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BIOMATERIALS AS ADDITIVES IN THE SYNTHESIS AND RECYCLING OF SUSTAINABLE ASPHALT ECOBINDERS

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Abstract

In recent years, the course of research has significantly shifted towards the development and testing of eco-friendly practices, products, technologies, policies, initiatives and incentives which are aimed at reducing or even reversing the effects of pollution and several other environmental issues facing the modern society. This approach, in the long run, will also bring about some form of green circular economy where resources are recycled in such a way that the environment is also protected. The use of biomaterials as additives in the production of sustainable asphalt ecobinders is a promising strategy to improve the performance and sustainability of asphalt pavements while safeguarding the environment. Biomaterials such as cellulose, lignin, and chitin, can be derived from renewable sources and have shown potential to enhance the mechanical, rheological, and environmental properties of asphalt mixtures. Materials also derived from waste recycling or blends of bio-based materials and their derivatives also have a huge potential in this regard. This dissertation provides a comprehensive review of bitumen, its structure, the role of additives in asphalt mixes, and the current state of research on the use of biomaterials as additives in sustainable asphalt ecobinders, including their effects on performance and sustainability. The experimental studies carried out in the course of the realization of this body of work revolve around rejuvenation of bitumen obtained from Reclaimed Asphalt Pavement (RAP), the development and use of several bio-based materials (especially from waste) as additives to improve the physico-chemical properties of bituminous mixes and emulsions, conversion of waste materials to substances used for the total or partial replacement of conventional asphalt binders and so on. This body of work also employed the use of innovative practices towards sustainability such as Warm Mix Asphalt (WMA) technology, recycling of RAP, Polymer-modified bitumen (PmB), Bitumen recycling agents and so on. All of this adds up to a significant effort towards a circular economy, resource and environmental conservation, and in general, sustainability. The use of bio-based materials in asphalt industry practices also significantly reduces the health hazards faced by the asphalt workers and the society at large as a result of the mitigation of the issue of greenhouse gas emissions. Several techniques such as Rheology, Scanning Electron Microscopy, Differential Scanning Calorimetry, Nuclear Magnetic Resonance, Infrared Spectroscopy, Atomic Force Microscopy, Light microscopy amongst others were used in the studies carried out in the course of the actualization of this body of work. Some of the results obtained indicate that these biomaterials have huge potential in replacing conventional synthetic additives on an industrial scale and also highlights the need for standardized testing methods and protocols to evaluate the performance and sustainability of these ecobinders. Ultimately, the use of biomaterials as additives in sustainable asphalt ecobinders coupled with recycling of aged bitumen has the potential to reduce the environmental impact of asphalt pavements while maintaining or improving their performance.

Chapter 1

Introduction

1.1 The need for sustainable eco-friendly technologies and policies in industrial practices

In today's world, scientific and technological advancement is constantly on the rise. Some of the factors that come alongside this advancement are resource depletion and/or limitation coupled with rising environmental concerns that stem from the application of these technologies in society. This brings about several major global issues because excessive use of non-renewable resources brought about by the ever-increasing economic development rate occurs at the detriment of the atmosphere and the environment in general [1]. Industrial and economic development do not necessarily overlap with the reduction of pollution and sustainable resource management or conservation [2] thus an approach that brings about balance in elevated resource consumption, industrial practices and economic development is highly needed.

This challenge has instigated the enactment of several eco-friendly policies and practices in industry and society in general which aim to mitigate the environmental problems such as elevated carbon footprint, greenhouse gas emissions and global warming. For instance, in order to conserve energy and reduce carbon emissions, several countries have established agencies and policies for environmental protection and sustainability such as the European Union's Restriction of Hazardous Substances Directive and limitation policies on chlorofluorocarbons enacted at the Johannesburg World Summit [3]. The European Union has adopted so many sustainable development policies such as the EU Sustainable Development Strategy (SDS), the Environmental Technology Plan and the 2015 Package on the Circular Economy. On a global scale, the Kyoto protocol was also brought about in order to commit industrialized countries and economies to greenhouse gas reduction requirements [4]. These pro-sustainability policies are the building blocks of so many initiatives that are now in place for safer, eco-friendly practices and technologies in industry.

1.1.1 Sustainable road pavements

Sustainability is the approach taken in the use of a resource in such a way that the resource is not permanently depleted or damaged. In a simpler context, it is the ability to meet our material needs without compromising the ability of the next generation to meet theirs. Sustainability encompasses environmental, economic and societal aspects. As researchers in the life sciences, we are capable of influencing the environmental and economic aspects of sustainability. Environmentally, via the synthesis of green materials and eco-friendly products such as eco-binders and green additives coupled with the development of safer protocols to modify existing paving operation processes which harm the environment. Economically, via the synthesis of recyclable, reusable road paving materials coupled with the development of improved quality materials to reduce maintenance and renovation costs.

The term "sustainable" in the context of road pavements refers to system characteristics which comply with the pavement's ability to:

- Achieve the engineering objectives for which the pavement was constructed.
- Preserve and (ideally) restore surrounding ecosystems.
- Use financial, human and environmental resources economically.
- Meet human needs such as logistics, health, safety, equity, employment and comfort.

All stakeholders in the road pavement sector should strive to achieve all four of the aforementioned criteria by adopting more sustainable practices and continually seek available technical information, support and guidance to improve these practices [5].

The road sector ranks highest for the emission of greenhouse gases (GHG's). It directly emits GHG's via fossil energy used during crude oil mining and fractionation processes, aggregate mining, transportation, paving operations and so on while it is also indirectly responsible for GHG emissions via vehicle emissions. The road construction sector is squarely facing the challenge of sustainability most especially because the raw materials are becoming increasingly scarce and eco-friendly policies regarding air, noise, land, and water pollution are getting stricter as time goes on. Challenges such as cost-effective and improved production, construction and of course, maintenance are the major issues facing the asphalt industry.

