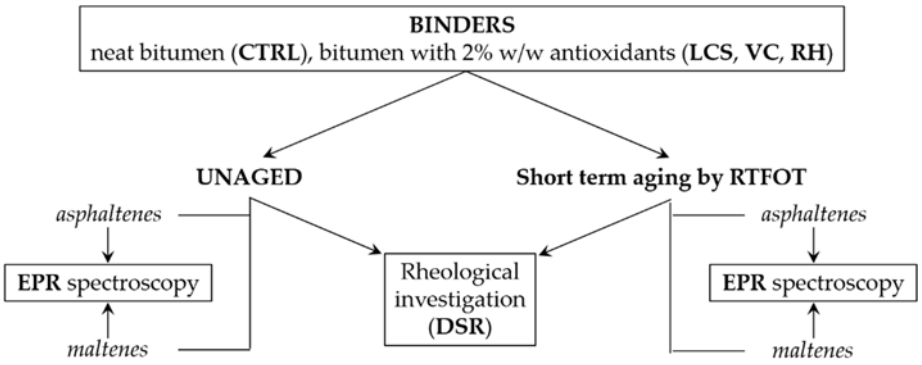

Figure 1. Flowchart of the experimental approach. The tested binders both neat bitumen as control CTRL, and bitumen modified with 2% w/w of natural antioxidants, namely, a mix of phospholipids (LCS), Vitamin C (VC) and rice husk (RH), are subjected to artificial thermal treatment by Rolling Thin Film Oven Test (RTFOT). Then, Dynamic Shear Rheological (DSR) tests carried out on artificially aged binders are compared to those performed on aliquots of unaged samples. A parallel EPR study is performed on both the asphaltene and maltene fractions obtained, respectively, from unaged binders and bitumens subjected to short-term aging by RTFOT.

2. Materials and Methods

2.1. Sample Preparation

A light brown bitumen (penetration grade 50/70), produced in Saudi Arabia and kindly supplied by Loprete Costruzioni Stradali (Terranova Sappo Minulio (RC), Italy), was used as base asphalt binder to test the effectiveness of natural compounds selected as anti-aging additives. The natural antioxidant additives selected for the present research were: (a) commercial mix of phospholipids in form of light yellow powder (hereafter LCS) provided by Kimical srl (Rende (CS), Italy); (b) Vitamin C, also known as ascorbic acid (hereafter VC) provided by Sigma-Aldich (Milano, Italy); (c) rice husk (hereafter RH) obtained from producers located in Mantova, Italy. The raw RH was first washed with distilled water and dried at 60 °C and then ground for 10 min in an electric mixer and sieved with 0.5 mm sieve to get fine powder prior mixing with bitumen. Three aliquots of the starting bitumen were first heated at 140–160 °C and then mixed with 2% by weight (w/w) of LCS, VC and RH, respectively. A fourth aliquot of the same bitumen source was used as reference (hereafter, CTRL). Each compound was separately added to bitumen, under vigorous stirring at the temperature of 150 °C and the stirring was maintained for a period of 30 min. Once the mixing procedure was finished, each of the resulting bitumen mixtures was separately poured into small sealed containers and then stored in a darkened thermostat at 25 °C to preserve morphology.

2.2. Bitumen Separation

Both unaged and artificially aged bituminous samples, either modified with antioxidants or not, were subjected to an experimental procedure based on the bitumen separation by n-pentane extraction according to the American Society for Testing Materials (ASTM) Standard method 4124 [28]. In details, 10 g ca. of bitumen were weighed into a 2 L Erlenmeyer flask and 300 mL ca. of n-pentane were added. A good dispersion of the bitumen was assured through vigorous stirring. The flask was then heated to 90 °C and kept at that temperature for about 1–2 h. Afterwards, the bottle was left overnight for cooling and sedimentation of solid fraction. The next day, the dispersion was filtered through a Büchner-funnel (Whatman 42 ashless) and the insoluble phase, called asphaltene phase, was collected and stored. Then, the n-pentane soluble maltene phase, appearing as a viscous liquid, was obtained after the solvent had been removed by evaporation under reduced pressure. In Table 1 the percentages of asphaltene collected from the unaged and aged samples are reported.

Table 1. The weight percentages of asphaltene fraction obtained from crude bitumen (CTRL) and bitumen modified with LCS, VC and RH additives, both unaged and subjected to artificial aging.

Sample	Asphaltene (% *w/w*)	
	Unaged	**Aged**
CTRL	26.8	34.2
Bitumen + LCS	29.2	32.8
Bitumen + VC	28.2	35.3
Bitumen + RH	29.5	35.7

2.3. Aging Test

In order to study the effects of aging in the laboratory, the method known as Rolling Thin Film Oven Test (RTFOT) [29,30] was adopted to simulate the short-term aging of asphalt binders that would occur during the hot-mixing process. The apparatus consists essentially of an internal double-wall furnace, in which the hot air circulates conveyed by an internal fan at the test temperature of 163 °C. The test consists in subjecting a thin layer of bitumen, ~1.25 mm, to a hot air jet for 75 min. Each modified bitumen, plus a reference binder free of additives, was divided into two aliquots, of which only one was subjected to the process of artificial aging. Both sets of aliquots were subsequently separated into the respective fractions of asphaltene and maltene by extraction in n-pentane, which were finally characterized through Dynamic Shear Rheology (DSR) and Electron Paramagnetic Resonance (EPR) spectroscopy tests (see the flowchart of the experimental approach in Figure 1).

2.4. Dynamic Shear Rheology (DSR)

Temperature sweep (time cure) rheological tests were performed to analyze the mechanical response of modified bitumens vs. CTRL upon artificial aging process. Experiments were carried out using a controlled shear stress rheometer (SR5, Rheometric Scientific, Piscataway, NJ, USA) equipped with a parallel plate geometry (gap 2.0 ± 0.1 mm, diameter 25 mm) and a Peltier system (±0.1 °C) for temperature control. Bitumen exhibits aspects of both elastic and viscous behaviors and is thus classified as a visco-elastic material [31,32]. DSR is a common technique used to study the rheology of asphalt binders at high and intermediate temperatures [33,34]. Operatively, a bitumen sample was sandwiched between two parallel plates, one standing and one oscillatory. The oscillating plate was rotated accordingly with the sample and the resulting shear stress was measured. The linear viscoelastic regime of both the reference free of additives (CTRL), and modified bitumens was checked by preliminary stress sweep tests. The temperature sweep tests were performed within the range 25–80 °C with ramp 1 °C/min in heating by applying the proper stress values to guarantee linear viscoelastic conditions at all tested temperatures. During the tests a periodic sinusoidal displacement at

constant frequency of 1 Hz was applied to the sample and the resulting sinusoidal force was measured in terms of amplitude and phase angle as the loss tangent (tan δ). RSI Orchestrator® software was used to determine the complex modulus (G^*), storage (G^t) and loss (G'') moduli, phase angle (δ) or tan $\delta = G''/G^t$. More details about the mechanical characterization can be found elsewhere [35].

2.5. Electron Paramagnetic Resonance (EPR) Spectroscopy

Nine GHz EPR (X-band) spectra were recorded on a Bruker Elexys E-500 spectrometer (Bruker, Rheinstetten, Germany). Capillaries containing the samples were placed in a standard 4 mm quartz sample tube containing light silicone oil for thermal stability. The temperature of the sample was regulated at 25 °C and maintained constant during the measurement by blowing thermostated nitrogen gas through a quartz Dewar. The protocol of EPR testing is sketched in Figure 2. The instrumental settings were as follows: sweep width, 120 G; resolution, 1024 points; modulation frequency, 100 kHz; modulation amplitude, 1.0 G; time constant, 20.5 ms. From preliminary power saturation tests, r.f. power levels 0.203 and 0.40 mW selected, respectively, for asphaltene and maltene fractions, were found to be sufficiently low to avoid saturation effects. Several scans, typically 4–16, were accumulated to improve the signal-to-noise ratio. Linewidths were measured from first-derivative curves (peak-to-peak). The spin concentration could be estimated by taking the ratio of area of the sample to that of a standard containing a known number of radicals. Therefore, the concentration of paramagnetic centers in both the asphaltene and maltene fractions of bituminous specimens were obtained by double integration of the experimental first-derivative spectrum and compared with EPR spectrum of a known amount of a MgO-MnO solid solution used as standard [36,37] (spin density = 6.83×10^{15} spin/g). The g-value (Landé factor) was determined from the condition $h\nu = g\beta B_r = g_s \beta B_s$, from which $g = g_s B_s/B_r$ where ν is the frequency of the used microwave radiation, β the Bohr magneton for electron, $g_s = 1.9810$ is the g-value for the standard [38,39], B_s and B_r are the magnetic field values of standard and sample, respectively.

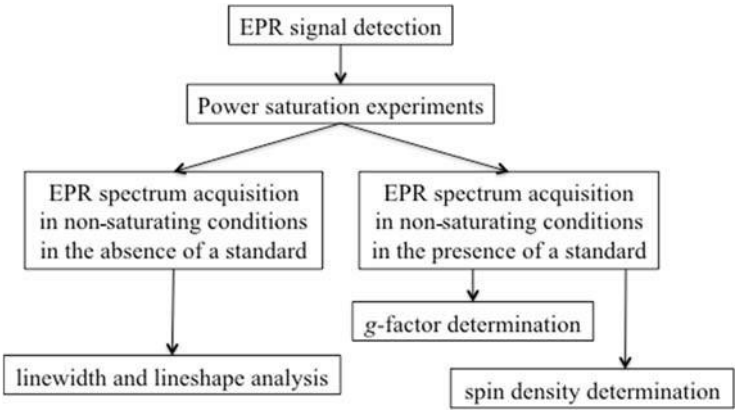

Figure 2. Flowchart of the Electron Paramagnetic Resonance (EPR) test protocol. The preliminary power saturation experiments are necessary to determine the power of the incident microwave beam to be used in the following steps.

3. Results and Discussion

3.1. Mechanical Behavior

Two important parameters are obtained from DSR tests on bitumen: the complex modulus, G^*, and the phase angle, δ. These parameters can be used to characterize both viscous and elastic behavior of the binder [40]. The dependence of these quantities on the temperature gives rise to the so-called time cures. As the temperature increases or frequency decreases, bitumen begins to lose the majority of its elastic behavior (the storage modulus, $G^t = G^* \cos\delta$, decreases) and starts to behave as a viscous fluid

(the loss modulus, $G'' = G^* \sin \delta$, increases). Thus, the limiting temperature in correspondence of which $\tan \delta \rightarrow \infty$ identifies the viscoelastic-sol transition temperature T_{TR} above which viscous behavior is highly predominant over elastic mechanical contribution. Figure 3 shows the time cure curves for virgin bitumen and bitumens modified with antioxidant additives and compared to analogous measurements performed after the aging process (RTFOT). Through data interpolation the asymptotic value of $\tan \delta$ intercepts the temperature axis and identifies T_{TR}. Actually, in Figure 3 the temperature difference $\Delta T = T_{TR}$ (aged) $- T_{TR}$ (unaged) can be read in each graph while the histogram of Figure 4 illustrates a direct comparison of ΔT for all the investigated samples.

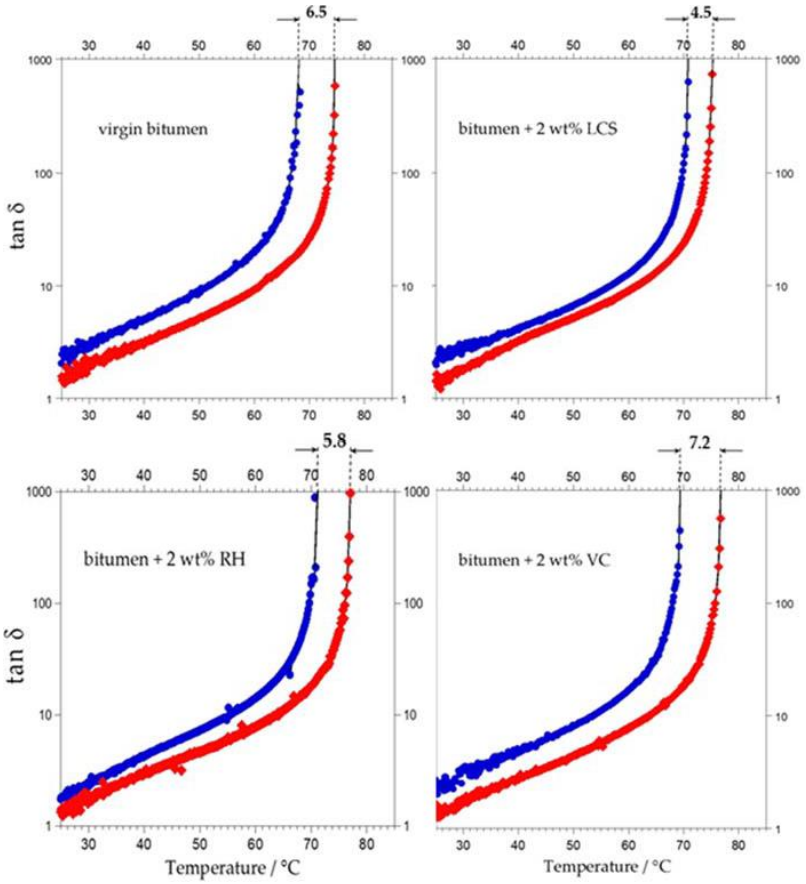

Figure 3. Time cure curves for virgin bitumen and bitumens modified with 2% w/w of LCS, RH and VC antioxidant additives, respectively. The increments of viscoelastic-sol transition temperature between aged (red symbols) and unaged (blue symbols) samples are indicated on the top axis of each graph.

Upon addition of 2% w/w of anti-oxidants a slight increase of T_{TR} is observed for unaged samples, 69.4 °C (VC), 70.6 °C (LCS) and 71.2 °C (VC) compared to virgin bitumen 68.1 °C. The shift ΔT (±0.2 °C as estimated error) of T_{TR} recorded upon heating treatment respect to the same unaged sample is an indication of an increase in hardening consistency of bitumen, which in turn can be correlated to the oxidation degree occurred in the material. Aging significantly changes both the chemical and physical properties of asphalts, which results in lower elasticity and higher stiffness. In absence of additive a shift of T_{TR} towards higher temperatures has been observed with ΔT_{CTRL} = 6.5 °C. Then, the following sequence of ΔT values has been detected for bitumen supplemented with inhibitors of free radicals: ΔT_{LCS} = 4.5 °C, ΔT_{RH} = 5.8 °C and ΔT_{VC} = 7.2 °C. Those data clearly indicate a superior performance manifested by LCS in retarding oxidative hardening compared to the other tested antioxidants. Hitherto, the use of raw mixtures of natural phospholipids has been confirmed to be a powerful method to increase both the adhesion properties of bitumen [34] and its mechanical

resistance to the action of thermal shocks [41]. Here, the discover of anti-aging properties of LCS adds another advantage of using these green compounds as multi-functional additives to enhance the bitumen performances. The presence of polyunsaturated fatty components in phospholipids providing carbon sites susceptible of oxidation may be responsible for the observed antioxidant activity [42] as it will be also confirmed by the analysis of EPR spectra.

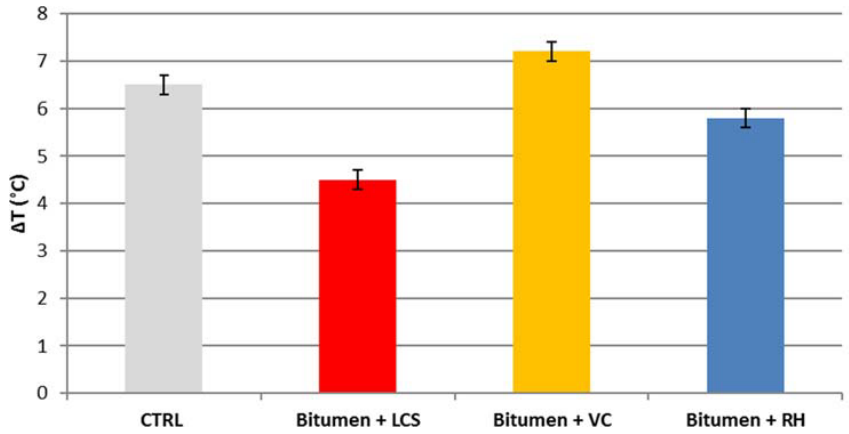

Figure 4. Comparison of $\Delta T = T_{TR}$ (aged) $- T_{TR}$ (unaged) for the series of investigated samples.

3.2. EPR Spectroscopy Investigation

EPR measurements clearly confirm the presence of unpaired electrons in all the investigated systems, according to previous studies [22,43]. The X-band EPR spectra of the bituminous signals consist of two non-overlapping EPR signals, one centered at about 3480 G due to vanadyl ions (spin 7/2), and the second in a range between 3510 and 3530 G associated to organic radicals (see Figure 5 for the asphaltene fractions).

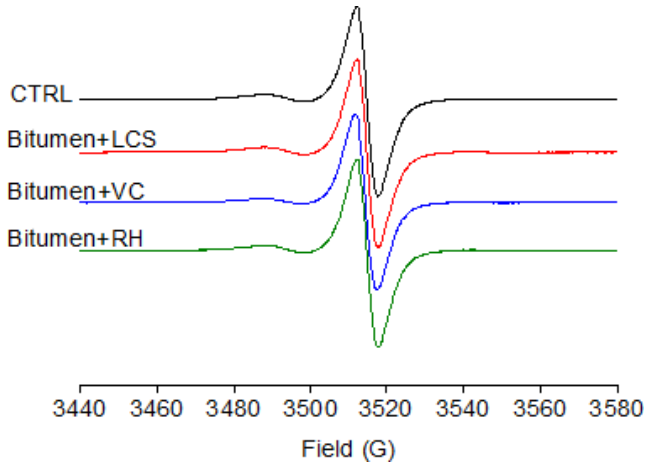

Figure 5. X-band EPR spectra of unaged asphaltene samples mixed with 2% *w*/*w* of antioxidants registered at room temperature. CTRL indicates the control sample with no antioxidant added.

A complete set of spectra acquired for both the asphaltene and maltene fractions is illustrated in Figure S1 of Supplementary Material. Free radicals associated with non-localized π system, stabilized by resonance in polyaromatic centers, can be studied by EPR spectroscopy owing to the influence of the environment on the radical magnetic properties. Therefore, various parameters can be derived from the analysis of spectra, furnishing different pieces of information, sometimes complementary, sometimes partially overlapping.

3.2.1. The *g*-Factor

The *g*-factor (or Landé factor) indicates the magnetic field of resonance (position in the spectrum); it is a parameter sensitive to the chemical environment of the unpaired electron, i.e., to the specific features of the orbital in which it is localized.

The *g*-factor increases in the presence of heteroatoms, owing to their contribution to the electron molecular orbital. In fact, the heteroatoms shift g to values higher than 2.0023 corresponding to free electron [44]. For all the asphaltene samples, whether unaged or aged, the peak assigned to organic radical gives g = 2.0027–2.0028 (see Table S1 in Supplementary Material) very close to the free electron value, thus indicating that if present in these radicals, heteroatoms are not likely to participate in the molecular orbital of the unpaired electron to any significant degree. Even for maltene samples, the Landé factor remains substantially constant in the range 2.0025–2.0029 (see Table S1 in Supplementary Material) comparable with that obtained for asphaltene. A weak reduction has been found only in the case of maltene fraction isolated from CTRL upon RTFOT treatment (2.0028 → 2.0025). The effects of the oxidation process are in fact more evident on the reference system free of antioxidants, which inevitably favors the aggregation and condensation of adjacent units, forming more complex structures. The latter are accompanied by an increase in the level of aromaticy responsible for the shift of *g*-factor towards lower values. Finally, the *g*-value for the signal of the vanadyl group does not undergo any variation as a result of the oxidation process for both asphaltene (2.0018–2.0019) and maltene (2.0011–2.0014) fractions analyzed (see Table S1 in Supplementary Material). This condition is in accordance with the fact that in the primary aging process simulated by heat treatment the vanadyl group is not involved in any way.

3.2.2. The Spin Density

Spin concentration is a measure of the number of unpaired electrons in a given amount of sample. Overall, the EPR results show that the spin density of the maltene fraction, in both unaged and aged samples, is around 5% of that determined in the asphaltene phase. This is a further confirmation that the main contribution to the organic radicals detected in bitumen samples comes from unpaired electron in non-localized π system stabilized by resonance in extended polyaromatic macromolecules.

Interestingly, natural antioxidant additives affect the bitumen spin density even in the absence of the aging treatment, just as an effect of mixing. This is specifically true for LCS, the addition of which results in a lower radical content in the asphaltene fraction, ascribable to an effective scavenging action (see Figure 6).

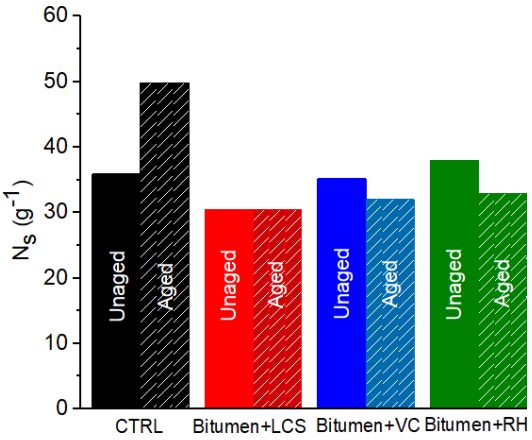

Figure 6. Spin density of asphaltene samples mixed with 2% *w*/*w* of antioxidants, as determined from the X-band EPR spectra registered at room temperature. CTRL indicates the control sample with no antioxidant added. Full bars: unaged samples; striped patterned bars: samples artificially aged through the Rolling Thin Film Oven Test (RTFOT) method.

The RTFOT treatment causes a significant increase of the spin density in the CTRL asphaltene sample, and, to a lower extent, in the corresponding maltene fraction. This indicates aging causes an increase in the average size of the polyaromatic asphaltene molecules, thus resulting in a further stabilization of the unpaired electrons in the extended π systems.

The anti-aging effect of natural antioxidant additives can be evidenced by observing the differences in concentration relative to the aged CTRL. In fact, upon the aging treatment, the addition of LCS, VC and RH leads to a reduction in the density of free radicals in asphaltene fraction of 39%, 36% and 34%, respectively (see Table 2).

Table 2. Concentrations of paramagnetic centers N_s determined in asphaltene and maltene fractions obtained both from unaged bituminous samples and after artificial aging through RTFOT. Relative concentration differences with respect to the aged CTRL have been also indicated in brackets.

Sample	Organic Radical Density N_s in 10^{17} Spins·g^{-1}			
	Asphaltene		Maltene	
	Unaged	Aged	Unaged	Aged
CTRL	35.9	49.8	2.27	2.68
Bitumen + LCS	30.5	30.5 (39%)	1.92	1.27 (53%)
Bitumen + VC	35.2	32.0 (36%)	1.79	1.36 (49%)
Bitumen + RH	38.0	32.9 (34%)	1.96	2.23 (17%)

In particular, among all the additives tested, LCS is the only one able not only to lower the free radical content of the asphaltenic component in response to the heat treatment to which the bitumen is subjected, but also to keep the spin density unchanged before and after aging stress. The relative antioxidant effect recorded on the maltene fraction is much more pronounced compared to the aged CTRL, showing a strong reduction in the concentration of paramagnetic radicals for bitumens modified, respectively, with LCS (53%) and VC (49%) while the effect of RH is somewhat weaker (17%).

3.2.3. Linewidth and Lineshape

The width of an EPR band is inversely proportional to the lifetime of the absorbing species in its excited state. It depends on the interaction between the unpaired electrons and their surroundings; the greater the interaction, the wider the band. Moreover, for complex and chemically heterogeneous samples, spectrum broadening could be the result of unresolved hyperfine structure; in bitumen samples, broadening of EPR signals due to unpaired electrons delocalized in aromatic π systems could arise from the hyperfine coupling with the adjacent aromatic H atoms [45].

The spectral linewidth is generally quantified by measuring, in gauss (G), the peak-to-peak distance (H_{pp}) of the first-derivative curve, which is the experimental output of the instrument. The (H_{pp}) values determined for the examined samples, collected in Table 3, show that, overall, the linewidth of the organic radical signal is only marginally affected by both aging and antioxidant addition. This indicates that both the molecular structure and the supramolecular organization of the sample do not change. Perusal of the table only reveals a slight narrowing for asphaltene in the presence of the LCS additive, thus suggesting reduced local interactions.

Further information can be obtained from the analysis of the EPR signal lineshape. In general, it is affected by the unresolved hyperfine structure and the anisotropic effects and is classified as either Lorentzian or Gaussian. EPR lines have a trend toward a more Lorentzian character with increasing aromaticity [46]. However, radical species with different relaxation behaviors give rise to independent narrow absorptions, which yield a Gaussian-shaped envelope [46]. The accordance with one lineshape rather than another can be estimated by evaluating the ratio R_n of H_n to H_{pp} where H_n is the width at the position $1/n$ of the peak-to-peak height of the first-derivative curve. For n = 5, the expected R_5 values for a Lorentzian and Gaussian lineshape are 1.72 and 1.17, respectively [46].

The peak-to-peak separations of the asphaltene and maltene EPR derivative signals (H_{pp}) and the lineshape ratio $R_5 = H_5/H_{pp}$ are reported in Table 3. It is observed that for both the series of unaged and aged asphaltenic samples, the reference parameter R_5 remains almost constant and intermediate between Lorentzian and Gaussian lineshape, implying that the core size of the polyaromatic clusters remains essentially unchanged upon thermal treatment.

Table 3. Peak-to-peak separation of the derivative peak (H_{pp}) and lineshape parameter (R_5) of EPR spectra of asphaltene and maltene fractions obtained both from unaged bituminous samples and after artificial aging through RTFOT.

Sample	Asphaltene				Maltene			
	H_{pp} (G)		R_5		H_{pp} (G)		R_5	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
CTRL	6.2	5.8	1.4	1.5	5.4	4.9	1.5	1.5
Bitumen + LCS	5.9	5.6	1.4	1.5	5.2	5.3	1.5	1.3
Bitumen + VC	5.9	5.8	1.4	1.4	5.6	5.4	1.4	1.4
Bitumen + RH	5.7	5.7	1.5	1.4	5.7	5.6	1.4	1.4

An exception of this feature regards the unaged sample modified with RH additive, in correspondence of which a significant increment of R_5 is recorded compared to the asphaltene samples of the same series. Considering the maltene fraction, calculated R_5 data are slightly scattered compared to asphaltene, though manifesting the same intermediate character of the signal lineshape. Only for the sample supplemented with LCS a marked Gaussian tendency is observed in response to the aging treatment. In this case, this tendency is probably due to the presence of radical species characterized by quite different (less homogeneous) relaxation times, leading to independent absorptions.