1.1.2. **Eco-friendly initiatives in the asphalt industry**

There are several eco-friendly initiatives currently in place in the asphalt industry with a few of these initiatives already gaining popularity and acceptance among asphalt industry stakeholders and enthusiasts. The most important sustainable initiatives in the asphalt industry are highlighted as follows:

- Reclaimed Asphalt Pavement (RAP): This is the material removed from existing pavement infrastructure which consists of bitumen and aggregates and is reprocessed for use in new road paving operations. Since RAP is composed of two non-renewable resources (aggregates and bitumen binder), its recycling fulfils the sustainability of asphalt pavement construction. The bitumen binder contained in the RAP is extracted and rejuvenated and can be incorporated into new bituminous mixes for new road pavement operations while the residual aggregates are milled and crushed for reuse in new road pavement construction. The use of RAP products in 2018 saved 4.1 million tons of virgin bitumen binder and 78 million tons of aggregates in USA alone [6]. A large part of the work carried out in this PhD project is based on the recycling and rejuvenation of aged bitumen binder contained in RAP.
- Warm Mix Asphalt (WMA): This is an asphalt produced at 20 – 40° C lower than a conventional Hot Mix Asphalt (HMA) which is usually produced between 150° C – 200° C. WMA which is usually produced at temperatures between 100 – 150° C has several benefits to the environment and asphalt workers. Some of these benefits include less energy expenditure during paving processes due to lower compaction temperatures, less emissions and safer working conditions of asphalt pavement workers [7].
- Use of biomaterials/biopolymers as additives for bitumen: To improve bitumen's properties, additives provide a viable option. However, most of the conventional additives currently used are consist of substances which are harmful to the environment such as strong acids or bases. In recent years, research has drifted towards the synthesis of sustainable eco-friendly functional materials as bitumen additives to substitute the harmful substances currently in use. Additives obtained from natural materials such as bio-oils, natural rubber, plant-based substances, biosurfactants and so on are gaining widespread acceptance in the asphalt industry [8].
- Cold Mix Asphalt (CMA): Cold mixes are produced using unheated aggregates and bitumen emulsion or foamed bitumen [7]. CMA saves a lot of energy in its production since the aggregates do not need to be heated and the binder is in the form of an emulsion. This greatly reduces production costs while totally eliminating GHG emissions during paving. A lot of research is still

going on in this regard in order to achieve road pavement quality which is better than or at least equivalent to conventional methods.

1.1.3. **Additives and their classification**

There are several types of additives used in the asphalt industry and they can be grouped into three main classes; asphalt mix modifiers [9], asphalt mixture reinforcement materials [10] and recycling agents [11]. In this PhD project, all three of these classes of additives were used.

- Asphalt Mix Modifiers: These additives can be further divided into two groups. The first group consists of the additives which are added directly to the hot asphalt mixtures. These additives usually have a low melting point to facilitate their incorporation into the asphalt mix [12]. The second class of additives are added to the bitumen binder and then the resulting modified bitumen is added to the asphalt mixture. This second group consists mainly of elastomeric copolymers [13].
- Asphalt Mixture Reinforcers: This group of additives enhance asphalt mixes by improving the shortcomings of these mixes. Asphalt mixes containing asphalt reinforcers are mostly used to pave heavy-duty roads because they improve the tensile strength of the road pavement. This increase in tensile strength is brought about by the formation of cross-linked networks with the matrix of the bituminous binder [10].
- Recycling Agents: These are plant-based or petroleum-based oils and resins which are added to the bituminous mixes or directly to the asphalt mixture depending on the functionality and nature of the product. These additives are used to restore the properties of aged bitumen binder which have been lost to oxidative aging and mechanical stress that the road pavements are subjected to during their service life [14].

1.2 **Problem Statement**

In order to achieve sustainable asphalt ecobinders on a large scale, the impact of the paving process should bring about no real damage to the environment. Conventional additives currently used in asphalt paving are toxic materials which are either very acidic or vary basic in nature. To solve the problem of environmental pollution brought about by asphalt paving and its processes, these harmful additives need to be substituted with eco-friendly biomaterials. Non-renewable resources used during road paving processes need to be recycled thus conserving natural resources and also promoting a circular economy. Energy consumption and GHG emissions during conventional road paving processes also need to be lowered. The need for sustainable asphalt technologies to be brought to the forefront of the asphalt industry's conventional practice is crucial now more than ever.

1.2.1 **Biomaterials for sustainable road paving**

Road paving is a crucial aspect in the development of modern infrastructure but the production, transportation, and maintenance of conventional asphalt materials have a significant negative impact on the environment. However, paving roads with biomaterials is becoming a more sustainable and environmentally friendly alternative.

Biomaterials are substances derived from living things like plants, animals, or microbial activity. As opposed to conventional paving materials, these materials are more durable and have a lower environmental impact [8]. Lignin, a naturally occurring polymer present in plant cell walls, is one example of a biomaterial used in the production of modified asphalt mixes. Asphalt can be

strengthened and made to last longer by adding a polymer made from lignin, which can be extracted from agricultural and forestry waste products [15]. The use of cellulose nanocrystals (CNCs) as a biomaterial for road paving is another example of the application of biomaterials as additives in road paving operations. CNCs are very tiny particles that can be taken out of plant-based materials like cotton and wood. They are perfect for reinforcing concrete or asphalt due to their excellent mechanical qualities [16]. CNCs are also renewable and biodegradable, which further emphasizes their status as an environmentally friendly choice.

Additionally, biomaterials may help to reduce the carbon footprint resulting from road paving operations. A viable approach to reduce waste and develop a circular economy is to use agricultural waste products to make biomaterials for paving roads. The need for petroleum-based materials, which are non-renewable and increase greenhouse gas emissions, can also be decreased by using biomaterials in road paving. By providing a greener alternative to conventional paving materials, biomaterials have the potential to revolutionize road paving. They have numerous advantages, such as reduced environmental impact, improved strength and durability, and lower carbon footprint [17]. With the advancement of research into biomaterials, it is likely that biomaterials will be gain more widespread acceptance in the field of road paving.

1.2.2 **Recycling of aged road pavements via rejuvenation of Reclaimed Asphalt Pavement (RAP)**

Asphalt pavements during their service life become increasingly susceptible to oxidative aging and fatigue brought about by extended use of the road pavement. These pavements are susceptible to rutting, cracking, and other types of distress as they get older, which can compromise their performance and safety. In order to mitigate these problems, many agencies and contractors have turned to using reclaimed asphalt pavement (RAP) to recycle old road pavements.

RAP is the material that is obtained when old asphalt pavements are removed and milled into small particles. The bitumen binder present in this reclaimed asphalt is also extracted with the aim of recycling it by rejuvenating it to restore its viscoelastic properties which have been lost to aging. The proportion of RAP that is typically included in new asphalt mixtures varies depending on the requirements and specifications of the individual project. However, there are limitations to the amount of RAP that can be used in a mix, as too much RAP can compromise the quality and durability of the new pavement [18]. The rejuvenation of RAP is one method for overcoming this limitation. This rejuvenation involves the addition of a rejuvenating agent to the RAP material (in this case, the extracted bitumen binder) to restore its original viscosity, elasticity, and durability. This rejuvenation involves the replenishing of hydrocarbons, aromatic compounds and other structural components of the bitumen binder thereby restoring it to a state similar to that of the initial virgin bitumen used for the initial paving operation.