3.2.4. Saturation Curves

Analysis of saturation curves of asphaltene samples shows a typical homogeneous saturation trend, as shown in Figure 7, characterized by the presence of a maximum followed by a decrease of the signal, which indicates the onset of spin saturation process. The homogeneous saturation trend is generally observed when a given set of spins is exposed to the same net magnetic field and has a uniform distribution in space. In fact, decrease of amplitude with increasing microwave power is characteristic for free radicals homogeneously located in the sample. Homogeneous saturation occurs when all free radical spins behave as a single spin system with the same relaxation behavior. In other words, the energy absorbed from the microwave field is distributed to all the spins and thermal equilibrium of the spin is maintained through resonance.

The observed homogeneous saturation is in agreements with the molecular structure of asphaltenes, which can be visualized as polycondensates of a multicomponent system made up of individual molecules of aromatics, paraffins, naphthenics, macrocyclics, and heterocyclics characterized by extensive conjugation and wide electronic delocalization. As illustrated in Figure 7, all the saturation curves are affected neither by the presence of additives nor by the aging process.

Analogous tests have been carried out on maltene samples isolated from both CTRL and bitumen modified with LCS, VC and RH additives, respectively. The correspondent power saturation curves, shown in Figure 8, manifest a definitely more complex trend.

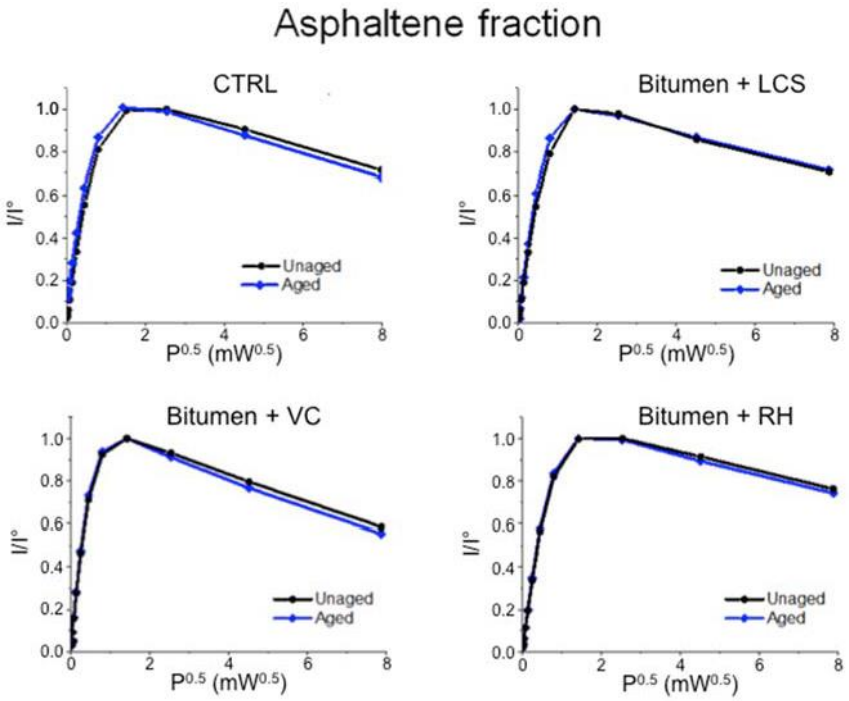

Figure 7. Power saturation profiles for asphaltene samples mixed with 2% w/w of antioxidants, as determined from the X-band EPR spectra registered at room temperature. CTRL indicates the control sample with no antioxidant added. Black lines, full circles: unaged samples; blue lines, full diamonds: samples artificially aged through the RTFOT method.

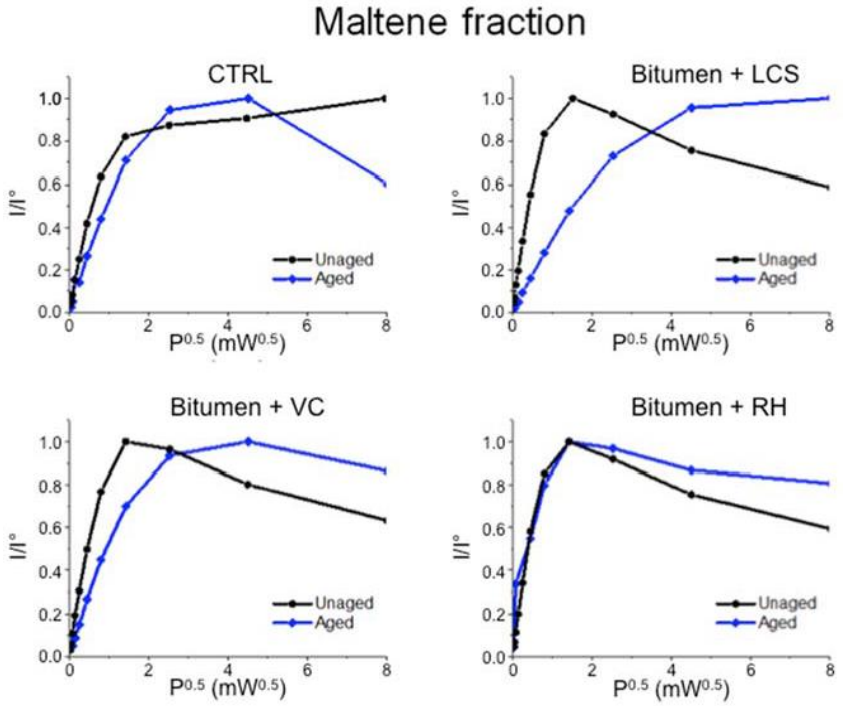

Figure 8. Power saturation profiles for maltene samples mixed with 2% w/w of antioxidants, as determined from the X-band EPR spectra registered at room temperature. CTRL indicates the control sample with no antioxidant added. Black lines, full circles: unaged samples; blue lines, full diamonds: samples artificially aged through the RTFOT method.

Maltene phase free of antioxidants shows a heterogeneous trend characterized by the absence of a maximum, which becomes homogeneous by following the simulated aging process in the laboratory, (see Figure 8). This circumstance may occur because aging of bitumen promotes a progressive increase of aromaticy accompanied by a consequent decrease in mass of saturated oils and resins [1]. The presence of antioxidant agents imparts an inversion of trend shown by the reference, i.e., from homogeneous to heterogeneous saturation upon RTFOT treatment. This aspect might be a consequence of a reduced oxidability of the organic matrix due to the antioxidant activity, the efficiency of which qualitatively increases along the series RH < VC < LCS.

4. Conclusions

The effectiveness of natural compounds as anti-aging additives in the reduction of age-hardening effect and concomitant bitumen protection against oxidative aging was evaluated by measuring the rheological properties and EPR spectra of asphalt binders in unaged samples and after artificial thermal treatment. Addition of phospholipids turned out to be beneficial in minimizing the shift of viscoelastic-sol transition temperature towards higher values in temperature sweep rheological tests, which is a typical fingerprint of bitumen hardening in response to oxidative phenomena. The apparent scavenging action manifested by phospholipids was confirmed by a lower radical content detected in the asphaltene fraction compared to the reference system as observed by EPR results. An increase of heterogeneity of distribution of radicals in maltene fractions was inferred by the power saturation profiles determined from the X-band of EPR spectra upon addition of natural anti-aging compounds. However, that effect was more pronounced in presence of phospholipids, in a minor degree for vitamin C and even less for rice husk, thus indicating a greater aging inhibitory effect promoted by the former additive. The present study confirmed the usefulness of considering green compounds from renewable resources of reduced carbon footprint as anti-aging additives for bituminous materials.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/8/8/1405/s1, Figure S1: X-band EPR spectra of asphaltene and maltene fractions obtained from bitumen samples mixed with 2% *w*/*w* of antioxidants, Table S1: Landé factor (*g*) of EPR signals of asphaltene and maltene fractions obtained both from unaged bituminous samples and after artificial aging through RTFOT.

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Chapter 6

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Composition and rheological characteristics of bitumen in short-term and long-term aging

Состав и реологические характеристики битума при кратковременном и длительном старений

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Key words: blown bitumen; short-term aging; long-term aging; dynamic shear rheometer; bending beam rheometer; complex shear modulus; phase angle; stiffness

Ключевые слова: окисленный битум; кратковременное старение; длительное старение; динамический сдвиговой реометр; реометр с изгибаемой балкой; комплексный сдвиговой модуль; фазовый угол; жесткость

Abstract. This paper investigates the impact of sequential short-term and long-term aging of blown bitumen of the grade BND 70/100 on its mechanical characteristics in the temperature interval from 76°C to -36 °C. Group chemical composition of the bitumen has been determined by the method of liquid adsorption chromatography by the chromatograph “Gradient M”. Short-term aging has been performed in the vertical rolling thin film oven (RTFOT) under the standard of AASHTO T 240-08, and the long-term aging - in the pressure aging vessel (PAV) under the standard of ASTM D 6521-08. Mechanical characteristics of the bitumen are complex shear modulus *G** and phase angle *δ* at the mean and high temperatures (from 4 °C to 76 °C) have been measured by dynamic shear rheometer (DSR) under the standard of AASHTO T 315-08. Bitumen stiffness S at low temperatures (from -24 °C to -36 °C) has been measured by bending beam rheometer (BBR) under the standard of AASHTO T 313-08. It has been determined that during short-term aging the content of oils in the bitumen has been decreased for 1.5 %, and the content of asphaltenes has been increased for 2 %. After the long-term aging, performed after the short-term aging, the content of oils in the bitumen has been decreased for 7 %, and the content of asphaltenes has been increased for 6.3 %. The content of resins in the bitumen remains practically constant at both types of aging. At the mean and high temperatures the short-term and long-term aging increase the complex shear modulus up to 2 and 7 200 times respectively and decrease the phase angle at average for 4-6° and 8-10° respectively. At low temperatures the short-term aging and long-term aging increase the bitumen stiffness in 1.5 and 2.5 times respectively.

Аннотация. В настоящей работе исследовано влияние последовательных кратковременного и длительного старений окисленного битума марки БНД 70/100 на его механические характеристики в температурном интервале от 76 °С до -36 °С. Групповой химический состав битума был определен методом жидкостно-адсорбционной хроматографии на хроматографе «Градиент М». Кратковременное старение было осуществлено в вертикальной тонкопленочной вращающейся печи (RTFOT) по стандарту AASHTO T 240-08, а длительное старение - в сосуде высокого давления и температуры (PAV) по стандарту ASTM D 6521-08. Механические характеристики битума – комплексный сдвиговой модуль G* и фазовый угол *δ* при средних и высоких температурах (от 4 °С до 76 °С) были измерены динамическим сдвиговым реометром (DSR) по стандарту AASHTO T 315-08. Жесткость битума S при низких температурах (от -24 °С до -36 °С) была измерена реометром с изгибаемой балкой (BBR) по стандарту AASHTO T 313-08. Установлено, что при кратковременном старении содержание масел в битуме уменьшается на 1,5 %, а содержание

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асфальтенов увеличивается на 2 %. После длительного старения, осуществленного после кратковременного старения, содержание масел в битуме уменьшается на 7 %, а содержание асфальтенов увеличивается на 6,3 %. При обоих видах старения содержание смол в битуме остается практически постоянным. При средних и высоких температурах кратковременное и длительное старения повышают комплексный сдвиговой модуль до 2 и 7 200 раз соответственно и уменьшают фазовый угол в среднем на 4-6° и 8-10° соответственно. При низких температурах кратковременное и длительное старения повышают жесткость битума в 1,5 и 2,5 раза соответственно.

1. Introduction

It is well-known that bitumens in the conditions of their storage, preparation of an asphalt concrete mix, its transportation, laying, and compaction and during operation of an asphalt concrete pavement are subject to aging [1–3]. Due to aging bitumens usually become more viscous and more brittle at low temperatures. Therefore, the quantitative evaluation of the impact of bitumen aging on their properties is important for road engineering.

At present many countries of the world use widely three methods of artificial aging for bitumens. The first two of them [4] imitate the aging of a bitumen during preparation of an asphalt concrete mix, its transportation, laying, compaction, and the third method models the aging of a bitumen during operation of an asphalt concrete pavement. The latter two methods have been developed quite recently and included into the known American technical system Superpave [5].

The review of the published works [6–13] has shown that at present the intensive investigation is performed for the impact of bitumen aging on the properties of the bitumens themselves [8–10] and asphalt concretes with their use [11–15]. Meanwhile, practically always bitumen aging has been performed under the methods, included into Superpave. Practically all investigations are experimental ones and the impact of short-term and long-term aging has been evaluated in them on the rheological properties [5, 8–12], structural changes [9], standard characteristics [11, 12] of bitumens and asphalt concretes [9–13].

This paper investigates and gives the quantitative evaluation of the impact of short-term and long-term aging of the blown bitumen of grade BND 70/100 on its group chemical composition and mechanical (rheological) characteristics within the temperature interval from 76 °C to -36 °C by dynamic shear rheomoter (DSR) and bending beam rheometer (BBR).

2. Materials and Methods

2.1. Bitumen

Bitumen of grade BND 70/100 has been selected for experimental research of its rheological characteristics at various temperatures in three conditions: non-aged, after short-term aging (RTFOT) and after long-term aging (RTFOT+PAV). Bitumen has been produced at Pavlodar petrochemical plant from crude oil of Western Siberia (Russia) by method of direct oxidation. Its characteristics satisfy the requirements of the standard of Kazakhstan ST RK 1373-2013 [16]. Grade of bitumen under Superpave: PG 64-40 [5]. The main standard characteristics of the bitumen in the initial condition are shown in the Table 1.