Agencies and contractors can use more recycled material in their asphalt mixtures by rejuvenating RAP, reducing the demand for virgin asphalt and the associated environmental impacts of its production. Additionally, since the material is typically less expensive than virgin asphalt, using rejuvenated RAP is less expensive thereby reducing production costs and creating a circular economy around asphalt paving operations. In general, recycling old road pavements through the rejuvenation of RAP is a sustainable, practical and affordable method of pavement rehabilitation, maintenance and even construction of new asphalt infrastructure. In this light, it is a valuable tool in the ongoing effort to maintain and improve our transportation infrastructure.

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Chapter 2

Literature Review

2.1. The Structure of Bitumen

Bitumen is the gluey material that functions as an asphalt binder and keeps the mineral aggregate particles together in the composite used in road paving processes. It is the product of a refinery operation whereby a residuum obtained after the distillation of crude oil is treated by air blowing or by a solvent method to produce a product that meets specifications for a variety of road/highway construction and other uses [1,2]. Bitumen is also the name given in Europe to a manufactured product, while asphalt binder is used in North America and many other countries.

Nowadays, a significant amount of bitumen derived from petroleum is channeled into road paving processes, while the rest is utilized for other construction processes, such as painting, varnishes, roofing, insulation, the production of rust-protective compositions, battery boxes, and as one of the starting materials that go into the production of rubber products, brake linings and fuel briquettes. A variety of standard tests are available to define the quality and viscosity specifications of bitumen [2]. Bitumen can be fractionated into four general (but not chemical [3]) classes of compounds (SARA) [4]: (i) saturate hydrocarbons, correlated with the softening point of the material and empirically measured by the penetration index; (ii) aromatic and naphthene constituents, which are partially hydrogenated aromatic compounds; (iii) resin constituents, in some cases referred to as polar aromatic constituents, which contain a variety of alkyl residues and functional groups, and (iv) asphaltene molecules, constituted by a conjugated carbon core, having functional groups and heterocyclic compounds and carrying alkyl sidechains grafted directly to these cores. Asphaltenes (henceforth the term asphaltene(s) will be denominated with the acronym ASP) are associated with highly aromatic (H/C ~ 1.0–1.3) and high-molecular weight (MW) molecules [5], while resins have a higher H/C ratio (1.2–1.7), lower aromaticity, and lower MW compared to ASP [6,7].

Among the other fractions of bitumen, ASPs are the least soluble fraction of an almost continuous spectrum of several polyaromatic molecular species and can be extracted or separated from the other fractions through precipitation via the addition of a large volume of n-alkane to a crude oil (ASTM protocol D6560) [8]. The term resin is generally used to refer to a substance that has undergone elution from several solid adsorbents, while the term maltenes (petrolenes or de-asphalted oil) refers to a mixture of the resin and oil constituents that are obtained from the filtrates via the precipitation of ASP [9].

ASPs are often referred to as the “cholesterol of petroleum” [10], a term borrowed from medical terminology to define the clogging effect occurring in wellbores and transportation pipelines caused by the precipitation, deposition and dense flocculation of ASPs subjected to certain physicochemical conditions [11]. Each year, the damage caused by the deposition of ASP results in the loss of billions of dollars in the oil industry, which also is reflected in reduced production capacity, wells prematurely shutting-in, and implications for management techniques [12]. ASPs are therefore the lyophobic components of bitumen, and their dispersion is affected by several factors such as the nature of the dispersing medium (paraffinic or aromatic), as well as the chemical structure and relative proportion of resins and ASP [6,13–15]. Indeed, a high con-tent of resins imparts to a product an adhesive property and plasticity, whereas high ASP content is usually responsible for harder, more brittle bitumen, as evidenced from the structure and rheological properties of modified bitumen. Bitumen containing a high resin content translates to higher product adhesiveness, as well as a high level of plasticity, while on the other hand, a high ASP content imparts hardness and results in a more

brittle bitumen [16–20]. Furthermore, the presence of ASP is usually responsible for a significant increment in the viscosity of crude oil [21,22], thus making its transportation and processing more difficult. These properties and many others are dictated by the microstructure of bitumen, that is, the structure and dynamics of ASP aggregates dispersed in the maltene moiety.

This section of the literature review aims at illustrating bitumen, its colloidal structure, asphaltene behaviour which gives bitumen its characteristics which are still not yet fully understood. For example, in their review, Ghosh et al. [23] discussed ASP aggregation via spectroscopy methods, while Zhang et al. [24] focused on the relationship between microstructure and properties of bitumen, as highlighted by four microscopic testing approaches (FTIR, NMR, GPC, and AFM). This section retraces the evolution of salient results which with time have led to the general consensus of bitumen's colloidal model.

Asphaltenes and the Colloidal Nature of Bitumen Microstructure

The early models on bitumen microstructure borrowed the concept of "micelle" from colloid science, and suggested that ASP floats in suspension in the form of self-associated aggregates in a matrix of maltenes [25–27]. In its simplest form, this first model refers to bitumen as a colloidal system in which a suspension of ASP micelles is peptized by resins in an oily medium [28–30]. In particular, three different models of colloidal structure, namely, the solution sol, the elastic sol, and the gelatinous gel, were initially proposed [26]. Using these models, early petroleum scientists were able to explain the variations in the mechanical behavior of different types of bitumen, which have been observed experimentally. Since the early 1960s, Yen has been a pioneer in proposing a hierarchical scheme of ASP self-association, illustrating aggregation mechanisms ranging from the molecular state up to the cluster state [31,32]. Indeed, thanks to the first X-ray diffraction studies carried out on "pure" solid ASP, the initial version of the Yen model captured the stacking phenomenon of ASP, as illustrated in Figure 1.

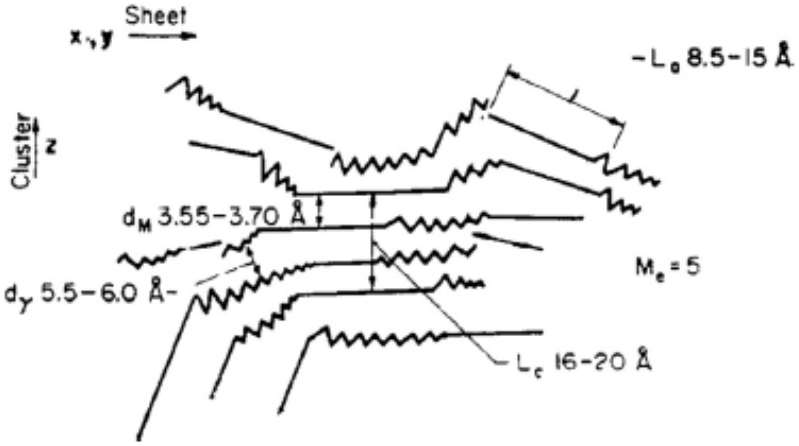
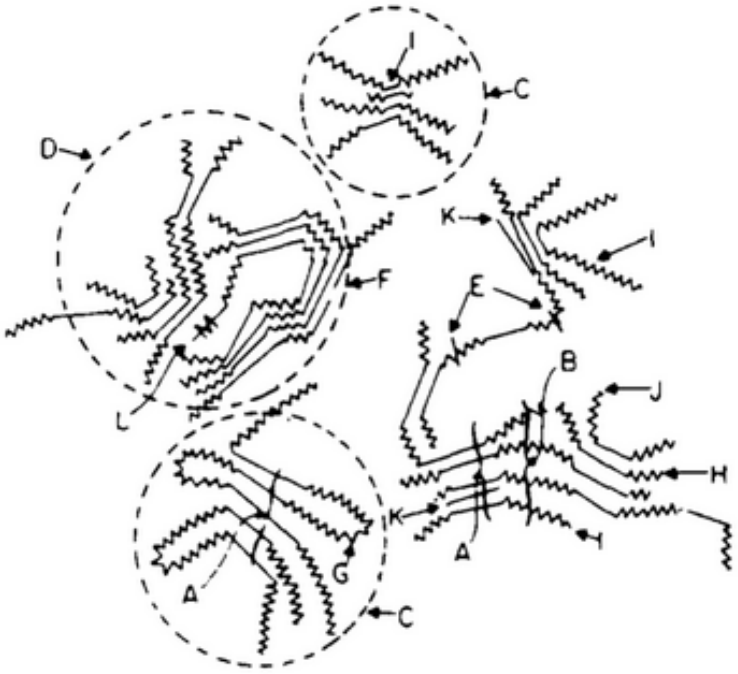


Figure 1: Dimensions of the proposed lamellar structure of asphaltene. Reproduced from ref. [33] with permission from ACS Publications.

ASPs, which have a strong tendency towards self-association, were considered capable of forming self-associated cores as the central unit of micellar-like supramolecular aggregates [34]. In particular, in the Yen model, ASP molecules were treated as plate-like structures capable of stacking together and forming a series of layers stabilized by various types of intermolecular interactions (π–π bonding, H-bonding and van der Walls interactions). It allowed us to gain an insight into the ASP macrostructure, such as the separation distance between two aromatic planes (dM), the aromatic layer diameter (La), the height of the unit cell (Lc) and the number of planes that con-tribute to the stacking of aromatic rings, and lastly, the distance between two neigh-boring aliphatic chains (dγ).

In the micelle structure of the Yen model [34], bonds of sulfide, ether, aliphatic chain, and/or naphthenic rings constitute the bridge among other building rings. In this model, the micelle was said to be about 16–20 Å high and 8–16 Å wide. Yen's proposed hierarchical view visualized the ASP state at different length scales, particularly inclination toward aggregation (Figure 2). The structure of the ASP molecule consists schematically of an aromatic region linked to aliphatic chains. The stacking phenomenon of several planar aromatic parts of the molecules leads to the formation of particles or crystallites, probably brought about by H-bonding or π–π association. Particles further associate into micelles, which in turn could form large aggregates.



Macrostructure of Asphaltics

A. Crystallite	G. Intracluster
B. Chain Bundle	H. Intercluster
C. Particle	I. Resin
D. Micelle	J. Single Layer
E. Weak Link	K. Petroporphyrin
F. Gap and Hole	L. Metal (M)

Figure 2: Hierarchical structure of asphaltenes at different length scales (reprinted from [33]).

Then, some debate was launched about whether the micellar unit in petroleum is made up of a material of a homogenous nature, since it consists of only ASP molecules, or if it consists of ASP and resin molecules. An alternative point of view was proposed by Altegelt and Harle [35], who regarded bitumen as a solution of disaggregated ASP dissolved in maltenes as the solvent. Koots and Speight [36] inferred that resins or maltenes are fundamental, in that their role is to keep the ASP constituents in suspen-sion, and therefore the micellar structure should be considered as an ASP–resin complex rather than an ASP–ASP micelle. Petersen [37] emphasized the importance of the different molecular components of bitumen interacting with one another so as to form a compatible or balanced system. Explaining the physical and chemical properties of bitumen using the solubility approach came to sometimes be known as the "Petersen model" [38]. Later, many investigations

began to work around the mechanism(s) by which ASPs self-associate both in solution and in crude oil [39,40].

The proposal of an outright alternative compositional model and a direct confrontation to the colloidal model was put forward by Anderson et al. [41], who pro-posed the dispersed polar fluid (DPF) model, in which bitumen was envisioned as a fluid that consists of a continuous distribution of variably sized molecules and different polar functionalities. The associations between these molecules were attributed to H-bonding, π–π bonding, van der Waal bonds and polar–polar electrostatic interactions. The notable difference consists in the fact that while the colloidal one presumes the existence of a continuous, low-polar phase and a dispersed, highly polar phase [42], the DPF model assumes that bitumen is a single-phase system, i.e., a simple homogenous liquid [41]. However, the general acceptance of DPF by bitumen scientists as an alternative model to the colloidal one is still yet to be established.

With the beginning of the 2000s, research in petroleum science focused on the effects of chemical structure and other components of bitumen on the aggregation mechanism of ASP [43,44]. A new model was proposed by Redelius [45], based on the mutual solubility of solvents. It incorporated information about cohesion, molecular volume, dispersive and polar interactions, as well as H-bonding. In particular, he developed a method to separately measure H-bonding and other polar interactions in aged asphalts and asphalt–flux mixtures. Concomitantly, the concept of micelles as the basic units of the colloidal model of bitumen continued to be tested in its validity.

As it was observed by Lesueur [46], resins could play a surfactant-like role and stabilize ASP into micellar aggregates. Accordingly, the ASP micelles were visualized as consisting of an insoluble molecular core associated with resins, thus imparting steric stabilization that disfavors the flocculation and precipitation processes. The ASP phase's separation after adding a non-polar solvent to the crude oil could thus be conceptualized in terms of reducing the polarity or the solubility parameter of the hydrocarbon. A thermodynamic equilibrium between individual ASP species and micelles was then invoked to explain ASP stability in hydrocarbon media and the stabilizing influence of the resins [47]. According to this model, the ASP colloidal particles were thus presumed to possess structures in the form of a core encompassed in a shell. The cores presumably form "insoluble" aggregates of stacked ASP, which are stabilized by ASP molecules with a higher solubility [48]. This model agrees with the basic concept of Acevedo's proposed description of the aggregation phenomenon [49].