Table 1. Main standard characteristics of bitumen in initial condition

Indicator	Measurement unit	Requirements of ST RK 1373-2013	Values
Penetration depth of the needle, 25°C, l00 g, 5s	0.1 mm	70–100	75
Penetration Index	-	-1.0...+1.0	-0.87
Ductility at the temperature of: 25°C 0°C		 ≥75 ≥3.8	 118 5.2
Softening point	°C	≥ 45	47.5
Fraas brittle point	°C	≤ -20	-28.5
Dynamic viscosity at 60°C	Pa·s	≥145	229
Kinematic viscosity at 135 °C	mm^2/s	≥250	428

2.2. Short-term aging

Short-term aging of the bitumen in the vertical rolling thin film oven have been performed under the standard of AASHTO T 240-08, which models the bitumen aging during preparing of an asphalt concrete mix, its transportation, laying and compaction. The samples of the bitumen were in the oven at the temperature of 150 °C for 75 minutes.

2.3. Long-term aging

Long-term aging of the bitumen in the special pressure aging vessel has been performed under the standard of ASTM D 6521-08, which models the bitumen aging during operation of the asphalt concrete pavement. The samples of the bitumen, after the short-term aging, were in the vessel under the pressure of 2070 kPa and at the temperature of 100 °C for 20 hours.

2.4. Dynamic shear rheometer

The mechanical characteristics of the bitumen at the mean and high temperatures (from +4 °C to +76 °C) have been measured by dynamic shear rheometer (Figure 1) under the standard of AASHTO T 315-08. The samples of the bitumen in the shape of round plate with diameter of 25 mm and thickness of 1 mm have been tested under the impact of sinusoidal varied strain, which has the amplitude of 12 % and frequency of 10 rad/s. Before testing the samples have been kept at the specified temperature not less than for 10 minutes. Shear deformation γ, shear stress τ and the phase angle δ have been measured as the test results.

The value of the complex shear modulus G* of the bitumen has been calculated under the formula [17–19]:

$$G^* = \frac{\tau_{\max} - \tau_{\min}}{\gamma_{\max} - \gamma_{\min}}, \quad (1)$$

where $\tau_{\max} - \tau_{\min}$ are maximum and minimum shear stresses respectively;

$\gamma_{\max} - \gamma_{\min}$ are maximum and minimum shear strains respectively.

The shear stresses τ_{max}, τ_{min} and shear strains γ_{max}, γ_{min} occur on the same plane, and their differences in the values are caused by sinusoidal load.

Figure 1. Dynamic shear rheometer (DSR)

2.5. Bending beam rheometer

The mechanical characteristics of the bitumen at low temperatures (-24, -30 and -36°C) have been measured by bending beam rheometer (Figure 2) under the standard of AASHTO T 313-08. The samples of the bitumen for tests had the shape of a beam with dimensions of 6.25x12.5x125 mm. Before testing the samples have been kept at the tested temperature for 60 minutes. In the beginning of the test the load, equal to 980 mN, has been applied automatically for 1 second and it has been kept as the constant one for the following 240 seconds. The maximum deflection of the middle of the beam has been measured automatically.

Figure 2. Bending beam rheometer (BBR)

Maximum stress on the bottom surface of the bituminous beam in its middle has been calculated under the formula:

$$\sigma = \frac{3 \cdot P \cdot \ell}{2 \cdot b \cdot h^2} \tag{2}$$

where P is a load, mN;

h, b, ℓ are height, width and length of the beam respectively, mm.

Maximum strain of the bottom surface of the bituminous beam in its middle at the time moment *t* has been calculated under the formula:

$$\varepsilon(t) = \frac{6 \cdot h}{\ell^2} f(t) \tag{3}$$

where $f(t)$ is the maximum deflection of the middle of the bituminous beam, mm.

The stiffness of the bituminous beam at the time moment *t* has been calculated under the formula

$$S(t) = \frac{P \cdot \ell^3}{4 \cdot b \cdot h^3 \cdot f(t)}. \tag{4}$$

2.6. Group chemical composition of bitumen

Group chemical composition of the bitumen has been determined by liquid adsorption chromatography method on the chromatograph “Gradient M” (Figure 3), manufactured by the Institute of petrochemical processing of the Republic of Bashkortostan (Russia). Chromatograph consists of two parts: analytical and detecting. The analytical part is the glass capillary column with the length of 300±5 mm and diameter of 1.2–1.4 mm, filled with the modified silica gel. Separating of the sample into maltenes (oils and resins) and asphaltenes with the use of complicated mixes of the solvents taken in different proportions (isooctane, dichloroethane, diisomayl ether, ethyl acetat, ethyl hydroxide and chlorbenzene). Detection for the groups of chemical compounds has been performed according to their heat conductivity at the temperature of 680 °C.

Figure 3. Liquid adsorption chromatograph

3. Results and Discussion

3.1. Group chemical composition of bitumen

Group chemical compositions of the investigated bitumen in three conditions has been shown in the Figure 4, where the impact of aging on the chemical composition is clearly seen: one can consider that the content of resins is practically constant at double aging (short-term and long-term); short-term and long-term aging decrease the content of oils for 1.5 % and 5.5 % respectively and increase the content of asphaltenes for 2.0 % and 4.3 % respectively. In general, the sequential double aging decreased the content of oils for 7.0 %, and the content of asphaltenes has been increased for 6.3 %.

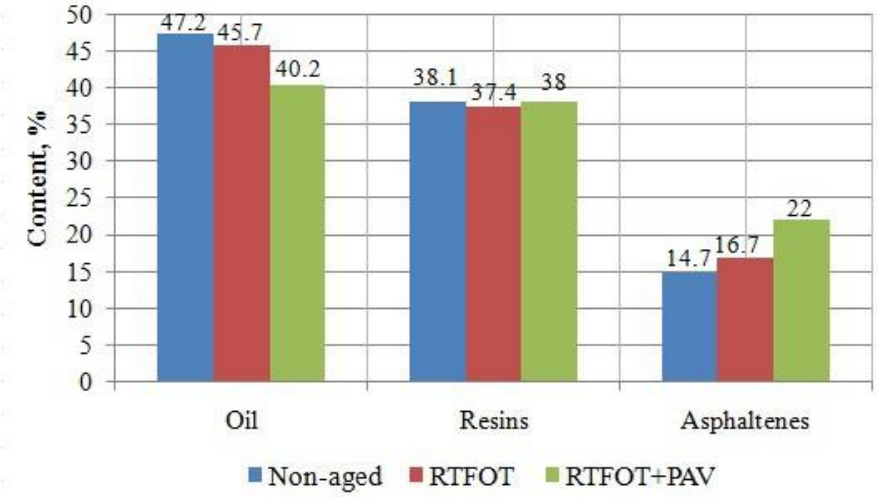

Figure 4. Group chemical composition of bitumen

3.2. Mechanical characteristics

3.2.1. At the mean and high temperatures

The graphs for dependence of the complex shear modulus G* and phase angle δ of the bitumen in three conditions on the temperature have been represented in Figures 5 and 6. It is seen that the aging changes the mechanical characteristics of the bitumen. Thus, after the short-term aging G* has been increased at the temperatures of 4 °C and 76 °C in 1.3 and 2.1 times respectively. And the impact of long-term aging on G* was great: the increase of G* was 5 300 and 7 200 times at the temperatures of 40 °C and 76 °C respectively.

In semi-logarithmic coordinates the temperature dependences of G* of the bitumen in the initial condition and after the short-term aging are nearly the straight lines. These straight lines are nearly parallel, i.e. the thermal sensitivity of the bitumen G* is practically similar in the specified conditions. Dependence of G* on the temperature after the long-term aging is of some other nature: within the range of temperatures from 26 °C to 76 °C it is a straight line, but with the less thermal sensibility; from 4 °C to 13 °C it is also described by the equation of straight line, but with considerably less thermal sensitivity; and temperature range from 13 °C to 26 °C is a transition one, within which the non-linear decrease of thermal sensitivity of the bitumen G* occurs.

Thus, the short-term aging of the bitumen, during which the content of oils has been decreased for 1.5 %, and the content of asphaltenes has been increased for 2 %, determined the increase of shear modulus G* at the mean and high temperatures in 1.3 and 2.1 times; long-term aging, resulting in the oil content decrease for 7 %, and the asphaltenes content increase for 6.3 %, has lead to the increase of G* at high temperatures up to 7 200 times.

The graphs in Figure 6 show clearly the impact of temperature and aging on phase angle δ. The phase angle is an important mechanical characteristic of the viscoelastic materials [20–22]. It shows the ratio of the elastic and non-elastic deformations. Its value varies from 0° to 90°. For the pure elastic material it is equal to 0° and for pure plastic material it is equal to 90°.

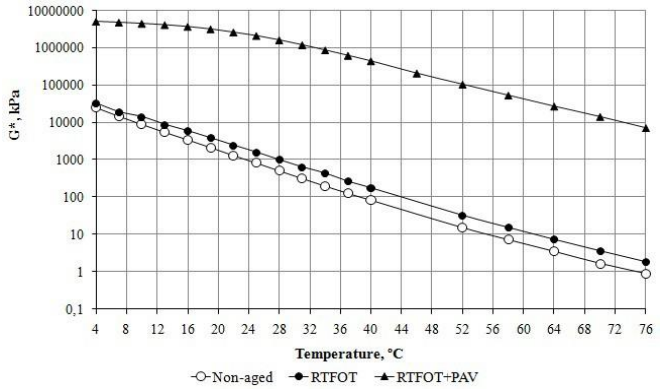

Figure 5. Dependence of complex shear modulus of bitumen on temperature

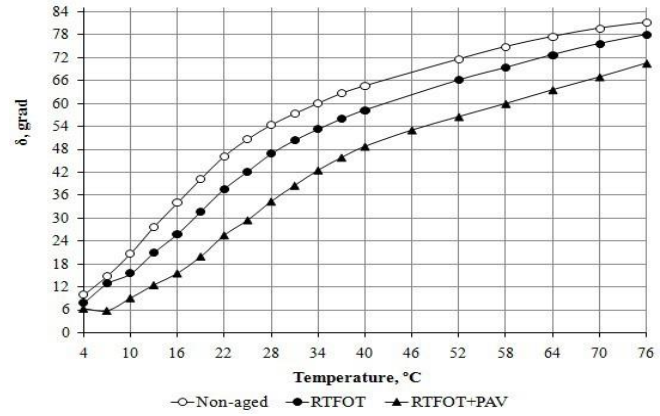

Figure 6. Dependence of phase angle of bitumen on temperature

It can be said that the short-term and long-term aging in the whole considered interval of temperatures (from 4 °C to 76 °C) decrease the phase angle of the bitumen at average for 4-6° and 8-10° respectively.

As could be expected, *δ* increases with the temperature increase. Temperature dependence of *δ* can be considered as bilinear one. There is a transition section in each condition of the bitumen (non-aged, RTFOT, RTFOT+PAV) between the first (at mean temperatures) and the second (at high temperatures) linear sections. The first linear section is characterized by higher indicator of thermal sensitivity of δ, and the second one has some lower thermal sensitivity. Smooth non-linear decrease for the indicator of thermal sensitivity of the phase angle occurs within the transition section. As it is seen from the Table 2, with the increase of aging level of the bitumen the position and characteristic (mean) temperature of the transition section on the temperature dependence of the phase angle shifts towards higher temperatures, and the width of the section has been decreased.

Table 2. Characteristics of transition section in temperature dependence of phase angle of bitumen

Condition of bitumen	Characteristics of transition section			
	initial temperature, °C	final temperature, °C	width of section, °C	conventional temperature of transition, °C
Non-aged	24	52	28	30
RTFOT	28	50	22	35
RTFOT+PAV	36	40	4	38

The works [9, 11–14] according to the results of experimental investigations determine that at high temperatures the short-term, as well as the long-term aging, increase complex shear modulus G* and decrease phase angle *δ* of the bitumens. But the authors do not mention numerical value for variation of G* and *δ* of the bitumens, provided by the impact of aging. It is obvious that it is connected with the fact that the issue of impact of aging on mechanical and other properties of bitumens is on the stage of studying and accumulating of experimental data, and researchers refrain themselves from general conclusions.

3.2.2. At low temperatures

The graphs for the stiffness of the bitumen at various low temperatures and conditions according to the aging are represented in Figures 7–9, where it can be clearly seen that the short-term and long-term aging impact essentially on deformability of the bitumen at low temperatures. At all low temperatures and conditions the bitumen stiffness decreases essentially under the exponential law within the time interval from 8 s to 240 s. At small load durations (8 s) the short-term aging increases the bitumen stiffness at the temperatures of -24 °C, -30 °C and -36 °C in 2.2; 1.3 and 1.5 times respectively, and the long-term aging in 2.8; 2.5 and 2.3 times respectively. Averaging the data, mentioned above, one can adopt that at average the short-term and long-term aging at small load durations increase the bitumen stiffness in 1.7 and 2.5 times respectively.