In Acevedo's rosary-type aggregate structure, the core of the particle is constituted by the least soluble fraction, A1, encompassed by a more soluble fraction, A2 [50,51], which functions as a solvating/dispersing agent [52] (see Figure 3). Studies involving the aggregation and dissociation of asphaltene solutions in maltene (solvent) showed that the colloidal aggregates could be increased by the addition of insoluble A1 asphaltenes, while on the other hand, the A2-type asphaltenes, which have a tendency to be more soluble, remained dissolved in maltene phase [53]. It has been indicated that the A1–A2 colloidal aggregates in this rosary-like structure are linked by the alkyl chains without necessarily being stacked via the π–π system. Even though the A1 monomer structure was rigid, the alkyl chain connection conferred flexibility to the rosary-type structures and a huge amount of both folded and unfolded conformers could be visualized [52].

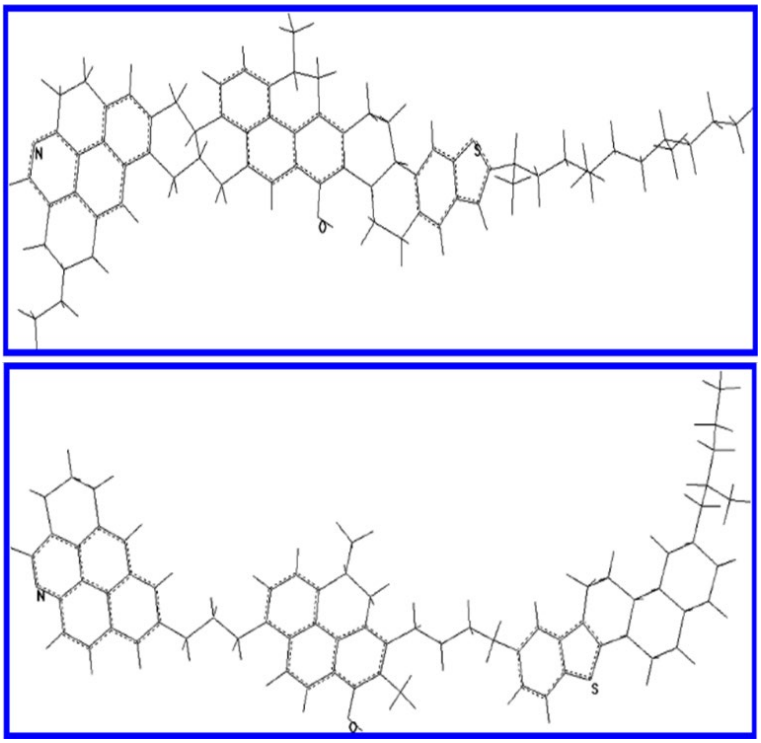


Figure 3: Condensed rigid structure of asphaltene for the insoluble fraction, A1 (above), and ro-sary-type flexible structure of an asphaltene model used to simulate compounds in the soluble fraction, A2 [52].

Afterwards, to explain solubility and compatibility, a physical model of the oil residue was proposed by Wiehe et al. [54], which was believed to be an aggregation phenomenon as a result of the changes in solubility. This proposed micelle structure was the backbone of the colloidal model. In this model, the resin molecules (R) form a layer around the asphaltene core (A), which in turn is further covered by a subsequent layer of aromatic molecules (a), all enveloped by an outer shell consisting of saturated substances (s) (see Figure 4).

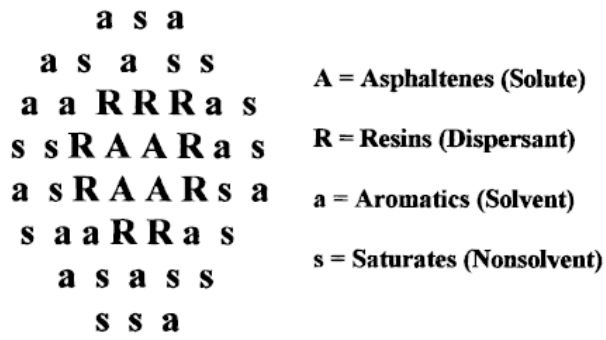


Figure 4: The Wiehe model of oil residue based on solubility [54].

In the context of the colloidal model, the classification of bitumen in terms of its ASP content is mentioned here to differentiate low-ASP (sol-type) binders (which are ductile, have low degrees of complex flow and show large variations in viscosity with temperature) from gel-type binders, with a high ASP content and characterized by non-Newtonian rheological behavior, relatively low viscosity variation with temperature, low ductility and susceptibility to hardening by oxidative aging [46]. Bitumen with intermediate ASP content has properties intermediate between the extremes of sol- and gel-type behavior. The transition from sol- or sol–gel- to gel-type materials that accompanies the increase in ASP content has been postulated by many researchers as the cause for bitumen failure by embrittlement and cracking [59].

Then, two questions began to arise: what forces are behind the association of the ASP molecules and at what point does aggregation result in precipitation? The forces behind the association phenomenon somehow need to have a greater magnitude than those that maintain ASP in solution. As a matter of fact, aggregation and precipitation are driven by different intermolecular forces: strong forces instigate association, while precipitation occurs as a result of dispersive forces among the aggregates. The ASP flocculation phenomenon could be instigated by solubility changes (the addition of a paraffinic antisolvent). However, both questions could not be analyzed within the framework of the early version of the Yen model, as it suffered from severe setbacks. It was inferred from investigations on ASP (solid) powder, and it was not firmly proven, that the model held also in solution. Thus, the representation of the elementary units of micelles was modified by contemplating a further clustering into particles of larger sizes, which bear similarities to the physical structure of a flake [55]. The picture consisted of various combinations of unit sheets of molecules forming particles, micelles, and clusters of micelles with different mechanisms of molecular interaction.

Thus, the Yen model was subsequently modified by Mullins [33,56,57], which distinguished several different entities (Figure 5): the elementary molecule, the nanoaggregate particle, and the cluster of nanoaggregates. In the Yen–Mullins model, an ASP molecule is in the range of ~1.5 nm; a nanoaggregate consists of stacked aromatics with a small aggregation number (<10) and a size of ~2 nm, while higher concentrations form clusters of nanoaggregates, again with small aggregation numbers, starting at ~5 nm [58]. These different entities may be associated by several types of interaction. ASP could precipitate artificially or naturally if molecular interactions with resin constituents are disrupted [60].