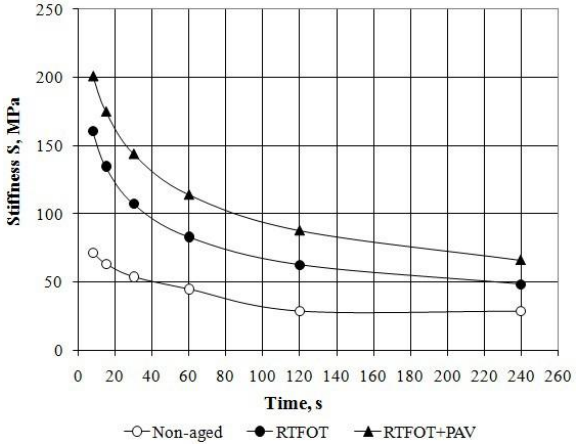

Figure 7. Time dependence of bitumen stiffness at the temperature of – 24 °C

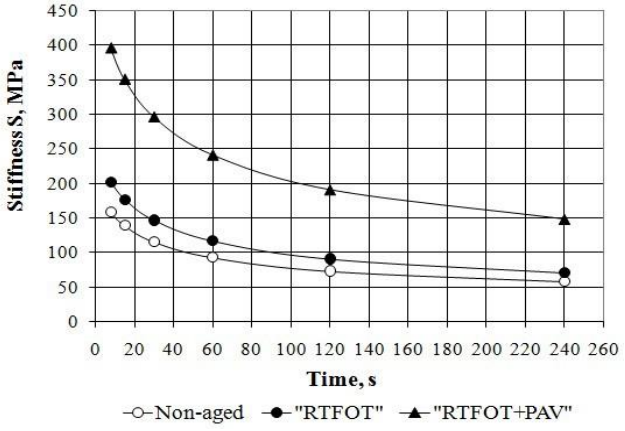

Figure 8. Time dependence of bitumen stiffness at the temperature of – 30 °C

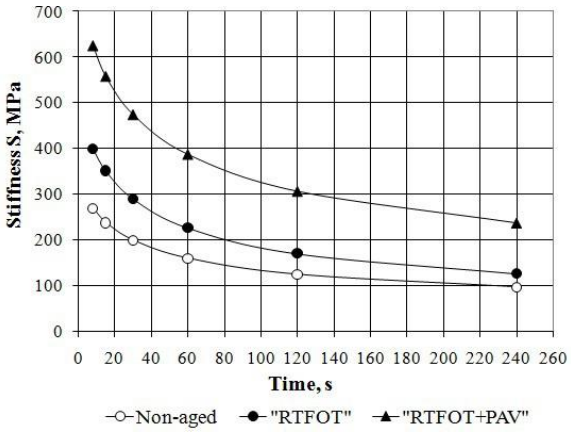

Figure 9. Time dependence of bitumen stiffness at the temperature of - 36°C

As it is known, one of the modern methodological systems in the world, aimed at more differentiated recording of the climatic conditions when defining the operational grade for the road bitumens, is Superpave [2]. The stiffness has been adopted at load duration of 60 seconds in Superpave as one of the bitumen indicators, characterizing its stability at low temperatures. For the tested bitumen the values of specific stiffness (at 60 s) at various low temperatures and aging conditions have been shown in Figure 10. The Figure shows clearly the cooperative effect of short-term and long-term aging and low temperature on specific stiffness of the bitumen: the specific stiffness has been increased with the aging level increase. For example, at the temperatures of -24 °C, -30 °C and -36 °C the short-term aging increases the specific stiffness of the bitumen in 1.8; 1.3 and 1.4 times respectively, and the long-term aging - in 2.5; 2.6 and 2.4 times respectively. At average the short-term aging and long-term aging increase the specific stiffness of the bitumen in 1.5 and 2.5 times respectively.

The literature review has shown that the investigations of the impact of aging on mechanical and other properties of bitumens at low temperatures are strictly limited. Only the work [10] investigates the impact of short-term and long-term aging on stiffness of bitumen PMB 45/80-65, modified by liquid surface

substance on the basis of amines within the temperature range from -10 °C to -28 °C. It has been determined that the long-term aging does not almost impact on bitumen stiffness, and the short-term aging increases it slightly: critical temperature, at which the bitumen stiffness is equal to 300 MPa, is increased only for 2.5 °C.

Our work investigates pure (unmodified) bitumen. It is obvious, that modification reduces the process of aging for bitumens, which can be a subject for future investigations.

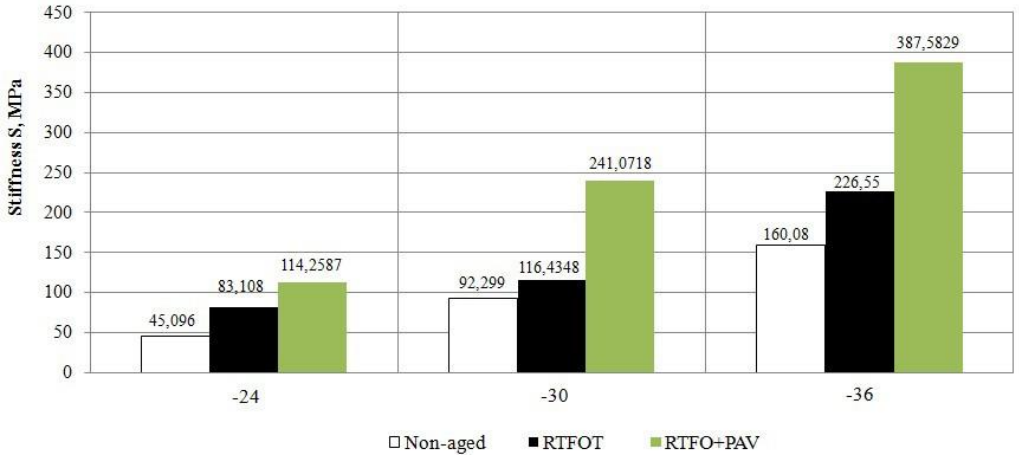

Figure 10. Bitumen stiffness at various low temperatures and aging conditions

4. Conclusion

1. At short-term aging of blown bitumen of grade BND 70/100 the content of oils in it has been decreased for 1.5 %, and the content of asphaltenes has been increased for 2 %. The long-term aging of the bitumen, performed after its short-term aging, compared with its initial condition, decreases the content of oils for 7 %, and the content of asphaltenes increases for 6.3 %. After two types of aging the content of resins in the bitumen remains practically constant.

2. The short-term aging determined the complex shear modulus G* increase at the mean and high temperatures (from 4 °C to 76 °C) in 1.3 and 2.1 times respectively, and the long-term aging increased G* at high temperatures in 7 200 times.

3. The short-term and long-term aging decrease the phase angle δ of the bitumen at the mean and high temperatures at average for 4-6° and 8-10° respectively.

4. The short-term and long-term aging increase the bitumen stiffness S at low temperatures (from -24 °C to -36 °C) in 1.5 and 2.5 times respectively.

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Chapter 7

A New Green Rejuvenator: Evaluation of Structural Changes of Aged and Recycled Bitumens by Means of Rheology and NMR

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Abstract. The functionality of a green additive, acting as bitumen rejuvenator was considered in the presented experimental work. The additive's effects on aged bitumen have been investigated through advanced rheological and NMR-relaxometry measurements. Bitumen ageing encompasses volatilization and oxidation which enable changes in the material molecular structure. Volatilization occurs mainly at high temperatures during production, transport and laying of the asphalt concrete. The oxidation, also caused by atmospheric oxygen and UV radiation, leads to an increased fragility and development of cracks in the asphalt layer. Fresh, aged, and doped recycled bitumens were tested. Rheology and NMR have been used to assess the structural differences between the bitumens and to understand the role of the proposed additive. A real rejuvenator helps to rearrange the colloidal structure of the oxidized bitumen, thus recreating one similar to the fresh bitumen. As a novel approach to bitumen characterisation, an inverse Laplace transform of the NMR spin-echo decay (T2) was here applied.

Keywords: Bitumen Rejuvenator Nuclear Magnetic Resonance Rheology

1 Introduction

Bitumen's organic complex are easily oxidized during paving and pavement service life, especially under thermal and/or ultraviolet radiation (UV) conditions (Hu et al. 2018). In general, an aged bitumen has higher reprocessing temperature because some of the aromatic components and resins, which are responsible for a certain grade of mobility, are oxidized to asphaltenes and reduced to saturates. Hence asphaltene micelles become larger so that the fluidity of the system is reduced. Compared with virgin bitumen, the aged bitumen is more brittle and has worse relaxation characteristics that make it

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vulnerable to cracking (Baldino et al. 2012). Once removed and processed, bituminous layers become Reclaimed Asphalt Pavement (RAP), which contains valuable asphalt binder and aggregates (Baldino et al. 2017). Over the past decades, researchers have conducted many investigations on the use of RAP materials in the production of recycled asphalt. As a result, rejuvenators are a solution that can be utilized to restore RAP binder properties towards its original state (Dinis-Almeida et al. 2016; Zaumanis et al. 2014). Today, rejuvenators play a crucial role in bitumen recycling methods aiming to an optimized performance of the reclaimed bitumen. Nevertheless, the rejuvenator affects are still not well understood and especially its impact on bitumen's supramolecular structure arrangement has not been fully investigated.

This research describes the physical-chemical characteristics of a new green rejuvenator, using the potentiality of Nuclear Magnetic Resonance (NMR) techniques to identify the main effect of chemicals on the regeneration process of the aged bitumen. The vegetable oils are a common flux for bitumen and many times, the flux of oil action has been mistakenly considered as regenerating operation. This confusion arises from the fact that oils simply soften the hard bitumen to match the macroscopic mechanical parameters according to specific requirements.

2 Experimental Work

2.1 Chemicals, Materials and Sample Preparation

A 100/130 pen virgin bitumen was sourced from Kazakhstan and supplied by Highway Research Institute (Almaty, Kazakhstan). The Vegetable Flux Oil (VO) and the green rejuvenator (HR) were provided by KimiCal s.r.l. (Rende, Italy).

The transformed bitumen was prepared with a high shear mixing homogenizer (IKA model, USA). Firstly, bitumen was heated up to 150 ± 5 °C until it fully flowed, then a given part of HR or VO (2% of the weight) was added to the melted bitumen under a high-speed shear of 400 to 600 rpm/min. Subsequently, the mixture was kept under mechanical stirring at 150 °C for 10 min in a closed beaker to avoid any oxidation process. After mixing, the resulting bitumen was poured into a sealed container and stored in a dark chamber at 25 °C to retain the obtained morphology. The in-service aging of the base bitumen was simulated with the Pressure Aging Vessel (PAV) according to the AASHTO/ASTM T179 standard.

All the prepared mixtures are listed and labelled in the paper as follows: Virgin bitumen: Sample A, PAV bitumen: Sample B, PAV bitumen + 2 wt% VO: Sample C and PAV bitumen + 2 wt% HR: Sample D.

2.2 Rheology, NMR Tests and Inverse Laplace Transform (ILT)

The rheological behavior at different temperatures was investigated by a Dynamic Shear Rheometer (DSR) time cure test at 1 Hz with a ramp rate of 1 °C/min (from 25 °C to 120 °C) within the linear viscoelastic range of the binders.

Relaxation experiments were performed by means of a purposely-built NMR equipment that operates at a proton frequency of 15 MHz. Those experiments were

done at temperatures lower than 15 °C which correspond to the respective temperature transition from viscoelastic to liquid (the temperature is chosen in order to standardize the structure of all samples). Inhomogeneity of field and surface effects usually causes the T_2 relaxation times to vary in the sample (Oliviero Rossi et al. 2015). The T_2 parameter is the spin-spin relaxation time as the relaxation relates to the exchange of energy only among spins and not with the surrounding environment. Hence, if inside the sample a continuous distribution of relaxation time exists, the amplitude A_n of the n^{th} echo in the echo train is given by:

$$A_n = A_0 \int_0^{\infty} P(T_2) e^{-2n\tau/T_2} dT_2 \quad (1)$$

where A_0 is a constant, τ is the half echo time and $P(T_2)$ is the ILT of the unknown function that fits the echo amplitude curve. Furthermore, $P(T_2)$ can be agreed upon as a distribution of rate (inverse of time) constant. $P(T_2)$ can be related to probability density function (PDF) accounting different macro-structures that compose the bitumen binder (Oliviero Rossi et al. 2015). In this work, ILT computation was performed by means of UpenWin (Bortolotti et al. 2009).

3 Results and Discussion

Rheology temperature-sweep tests were performed to collect information on the structural changes induced by temperature, trying to define a transition temperature range better than usual empirical tests (i.e. Ring and Ball) (Baldino et al. 2013). The elastic modulus (G′) is continuously monitored during a temperature ramp at a constant heating rate (1 °C/min) and at a frequency of 1 Hz (Fig. 1). The transition temperature is evidenced when G′ is plotted as a function of temperature. The initial trend is almost linear with temperature, when the material mainly behaves like a viscoelastic system. The subsequent decrease occurs in correspondence of the transition towards a liquid-like behavior (G′ plot disappears).

The aged bitumen (sample B) shows much higher transition temperatures than the unaged fresh material (Romera et al. 2006). This effect is due to an increased fraction of asphaltenes resulted from oxidation processes of the soft unsaturated organic part. The higher asphaltene fraction causes a hardening of the bitumen and higher inner connectivity, if compared to the less dense and weaker network of the virgin bitumen where the asphaltene domains are less connected. Both additives shift at lower temperatures the transitions from the viscoelastic to the liquid material. HR which is a surfactant, shows a stronger effect. Authors believe that its presence might reduce the associative interactions amid the asphaltene particles by interposition between them and the maltenes. As a result, the colloidal network can be weakened, which in turn may correspond to a reduction of the transition temperature.

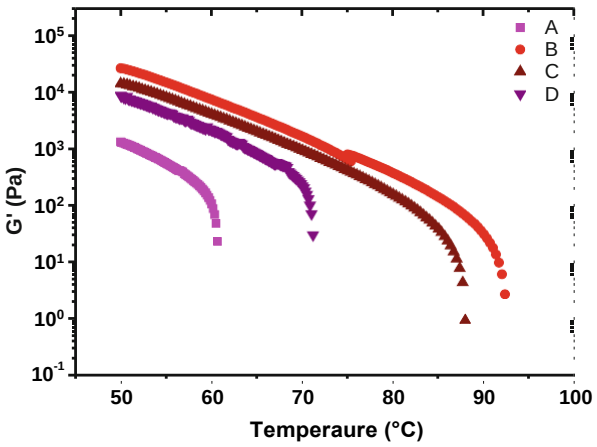

Fig. 1. Semi-log plot of high temperature ramp test for the A, B, C and D samples

3.1 NMR Study

The ILT analysis of the NMR echo signal decay was used to obtain the T2 relaxation time distributions. This technique allows finding the PDF distribution which associates to relaxation times that correspond to unrelated molecular aggregates inside the samples (Gentile et al. 2012). Results are presented in Fig. 2, where the time relaxation distributions PDFs are plotted as a function of the relaxation time. The T2 relaxation time distribution shows two peaks. The shorter T2 times correspond to more rigid supra-molecular aggregates, ascribed to asphaltenes, while longer T2 times are attributed to maltene fractions. For the virgin bitumen, one peak falls around 10 ms and it is due to asphaltene fraction; while the one centered at around 100 ms refers to maltenes.

The ILT of the aged bitumen again exhibits two peaks shifted towards shorter times and present very characteristic shapes. This more likely indicates a gradually increase of the material rigidity with the oxidation process. In particular, the asphaltene peaks are now closer to 1 ms for the aged bitumen. The hard consistency of the samples is strongly affected by the aging processes. During the oxidative aging, the concentration of polar functional groups becomes sufficiently high to immobilize an excessive number of molecules through intermolecular association. What is more, the molecules or molecular agglomerates lose sufficient mobility to flow past one another under thermal or mechanical stresses. The resulting embrittlement of the asphalt makes it susceptible to fracturing or cracking and resistant to healing. This presence of two peaks also supports the colloidal model of the bitumen. All experiments are performed at temperatures lower than 15 °C which is the respective temperature transition from solid to liquid (the temperature is chosen in order to standardize the structure of all samples). On the other hand, it is evident that the addition of VO and HR to the aged bitumen results in the asphaltene peaks shift to longer T2 times. The HR sample shows time distributions similar to the virgin bitumen, although VO simply shifts the distribution to longer times evidencing only its softening action.

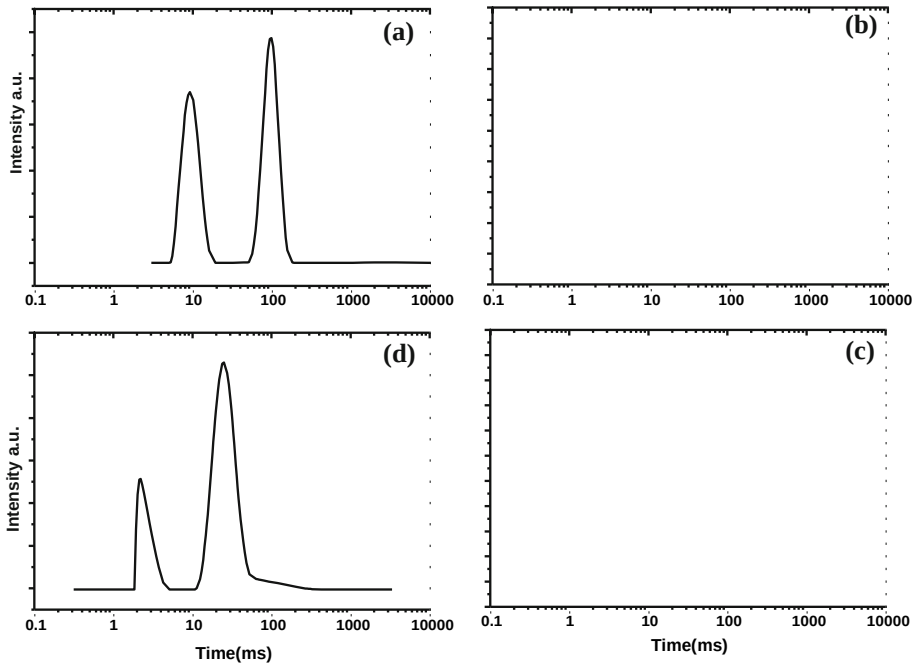

Fig. 2. ILT relaxation time distributions of bitumen samples at 15 °C lower than transition temperature (solid-liquid) determined by dynamic temperature ramp test experiment for each sample

4 Conclusions

This work shows the effectiveness of the HR additive in restoring both bitumen rheological (DSR) and physical (NMR) properties. This green additive tends to restore the mechanical properties of the oxidized bitumen. Moreover, the article aims to demonstrate the importance of testing the regenerated bitumen using structural techniques in order to distinguish between fluxed bitumen and real regenerated compound. Thus, bituminous systems can have alike macroscopic (ring and ball) or rheological properties, but unique supra-molecular structure. The bitumen with flux can be mistakenly considered as a real regenerated one according to the ring and ball test or to other simple rheological investigations.

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Chapter 8

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Organic-based recycling agents for road paving applications in cold-climate regions

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ABSTRACT

Because of the aged binder properties, high Reclaimed Asphalt Pavement (RAP) content asphalt mixtures are more susceptible to cracking failures than virgin mixtures. Thus the production of recycled Hot Mix Asphalt (HMA) for cold climate regions, in which asphalt pavement is subjected to severe thermal stresses, needs more considerations. The present paper deals with three recycling agents for producing recycled HMA with standard quality for paving applications in cold climate regions. These additives were three eco-friendly bio-based materials from which two of them were derived from Amine and Oleic acid reaction and the third was a solid compound of Furanone. As a complete study, the research plan consisted of both binder and mixture-phase tests investigating the efficiency of the additives as a recycling agent, particularly for cold region HMA paving applications. In the binder phase, the additives were investigated in two different scenarios: (I) first the reference asphalt binder was aged then the additives were added (2) first the additive was added to the virgin binder then the compounds were aged. This was mainly for investigating the efficiency of the additives as a softening agent. Considering the goal of this research, all the tests were carried out following the testing methods of the Republic of Kazakhstan and the obtained tests' results were compared to the requirements of its technical specifications.

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KEYWORDS
Reclaimed asphalt pavement (RAP); hot mix asphalt (HMA); cold climate regions; recycling agents; softening agent

1. Introduction

In spite of asphalt pavement recycling's 40 years of history, the main concern in the properties of using Reclaimed Asphalt Pavement (RAP) in Hot Mix Asphalt (HMA) is the characteristics of its binder, which is highly dependent on the choice of proper rejuvenation. It has been proven that the presence of RAP in recycled HMA increases the cracking susceptibility and decreases the durability of the mixture (Tran *et al.* 2012, Zaumanis and Mallick 2015). Obviously, the problem becomes more severe when the recycled HMA is laid in cold climates with high thermal stresses. On the other hand, many laboratory studies and filed practices have demonstrated evidence that even high-RAP containing pavements can achieve the desired pavement performances and durability similar to the conventional asphalt pavements (Sivilevicius *et al.* 2017). However, it should be noted that the level of success is highly dependent on the correct mix design and the choice of the recycling agent. Hence, careful selection of recycling agent is of paramount importance to provide the necessary short and long term properties for the recycled asphalt pavement.

To date, many different recycling agents have been introduced and used, from which recycling diesel oils and recycling oils from the food industry (either refined or not) have been the two main resources for this purpose (Zaumanis *et al.* 2014 and Gawel *et al.* 2010). In addition to these materials several, research works have represented new promising eco-friendly materials for HMA recycling purposes, which are effective both for mechanically and chemically restoring the aged binder of RAP (Oliviero Rossi *et al.* 2018 a, 2018b). In this respect, research has shown that the use of the Oleic acids as a bitumen flux could reduce the mixing and compacting temperature of recycled asphalt mixtures (Asli and Karim 2011).

Apart from the type of the used recycling agent, several researches have shown that the level of oxidation of the RAP and the correct choice of the dosage of the recycling agent play the key roles in the final properties of the recycled asphalt mixture (Cavalli *et al.* 2018 and Eskandarsefat *et al.* 2019). Regarding the differences between recycling agents, a complete study showed that the application of organic-based materials requires a smaller dosage to provide the same softening effect as a mineral recycling agent (Zaumanis *et al.* 2015 and Gawel *et al.* 2010). However, what should be taken into the account is that different recycling agents have the potential to address the deficiencies of aged binders in different extents. Despite the wide range of research works and studies investigating different types of recycling agents, just a few of them concen- trated on the properties of recycled asphalt mixtures at low temperatures. Considering this missing knowledge, the authors in this study aimed at investigating three new organic-based recycling agents for asphalt paving applications in cold cli- mates. Two of these materials were derived from Amine and Oleic acid reaction and the third is a solid compound based on Furanone. The test plan consisted of both binder and mix- ture-phase, which were conducted according to the Kazakhstan standard testing methods and specifications as a representative of a cold climate region in this research.

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The main objectives of this research were:

- Examining the effectiveness of three bio-based recycling agents for HMA paving applications in cold climate regions.
- Investigating the adhesive properties of asphalt binders containing bio-based recycling agents.
- Studying the effectiveness of three bio-based recycling agents as an additive for enhancing the low-temperature properties of virgin asphalt binders and asphalt mixtures.

2. Materials and methods

2.1. Materials

Based on the objectives of this research, which were concentrated on the cold-climate paving applications, a 100/130 (penetration grade) paving-grade bitumen (BND in Kazakhstan) was used in this research. Table 1 represents some of the fundamental physical properties of the used bitumen.

The recycling agents/additives in this study were three eco-friendly bio-based materials. From the chemical point of view, two of them were derived from Amine and Oleic acid reaction and the third was a solid compound based on Furanone, hereinafter in this paper called HR-I, HR-U, and FU, respectively. 1%, 2% and 3% on the weight of bitumen were the considered dosages in this study. It is worth mentioning that these dosages were selected according to the authors' primary investigations and experiences by other former researches of them. Before adding the recycling agents, the bitumen (virgin and aged based on the testing approach) was heated to 150°C and then the additive was added to the hot bitumen. Then the compound was stirred enough for providing a homogenous mixture. For manufacturing the asphalt mixtures, crushed sedimentary aggregates (previously fractionated), limestone sand and limestone filler were used according to mixture type B of the Republic of Kazakhstan technical specifications.

2.2. Methods

2.2.1. Sample preparation

The addition of the recycling agents/additives to the asphalt binder was carried out following two different approaches with different objectives:

(1) Investigating the effectiveness of the additives as an anti-aging agent. For this purpose, first the additive was added to the asphalt binder then the sample was subjected to short-term aging by means of Rolling Thin Film Oven (RTFO) and long-term aging by means of Pressure Aging Vessel (PAV).

Table 1. Some of the physical properties of the used asphalt binder.

Measured properties	Unit	Value	Standard
Penetration @25°C	0.1 mm	109	ST RK 1226 (2003)
Softening Point (R&B)	°C	46	ST RK 1227 (2003)
Ductility @ 25°C	cm	140	ST RK 1374 (2005)
Fraass Breaking Point	°C	−26	ST RK 1229 (2003)
Dynamic viscosity @ 60°C	Pa.s	128	ST RK 1211 (2003)

(2) Investigating the effectiveness of the additives as a recycling agent. For this purpose, first the asphalt binder was aged by means of RTFO and PAV, then the additive was added into the aged asphalt binder.

It is worth mentioning that from the practical point of view, while approach 1 could be useful for asphalt binder modification, approach 2 was introduced for restoring the aged asphalt binder's characteristics in the production of recycled asphalt concretes.

2.2.2. Research plan

As a complete research work, the tests were divided into two sections of the binder and mixture phases. Considering the main target of this research the tests were carried out following the testing standards and protocols of the Republic of Kazakhstan.

3. Results and analysis

3.1. Binder phase tests

3.1.1. Fundamental physical characterisation

At the first stage of this research, the binder phase, the fundamental physical properties of the reference asphalt binders and the compounds containing additives (both approaches) were determined. Tables 2 and 3 represent the result of the additive-containing aged compounds (first the additive was added then the compounds were aged; approach 1) and the aged additive-containing binder (first bitumen was aged and then additive was added; approach 2), respectively. The neat asphalt binder sample and the additive-containing compounds were aged by means of RTFO according to ST RK 1224, the Republic of Kazakhstan standards (simulating the short-term aging) and aged with PAV (Simulating long-term aging) following ASTM D 6521-13. According to the obtained results and compared to the test values of the reference asphalt binder, the additives always increase the penetration and decrease the softening point. While these effects were observed for the samples of both approaches, comparing the results reveals that the additives could be more effective on the aged asphalt binder (approach 2). However, according to the ductility test results, the additives were effective in enhancing the elastic properties of the compounds of both approaches.

3.1.2. Adhesion properties

The adhesion properties of the reference asphalt binder and the compounds were examined by means of boiling water adhesion test according to ST RK 1218 (2003) part 29. For this purpose, 4 dry aggregate grains were selected and threaded with thin wire. Then the grains were floated in the hot bitumen (140 ± 5°C) for 15 s. The coated grains were then kept for an hour at the room temperature as curing. Finally, the grains were suspended into the hot boiling water for 30 min. In the end, the grains were removed from the boiling water and cooled down in cold water for 3 min. Table 4 shows the average level of bitumen coverage, obtained by visual observation of three experts using the standard guide. Figure 1 shows the 2% HR-U

Table 2. Physical properties of the compounds in approach 1 (first additive was added then the compound was subjected to aging).