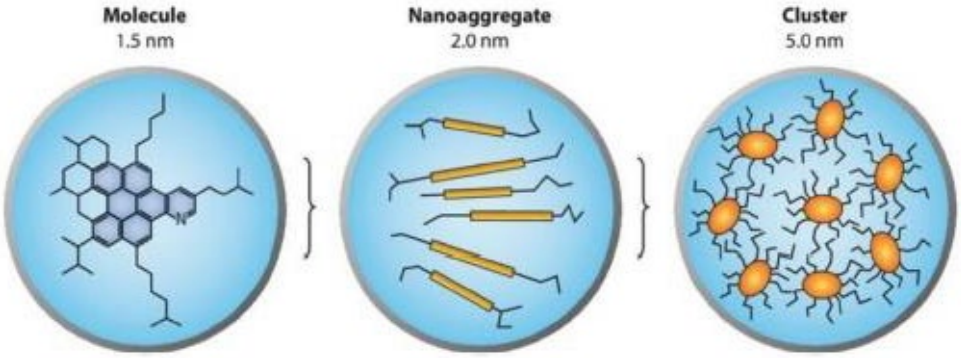


Figure 5: Yen–Mullins model of the asphaltene molecule, nanoaggregate (particle) and cluster [57].

Other NMR results were also found to be consistent and in concordance with the hierarchical Yen–Mullins model [61].

Aggregation of Asphaltenes in Bitumen and Model Solvents

The aggregation behaviour of ASP is plausibly influenced by the chemical composition, polydispersity and steric arrangement, or the interconnective network of functional groups in the single ASP monomers. This complex mixture is usually in a delicate equilibrium, which can be modified by a change in the temperature, pressure, or composition, resulting in asphalt precipitation [62]. Irrespective of the geographical origin and physical properties of ASP, the calorimetric data showed that ASP aggregates form a low-cohesion energy, polydispersed system [63]. Filtration has demonstrated size polydispersity, since varying quantities could be recovered by using varying pore size membranes [64]. The aggregation rate and equilibrium of aggregate dissociation are influenced

by concentration, temperature and time. Van der Waals forces are dominant in concentrated solutions, while coulombic forces are largely responsible for aggregation in diluted solutions [65].

Hence, a deep understanding of the mechanism of the association phenomena is critical for determining the true molecular parameters (weight and size), and also for developing solutions to the problems brought about by ASP's. A wide array of theoretical and experimental techniques has been applied for the study of such complexity. Unfortunately, the understanding and description of the structures of these complex fluids is still challenging and difficult due to the enormous number of their constituents. A simplified approach consists in the extraction of ASP from these fluids and its consequent dissolution in pure organic solvents, such as toluene, in order to access the structural parameters. However, it is worth noting that the observed behaviors in model solutions do not always have to reflect the actual state of crude oil, much less live crude oil. ASP particles in oil may be partially dissolved, partially micellar, and/or partially (steric) colloidal, depending on the polarity of the milieu. The addition of resins to ASP solutions was initially interpreted in terms of the effect of improving H-bonding due to specific interactions between resin and ASP [66]. Some part of the ASP fraction would be prone to associate and aggregate even in the best solvents, such as toluene. In dilute solutions, the concentration limit, which has been observed for the self-assembly of ASP monomers, was reported to be less than 10 mg/L [48]. Stacking as an inceptive mode of association might come about by the interaction of π-orbitals via complexes of charge transfer of the aromatic rings, as shown by the results of early X-ray diffraction analyses [32]. Stacking involves five to six layers of molecules, but only two or three according to existing research [32,67]. Stacking via interactions in the aromatic core was hypothesized to happen between colloidal particles as well [48].

According to Creek [68], the forces that influence precipitation and aggregation are the factors that differentiate every single one of these processes. He also differentiated aggregation from precipitation as definite steps in a process that is totally reversible. Strong interaction sites, which are found at the edges of the ASP molecules, promote aggregation phenomena, beginning with their reversible association in 2D sheets (lamellar array). Meanwhile, influenced by van der Waals forces of attraction between aggregates, precipitation eventually may occur [68]. Considering the arrangement of the ASP molecules in the aggregates, in principle, it should be different from a surfactant system, partially because of the inhomogeneity of the structures of the ASP molecules. How are ASP molecules arranged in an organic solvent in order to form aggregates, and what is the principal difference between the aggregate surface and its core? These are two fundamental questions that still have not been answered. Although there is some understanding about colloidal structures, the underlying mechanism of the packing of ASP molecules in an aggregate is as yet unknown.

Aging Phenomenon and Thermal Behavior of Bitumen

One of the typical phenomena occurring at low temperatures in bituminous materials under isothermal conditions is the thermoreversible aging caused by physical interactions, such as crystallization, phase separation and vitrification, all of which being reversible upon heating to sufficiently high temperatures [69]. Reversible aging can be divided into steric hardening, which occurs mainly in the intermediate temperature range, and physical hardening, which usually refers to a reversible phenomenon at low temperatures. Since the low-temperature properties of bitumen have important effects on pavement cracking performance, understanding these processes is crucial in evaluating the effects of physical hardening in both laboratory testing and field studies. Bitumen, as a viscoelastic material, is generally able to endure significant thermal stresses occurring under various cooling conditions. However, the ability to relax stress decreases when temperatures that are too low make the binder very stiff, and consequently there could be a risk that transverse cracks may occur throughout the entire paved section. Unlike oxidative aging associated with oxidation processes and

chain breaking in organic polymers, physical aging does not imply chemical change, and represents a reversible phenomenon of the amorphous glassy state. Indeed, heating the bituminous material erases the effects of physical aging, and the memory of its previous physical state is completely lost.

Bahia and Anderson studied physical hardening and glass transition in bituminous binders characterized by good and poor low-temperature performance [70]. A clear correlation was found between the physical hardening and glass transition process and the non-equilibrium state of bitumen in the range around the glass transition temperature (T_g). Anderson and Marasteanu illustrated several methods for describing the changes in viscoelastic moduli that result from physical hardening [71]. It was postulated that the physical hardening mechanism did not correspond to that typical of polymeric systems, and that this discrepancy could be attributable to the crystallizable fraction (waxes, paraffins, saturates) present in bitumen. The combined effect of both free volume collapse and wax crystallization was invoked to explain why isothermal hardening occurred at temperatures well above the T_g. Masson et al. conducted a systematic investigation to correlate the physical hardening phenomenon with the various SARA fractions constituting the crude oils, and concluded that while both ASP and resins made the main contribution to the hardening effect, maltenes could manifest a significant effect over the kinetic aspect of the whole process [72].

The effects of the crystallization of waxes and internal rearrangements of ASP were recognized by Hesp et al. as possible mechanisms to explain reversible aging [73]. By using AFM and neutron scattering techniques, Schmets et al. found that gradual phase separation at low temperatures was triggered by the nucleation of wax crystals, and a new hypothesis was developed for its effect on the cracking and healing potential of bitumen [74]. Tabatabaee and coworkers proposed a prediction model, based on a modified creep viscoelastic model, capable of describing the rate of physical hardening as a continuous function of time and temperature [75]. Fischer et al. investigated the kinetics of the crystallization process of bitumen by observing with AFM the development of the peri phase structures, which in turn was connected with an increase in stiffness and hardness [76]. Isothermal DSC measurements were also carried out, and the results were analyzed to interpret the observed AFM images.

Laukkanen et al. investigated the low-temperature mechanical properties of bitumen and considered the effect of reversible aging on the shape of the binder relaxation spectrum. They used the complex glass-forming liquids theory to explain the co-existence of liquid and glassy microphases in bitumen when annealed at low temperatures [77]. Ding and coauthors compared the low-temperature reversible aging discrepancy mechanism for binders with similar low-temperature performance grades, and evaluated the effects of the contribution of various pure waxes added to model bituminous materials [78,79]. Another work compared the effects of both types of hardening, namely, oxidative (irreversible) and thermoreversible aging, on the performance grade parameters, such as complex shear modulus, the elastic and viscous components of the complex shear modulus, and phase angle [80]. The authors analyzed the calorimetric data under the Ozawa theoretical framework, which has proven to be an effective method of predicting the rate of transition from an amorphous to a semi-crystalline state during isothermal annealing.

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2.2. Function of additives in Asphalt

Since the 1900's, Hot Mix Asphalt (HMA) has been the most common and generally accepted technology for asphalt pavement construction. Road pavements are made up of over 93% stones and less than 7% of bitumen functioning as a binder. Bitumen is a soft material made up of several components and it is a by-product of petroleum industry processes. Its chemical composition is complex and it can be characterized using special methods [1]. In order to ensure proper coating of aggregates and provide sufficient workability of HMA, both asphalt binder and aggregates are heated up to high temperatures between 150-180 °C. This results in high energy costs and the emission of several greenhouse gases (mainly CO2). The Kyoto Treaty was developed as a result in 1997 thus setting the objective for European countries to develop policies and technologies in order to meet greenhouse gas reduction requirements [2].

Warm Mix Asphalt (WMA) technologies were developed to produce asphalt at temperatures slightly above 100°C, with performances and characteristics equivalent to or even sometimes better than that of conventional HMA. WMA technologies mostly focus on the binder (bitumen) by adding different additives to improve its properties [3-7]. These technologies, which produce asphalt between 110-140 °C, facilitate proper coating of the aggregates and hence the workability and compactibility of the mix while also reducing production and compaction temperatures by 20-40 °C. This reduces energy consumption, minimizes fume and odour emissions and also creates a cooler working environment for asphalt workers [8]. Figure 1 shows the position of WMA among the different techniques ranging from cold to hot mixes.

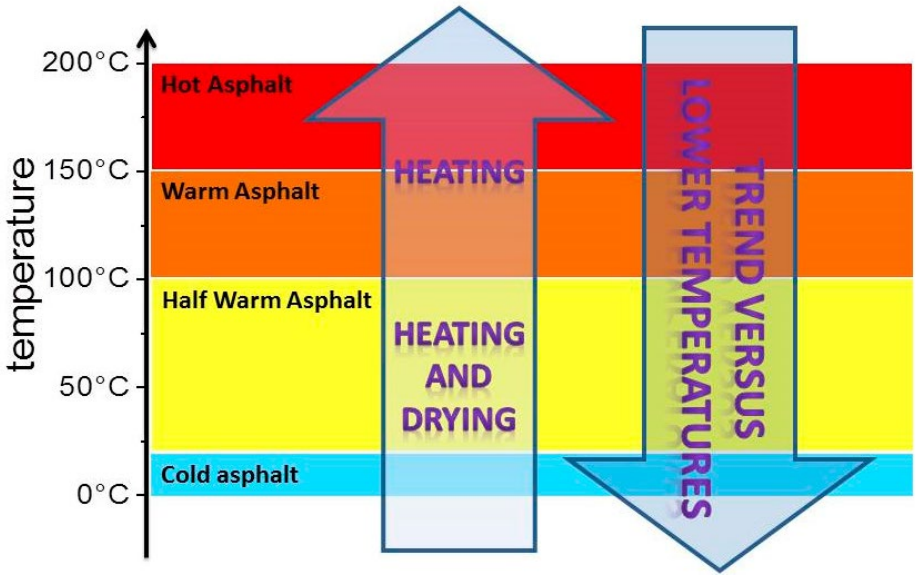

Figure 1: Classification by temperature range (EAPA, 2014)

Several techniques exist for the production of WMA. The three generally most accepted are those using (i) organic additives; (ii) chemical additives; and, (iii) foaming techniques [9]. Organic additives are usually waxes and fatty amides, which are able to reduce the viscosity of the binder above the melting point of the binder. Common waxes used in the production of WMA are Sasobit® and Asphaltan B®. On the other hand, chemical additives are usually emulsifiers and surfactants that

do not reduce the binder viscosity but improve the coating of aggregates by reducing the surface energy of the aggregate/binder interface and/or the inner friction. Products such as Rediset® and Evotherm® are often used [10]. Foaming techniques function by reducing the viscosity of the binder just like organic additive technique but only for a short period of time. This is achieved by introducing small amounts of water in the hot binder (bitumen) causing expansion of the bitumen and the formation of a large quantity of foam. Foaming techniques are subcategorized into (i) water-based processes, which entail the use of injection foaming nozzles; and, (ii) water-bearing additives, which involve the use of minerals in the form of zeolites [8,11].

Asides the aforementioned WMA techniques, there are also several combined technologies and products used to produce WMA, like zeolites or fibres with organic additives or pallets with fibres. These are called hybrid techniques. Hybrid techniques involve a combination of two or more technologies and are used less often. Examples of hybrid techniques are Low Energy Asphalt (LEA) and Tri-Mix Warm Mix Injection system which are both technologies that combine chemical and water-based techniques to achieve required results [2,12,13]. In addition to all of the commonly known techniques for WMA production, an uncommon technique that uses emulsions to pre-coat aggregates is sometimes used. This technique involves the use of stabilized bituminous emulsion to pre-coat aggregates before the main mixing procedure with asphalt binder. Due to the absence of hazardous additives in this specialized emulsion technique, it is designed to produce a more environmental friendly and cost effective procedure [14].

Just like any new technology, WMA needs a lot of further research and study. A few concerns like finding a mix design strategy and the need for a comprehensive specification have been identified thus far. Previous research [15,16] confirms that the lack of standardized mixture design procedure of WMA makes it important to identify the mechanism(s) of action of additives. The wide range of mechanisms through which several WMA additives act also provides a wide range of WMA additive product options when deciding how to formulate warm mixes. Also, since the set of instrumentation, machinery and apparatus available for WMA production contribute to determine the technique to be used, a good knowledge of how and why the additives work gives a realistic evaluation of methods and techniques to be used for future WMA technology. Table 1 shows the range of additives used in warm mix technologies.