		Penetration 0.1 mm			Softening point °C			Ductility cm		
Add. type	Dose (%)	Neat	RTFO	PAV	Neat	RTFO	PAV	Neat	RTFO	PAV
HR-I	1	135	84	55	43	49	56	111	73	16
	2	142	97	58	41	48	54	122	90	20
	3	150	114	68	38	44	51	130	110	31
HR-U	1	137	84	40	43	52	58	122	103	17
	2	143	100	49	41	45	56	135	129	21
	3	152	110	57	38	44	54	140	120	27
FU	1	112	71	40	45	53	61	92	57	9
	2	120	74	43	43	52	60	96	60	12
	3	127	76	46	40	51	59	116	75	14

Table 3. Physical properties of the compounds in approach 2 (first the binder was subjected to aging then additive was added).

Add. type	Dose (%)	Penetration 0.1 mm	Softening point °C	Ductility cm
(RTFOT + PAV)	–	44	60	9
HR-I	1	48	55	15
	2	67	53	30
	3	69	52	31
HR-U	1	52	55	18
	2	59	54	27
	3	66	52	29
FU	1	45	57	11
	2	49	58	13
	3	54	59	16

added asphalt binder covered grain before and after placing it into boiling water.

According to the results of Table 4, while HR-I and HR-U additives could improve the adhesion properties of the asphalt binder, the adhesion properties of the compound containing FU was similar to the reference asphalt binder. It is worth mentioning that in the table of the results 5 refers to complete bitumen coverage and 1 refers to limited bitumen spots.

3.1.3. Low-temperature performance

The low-temperature properties of the neat bitumen and the additive-containing compounds (via approach 1 and 2) were investigated by means of Bending Beam Rheometer (BBR). The knowledge obtained from this test is used for the determination of low-temperature susceptibility and thermal cracking sensitivity. According to Superpave, the low-temperature stability of an asphalt binder is ensured if the stiffness value be less than 300 MPa and the m-value be larger than 0.3. The m-value is the log-log of the creep curve at a given loading time. It is known that the value of stiffness (S) and m-value with a loading

Table 4. The level of asphalt binder coverage (approach 2, first aged then modified samples).

Add. type	Additive dose (%)	Degree of bitumen coverage
Virgin and neat bitumen	–	1
(RTFOT + PAV)	–	2
HR-I	1	3
	2	3
	3	4
HR-U	1	2
	2	2
	3	3
FU	1	1
	2	1
	3	2

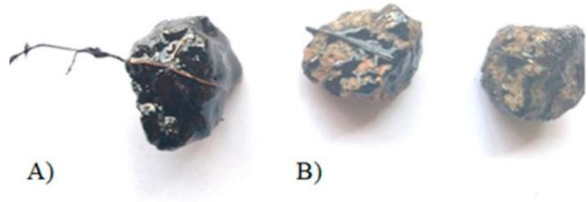


Figure. 1. (A) A covered grain before placing in the boiling water, (B) Grains after 30 min in boiling water.

duration of 60 s at the calculated low temperature is necessary to determine the low-temperature stability of an asphalt binder. The test was carried out according to ASTM D 6648−08 (2018) at three levels of temperatures: −24, −30, and −36°C. The BBR test results for the tested asphalt binders containing different dosages are presented in Figures 2−5.

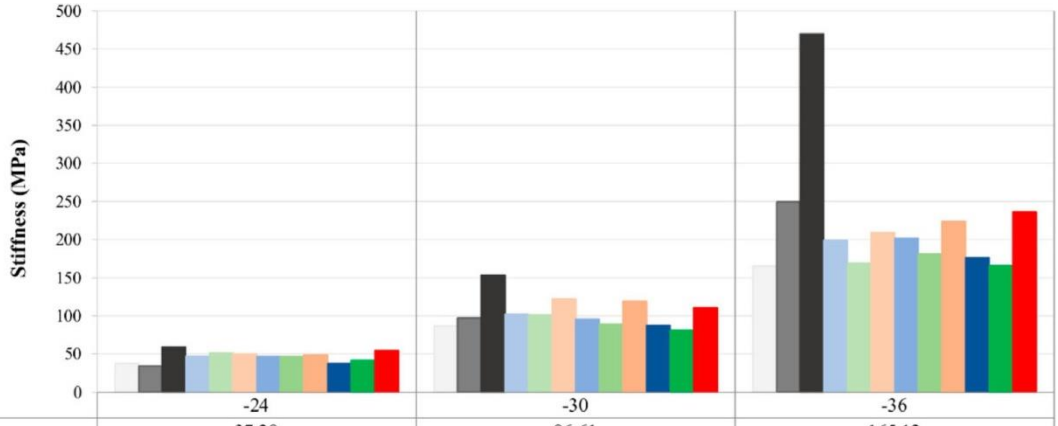
According to Figures 2 and 4 (Approach 1) it can be inferred that all the tested additives are effective in improving the properties of the aged binder even a small dosage. In addition, the test results indicated that HR-U is more effective in improving the low-temperature properties of the aged asphalt binder. This comes from the fact that lower stiffness values and higher *m*- values were recorded for the HR-U compounds at all the three test temperatures. However, it should be mentioned that the recorded difference between the compounds containing HR-I and HR-U was not significant and all the tested compounds complied with the Superpave requirements. From another point of view, it can be seen that except for the compounds containing FU additive, the larger dosage of the additives resulted in lower stiffness properties and increased m- values. Same to the test results of approach 1, according to Figures 3 and 5 (Approach 2) it can be seen that all the additives were effective for improving the low-temperature properties of the compounds and similarly the test results of HR-I and HR-U additives were more consistent.

Comparing the results of the two approaches, it can be concluded that adding the additives to the aged asphalt binder is more effective. This could be expected because in approach 1 the additives are also subjected to the aging process, which could reduce their effectiveness.

3.2. Asphalt concrete phase tests

3.2.1. Mix design and specimen fabrication

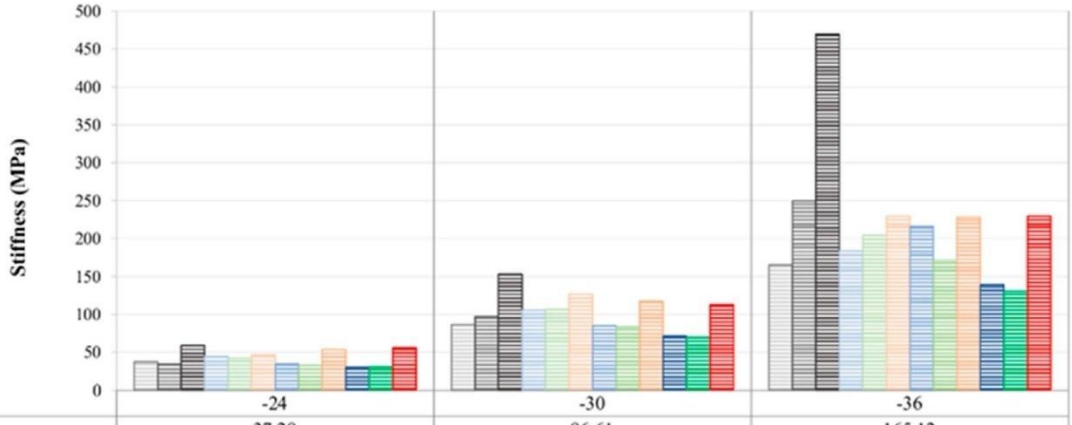
The first stage in the mixture phase was dedicated to the mix design. A dense-graded (Type B) mixture was selected



	-24	-30	-36
Neat Bit.	37.28	86.61	165.12
RTFO-aged Bit.	34.15	97.16	249.34
(RTFO+PAV)-aged Bit.	59.12	153.35	470.06
1% HR-I (RTFO+PAV)	46.89	102.13	198.84
1% HR-U (RTFO+PAV)	51.27	101.16	168.93
1% FU (RTFO+PAV)	50.12	122.31	209.36
2% HR-I (RTFO+PAV)	46.78	95.49	201.82
2% HR-U (RTFO+PAV)	46.53	89.2	181.57
2% FU (RTFO+PAV)	48.88	119.43	224.12
3% HR-I (RTFO+PAV)	37.28	87.21	176.12
3% HR-U (RTFO+PAV)	41.61	81.2	166.25
3% FU (RTFO+PAV)	54.38	110.61	236.68

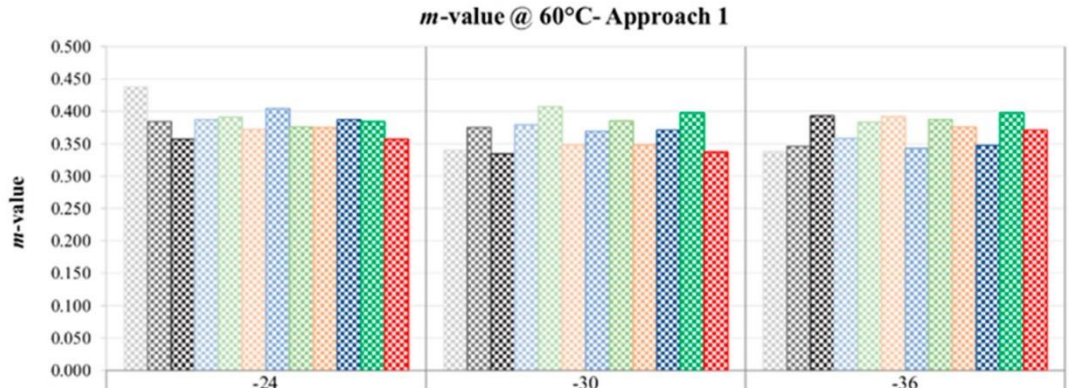
Figure. 2. BBR Stiffness using approach 1.

according to ST RK 1225 (2014) the Republic of Kazakhstan standards and optimised with the bitumen content of 4.8%. Table 5 shows the aggregate proportions. In this phase, a series of asphalt mixtures containing 1%, 2%, and 3% of HR-I, HR-U, and FU were manufactured and compared with the reference mixture without any additive (made with aged asphalt binder). It is worth mentioning that for producing the asphalt mixtures, the asphalt binder was first aged by means of RTFOT and PAV and then the rejuvenators were added to the binder (Approach 2).



	-24	-30	-36
Neat Bit.	37.28	86.61	165.12
RTFO-aged Bit.	34.15	97.16	249.34
(RTFO+PAV)-aged Bit.	59.12	153.35	470.06
(RTFO+PAV)+1% HR-I	44.51	105.54	183.49
(RTFO+PAV)+1% HR-U	42.60	106.71	204.45
(RTFO+PAV)+1% FU	46.55	126.23	229.62
(RTFO+PAV)+2% HR-I	34.99	85.13	216.41
(RTFO+PAV)+2% HR-U	32.84	83.11	171.13
(RTFO+PAV)+2% FU	53.63	117.48	227.88
(RTFO+PAV)+3% HR-I	30.56	71.51	139.29
(RTFO+PAV)+3% HR-U	30.81	69.51	130.25
(RTFO+PAV)+3% FU	55.98	112.79	229.54

Figure. 3. BBR Stiffness using approach 2.



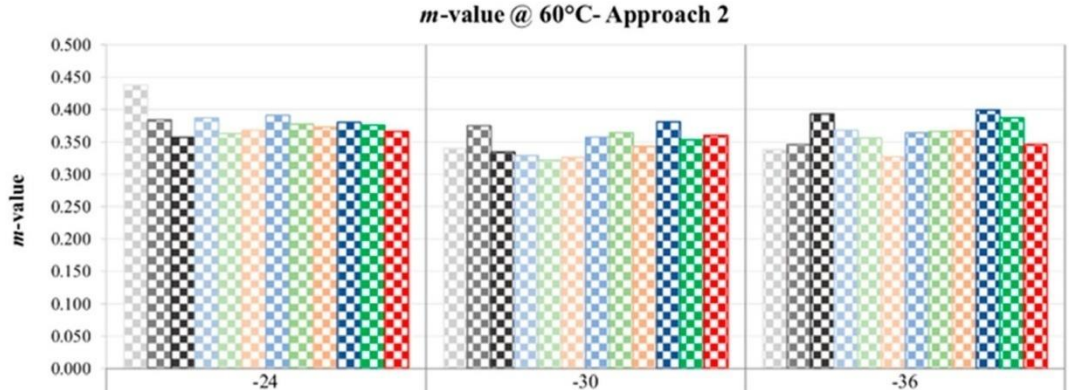
	-24	-30	-36
Neat Bit.	0.438	0.340	0.338
RTFO-aged Bit.	0.385	0.375	0.346
(RTFO+PAV)-aged Bit.	0.357	0.334	0.393
1% HR-I (RTFO+PAV)	0.387	0.379	0.358
1% HR-U (RTFO+PAV)	0.391	0.407	0.383
1% FU (RTFO+PAV)	0.372	0.348	0.392
2% HR-I (RTFO+PAV)	0.404	0.369	0.343
2% HR-U (RTFO+PAV)	0.376	0.385	0.387
2% FU (RTFO+PAV)	0.375	0.348	0.376
3% HR-I (RTFO+PAV)	0.387	0.371	0.347
3% HR-U (RTFO+PAV)	0.384	0.398	0.398
3% FU (RTFO+PAV)	0.357	0.337	0.371

Figure. 4. BBR *m*-values using approach 1.

The asphalt concrete specimens were manufactured according to 1218-2003 (2012) the Republic of Kazakhstan standards part 6. For this purpose, 680 g of the mixture was placed in a steel mould with a diameter of 7.14 mm and compacted with 40 MPa pressure of hydraulic press according to GOST 28840 Russian standard.

3.2.2. Moisture susceptibility

The test consisted of determining the moisture absorbed by the asphalt mixtures at a defined saturation mode. The test was carried out according to 1218 the Republic of Kazakhstan standards part 13. The test procedure consisted of placing a specimen with a known weight in a vacuum vessel, which is



	-24	-30	-36
Neat Bit.	0.438	0.340	0.338
RTFO-aged Bit.	0.385	0.375	0.346
(RTFO+PAV)-aged Bit.	0.357	0.334	0.393
1% HR-I (RTFO+PAV)	0.387	0.329	0.368
1% HR-U (RTFO+PAV)	0.363	0.322	0.356
1% FU (RTFO+PAV)	0.368	0.326	0.327
2% HR-I (RTFO+PAV)	0.391	0.358	0.364
2% HR-U (RTFO+PAV)	0.377	0.364	0.366
2% FU (RTFO+PAV)	0.373	0.343	0.367
3% HR-I (RTFO+PAV)	0.380	0.381	0.399
3% HR-U (RTFO+PAV)	0.376	0.353	0.387
3% FU (RTFO+PAV)	0.366	0.360	0.346

Figure. 5. BBR *m*-values using approach 2.

Table 5. Proportions of the fine and coarse aggregates.

Material type	Proportion (%)
Crushed Agg. 15–20	10
Crushed Agg. 10–15	14
Crushed Agg. 5–10	20
Sand	49
Mineral filler	7

Table 6. Moisture absorption test results.

Mixture type	Moisture content (%)
Ref. mixture	3.8
1% HR-I	3.8
1% HR-U	3.8
1% FU	3.7
2% HR-I	3.6
2% HR-U	3.3
2% FU	3.7
3% HR-I	3.3
3% HR-U	2.8
3% FU	3.5
Standard requirement	1.0–4.0

filled with water at 20 ± 2°C. The level of water above the specimen should be at least 3 cm. In this condition, the specimen is kept under 2000 Pa for one hour. Then the pressure is adjusted to atmospheric pressure while the specimen is in the vessel with water for 30 min. Finally, the specimen is removed from the vessel and the weight of it is determined underwater and after drying. Table 6 shows the average test results obtained from 3 replicates for each mixture. According to the results, it can be seen that all the mixtures have complied with 1225-2013 the Republic of Kazakhstan technical specification's requirements (Part 5, Table 7) and no significant difference was recorded between the results except for the mixture containing 1% HR-U and HR-I additive. In addition, the more the rejuvenator content, the less the moisture absorption was recorded. Comparing the mixtures shows that HR-U containing mixtures performed better than HR-I and FU. This could be due to the fact that HR-U has hydrophilic-base compared to the hydrophilic-base HR-I additive.

2.1.6. Compressive strength

The test was done according to the Republic of Kazakhstan standard number 1218 part 15. In this test, the 71.4 mm (in diameter) specimens were manufactured and tested at 0°C, 20°C, and 50°C. The specimens were subjected to a compressive pressure with a loading rate of 3.0 ± 0.3 mm/min until the specimens fractured. Table 7 represents the average compressive strength values compared with 1225-2013 Kazakhstan technical specification's requirements (Part 5, Table 6). According to the obtained compressive strength values, it can be seen that the addition of the additives always increased the compressive strength (stiffness) of the asphalt mixtures, in particular at 0°C. However, at medium and high temperatures (20°C and 50°C, respectively), the increased stiffness is not sig- nificant. However, all the tested asphalt mixtures fulfilled the requirements of the Republic of Kazakhstan's technical specifi- cations. From another point of view, it can be seen that the highest recorded value obtained from the mixtures containing HR-U additive.

Table 7. Compressive strength.

Mixture type	Compressive strength (MPa)		
	@ 0°C	@ 20°C	@ 50°C
Ref. mixture	4.9	3.0	1.4
1% HR-I	8.0	3.1	1.9
1% HR-U	8.9	3.4	2.0
1% FU	7.9	3.3	1.7
2% HR-I	8.5	3.3	2.1
2% HR-U	9.2	3.7	2.2
2% FU	8.6	3.5	1.8
3% HR-I	8.7	3.5	2.3
3% HR-U	9.3	3.8	2.5
3% FU	9.1	3.6	1.9
Standard requirement	<13	>2.5	>1.3

3.2.3. Water sensitivity

The main objective of the test is to assess the susceptibility of the mixtures to the presence of water. The test was carried out following the testing method, described in 1218 the Republic of Kazakhstan standards part 21. For this purpose, two subsets of asphalt mixtures are subjected to wet and dry conditioning. For the wet conditioning, the specimen is placed in water (at 20 ± 5°C) for 15 days and then the compressive strength of it is tested. The water sensitivity is determined as the compressive strength ratio of the wet to dry conditioned specimens. Table 8, represents the average values compared to the republic of Kazakhstan's technical specification's requirements (1225-2013, Part 5, Table 6). According to the results, all the mixtures showed an acceptable result and have complied with the minimum of the considered specification and no significant difference was recorded between the mixtures.

3.2.4. Marshall stability

The well-known Marshall stability and flow test was carried out according to 1218 the Republic of Kazakhstan standards part 18. Table 9 represents the test results in terms of shear stability and internal friction coefficient compared to the Republic of Kazakhstan's technical specification's limits. According to the results it can be seen that while the shear stability of the mixtures containing HR-I and HR-U increased with increasing the dosage, the mixtures containing FU additive worked similarly or even lower compared to the reference mixture. From another point of view, comparing the mixtures containing HR-I with HR-U shows that the mixtures made with HR-I outperformed even if the difference is not significant.

Table 8. Water sensitivity, shown as compressive strength ratio.

Mixture type	Compressive strength ratio
Ref. mixture	0.93
1% HR-I	0.97
1% HR-U	0.97
1% FU	0.95
2% HR-I	0.94
2% HR-U	0.95
2% FU	0.91
3% HR-I	0.97
3% HR-U	0.93
3% FU	0.94
Standard requirement	<0.85

Table 9. Shear stability and internal friction coefficient.

Mixture type	Shear stability (MPa)	Friction coefficient
Ref. mixture	0.41	0.87
1% HR-I	0.59	0.90
1% HR-U	0.56	0.91
1% FU	0.39	0.91
2% HR-I	0.66	0.91
2% HR-U	0.57	0.91
2% FU	0.40	0.92
3% HR-I	0.67	0.93
3% HR-U	0.64	0.92
3% FU	0.43	0.94
Standard requirement	>0.38	>0.83

Table 10. Indirect tensile strength at 0°C.

Mixture type	Indirect tensile strength (MPa)
Ref. Mixture	4.10
1% HR-I	3.10
1% HR-U	3.70
1% FU	3.50
2% HR-I	3.20
2% HR-U	3.20
2% FU	3.20
3% HR-I	3.40
3% HR-U	3.10
3% FU	3.10

3.2.5. *Level of tenacity*

As an important factor, particularly for cold climate regions, the tensile properties of the asphalt mixtures were evaluated by means of the Indirect Tensile Strength (ITS) test. In this research, considering the dominant low temperature of cold climate regions, the test was carried out at 0°C following the testing method of the Republic of Kazakhstan (1218, part 16).

Table 10 shows the average test results. From the obtained values and compared to the reference mixture it can be inferred that the presence of the additives could improve the thermal sensitivity of the mixture at low temperature by reducing its stiffness. From another perspective, it can be seen that the dosage of the additives was effective in enhancing the low-temperature tensile properties. The more the additive content, the less the stiffness recorded.

3.2.6. *Resistance to permanent deformation*

The resistance to permanent deformation (rutting) of the asphalt mixtures was evaluated by means of Wheel Tracking Device (WTD) following the testing procedure represented in ST RK EN 12697-22-2012, the Republic of Kazakhstan standard. The test is developed to assess the resistance of asphalt mixtures to rutting under laboratory conditions with simulating the effects of passing vehicles on a road pavement. For the test, the asphalt mixture slabs were prepared in a slab geometry (10.0 × 30.5 × 30.5 cm). The test was carried out at 60°C with applying 10,000 wheel passes in 6 h and a half.

Fig. 6 represents the cumulative deformation of the tested asphalt mixtures over the number of the wheel passes. It can be seen that the recorded cumulative deformation depth after 10,000 wheel passes decreased with increasing the concentration of the additives compared to the reference mixture. It is noteworthy that for all the three tested additives, the more additives concentration, the less final cumulative deformation was recorded. This could show the efficiency of the proposed additives in improving the resistance to permanent deformation. From another perspective, unlike the other tests' results, it can be seen that the FU additive with less final

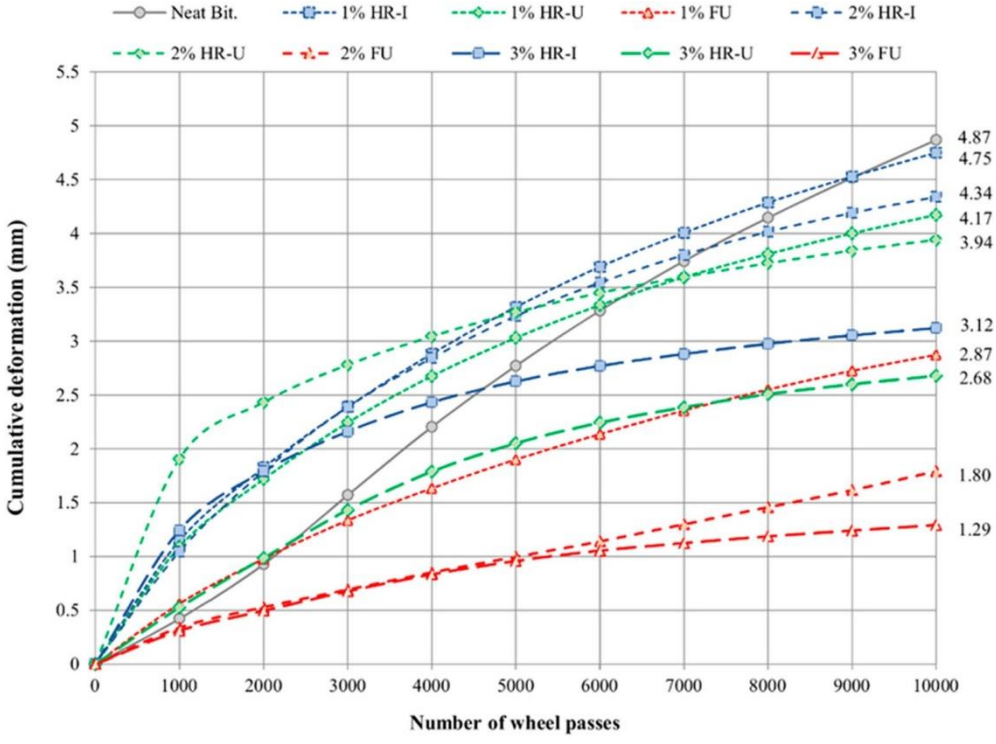


Figure. 6. Cumulative deformation of asphalt concretes vs. number of wheel pass.

cumulative deformation was more efficient in terms of permanent deformation resistance (Figure 6).

4. Conclusions

The present experimental research investigated 3 organic-based additives as a recycling agent for HMA paving applications in cold climates regions. For this purpose, considering the cold weather of Kazakhstan, the tests were carried out following its local standards and specifications. Based on the tests' results, the proposed additives showed promising results for improving the mechanical and performance properties of recycled HMA for being laid in cold climate regions. However, completing chemical and Rheological tests are recommended. Overall, the test results of both binder- and mixture-scale revealed that within most of the testing methods HR-U additive outperformed the two tested materials. However, the difference between HR-I and HR-U was not significant.

The followings are some of the remarks of this research:

- At the binder-scale phase, two different scenarios of adding the additives were studied. The results showed that approach 2 (first the binder was subjected to aging then additive was added) was more effective. This could be because of the fact that within approach 1 the additives were also subjected to aging (RTFO and PAV), which leads to oxidisation and reducing their effectiveness.
- The conventional physical tests on both the compounds of both HR-I and HR-U additives indicated similar results, both better than FU additive. The same was recorded within the adhesion test.
- The low-temperature properties of the compounds containing additives were investigated by means of BBR. The results showed the superiority of HR-U compared to the other two additives. However, the difference between HR-U and HR-I was not significant.
- The performance and mechanical properties of the asphalt mixtures made with the aged binder containing the additives were investigated in terms of moisture susceptibility, compressive strength, water susceptibility, level of tenacity, and resistance to permanent deformation. Overall the results showed the effectiveness of the additives in improving the mechanical and performance properties compared to the reference mixture.
- According to the shear stability test results, the mixtures containing HR-I and HR-U performed better compared to the reference mixture. These results were in line with the binder conventional tests' results.
- The level of tenancy of the asphalt mixtures containing additives was investigated by means of ITS test. The results showed that all the three introduced additives are capable to decrease the fragility of the asphalt mixtures at low temperature compared to the reference mixture.
- The resistance to permanent deformation of the mixtures showed the superiority of the mixture containing FU additive with the lowest final cumulative deformation. It is noteworthy that in this research, no correlation was observed between the test results of shear strength test (Marshall Method) and WTD. However, considering the conventional properties of the asphalt binders these results in the mixtures scale could be expected. This is due to the fact that the aged asphalt binder containing FU showed the lowest penetration with a high softening point.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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