Table 1. Products used in Warm Mix technology

WMA processes	Product	Company	Description	Dosage of Additive	Country where technology is used	Production temp. (or reduction range) °C
Organic additives						
FT Wax	Sasobit®	Sasol	Fischer-Tropsch Wax	1.0-2.5% by weight of binder	Worldwide	(20-30°C)
Montan Wax	Asphaltan B	Romonta GmbH	Montan Wax with fatty acid amide	2.0-4.0% by mass of bitumen	Germany	(20-30°C)

Fatty Acid Amide Wax	Licomont BS	Clariant	Fatty acid amide	3.0% by mass of bitumen	Germany	(20-30°C)
	3E LT or Ecoflex	Colas	Proprietary	Not specified	France	(20-30°C)
Chemical additives						
Emulsion	Evotherm® technologies	MeadWestvaco	Chemical packages with or without water	0.5-0.7% by mass of bitumen	USA, worldwide	85-115°C
Surfactant	Rediset	Akzo Nobel	Cationic surfactants & organic additive	1.5-2.0% by weight of bitumen	USA, Norway	(30°C)
Surfactant	Cecabase RT	CECA	Chemical package	0.2-0.4% by mixture weight	USA, Norway	(30°C)
Liquid Chemical	Iterlow	IterChimica		0.3-0.5% by mass of bitumen	Italy	120°C
Foaming Processes						
Water-containing	Aspha-Min®	Eurovia and MHI	Water-containing technology using zeolites	0.3% by total weight of mix	Worldwide	(20-30°C)
Water-containing	Advera®	PQ Corp.	Water-containing technology using zeolites	0.25% by total weight of mix	USA	(10-30°C)
Water-based	WAM Foam	Shell and Kolo-Veidekke	Foamed binder	2-5% water by mass of binder	Worldwide	100-200°C

Substantial information is known about the effects of additives on warm mix but the precise mechanism of how these additives work to confer the desired characteristics on WMA is still unclear. The main goal of this paper is to review the most relevant works appeared in literature on the subject to highlight the mechanism(s) of action of additives and relate them to the effects observed in the WMA technology.

The discussions presented in this section fostered by a review of previous research and studies highlight the following points about Asphalt mix additives:

1. Organic additives

- Organic additives in the form of waxes and fatty amides act as flow modifiers by melting below the melting point of the binder thus reducing its viscosity during mixing which improves coating and workability of the mix.
- During the cooling phase of the mix, waxes such as Sasobit start to crystallize and form a microscopic lattice structure in the binder which results in the increased stiffness of the asphalt pavement. This is responsible for the deformation resistance and reduction in the amount of air voids observed in wax treated WMA. It is speculated that the stiffness observed in the improved mix results from the alteration of binder hydrocarbon chain length by organic additives which are hydrocarbon-rich in nature.

2. Chemical additives

- Chemical additives in the form of emulsions and surfactants function at the microscopic interface of the binder and aggregates to regulate and reduce the frictional forces at that interface. This improves lubrication between binder and aggregates.
- Emulsifying agents such as Evotherm generally improve lubrication of the mix by altering Surface Free Energy components and parameters. This is responsible for asphalt mix particles moving more easily over each other in the mix which in turn translates to better coating of aggregates caused by an improved contact angle. Liquid chemical additives like Iterlow also act as emulsifying agents which contain amine groups and improves cracking resistance of the mix at low temperatures.
- Surfactants such as Rediset generally reduce surface tension of asphalt binder to improve wettability of aggregates. They also function in a similar fashion as the organic additives by reducing the viscosity of the binder to improve workability of the mix.

3. Foaming technologies in the form of Zeolites (aluminosilicates) and water-based processes (injection nozzles) generally reduce binder viscosity temporarily. This improves coating and mix workability. These processes are more susceptible to moisture damage due to the involvement of water in the foaming process thus anti-stripping agents are often added to the mix if it is not already contained in the product.

4. Hybrid techniques such as Sasoflex and Tri-Mix Warm Mix Injection system combine different categories of additives with specific desirable features to synthesize additives with versatile functions. This might be the future of WMA technology.

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2.3. **Eco-friendly materials as Bitumen additives**

Research on biomaterials has been pushed to the fore-front of scientific investigation in recent years due to concerns about the emission of greenhouse gases (GHG), global warming, demand for renewable resources and high energy consumption in general. The need for a circular economy and environmental sustainability makes it also important to reduce our dependence on non-renewable resources and drift to-wards alternative bio-renewable resources for industrial purposes and common day to day activities [1,2,3]. Apart from the economic advantage of the use of bio-derived materials which are less costly and reduce energy expenditure, biomaterials are also environmentally friendly as they are biodegradable, renewable and facilitate strategic resource conservation [4,5,6]. Biomaterials are also known to reduce greenhouse effect via CO2 conservation [7]. All of this goes a long way in promoting a circular economy and eco-sustainability in general. In asphalt technology, biomaterials can be used in different capacities; biomaterials with Warm Mix Asphalt (WMA), biomaterials with Reclaimed Asphalt Pavement (RAP) to rejuvenate aged bitumen, bio-binders as partial or total replacement of petroleum-based binders (bitumen) and so on [8].

The application of bio-binders in the asphalt industry differs depending on the aim of the research study in which it is being used. In the real sense, a bio-binder is a substance of biological origin that serves as an adhesive in the asphalt mix. Conventionally, in the asphalt industry, bitumen functions as the binder but as a result of the continuous research in the field of material science, other more bio-degradable bio-binders are being investigated. The experimental application of bio-binders can be classified thus [9]:

a) Direct alternative (75-100% bitumen substitute)

b) Bitumen extender (10-75% bitumen substitute)

c) Bitumen modifier (<10% bitumen substitute)

Although the total substitution of conventional asphalt binder is advantageous and preferrable, most bio-based binders do not have the necessary properties to produce high quality pavement and for now cannot be a complete substitute for asphalt bitumen [10,11,12]. Research is however still going on in this regard. This section focuses on the third category listed above i.e., biomaterials as bitumen modifiers (<10% bitumen substitute) because in existing literature, it is currently the most practically feasible approach to the application of biomaterials to asphalt technology. Also, studies involving biomaterials as bitumen modifiers are the most abundantly available on scientific database due to the fact that there are more researchers working on this aspect [8]. Several types of biomaterials have been used in recent years as bitumen additives and quite a number of them have yielded positive results by improving specific characteristics of bitumen.

Biomaterials are materials that partially or totally constitute a bio-binder. Biomaterials such as natural waxes, bio-oils, biopolymers, organic waste and bio-based nanomaterials have all been reported in literature to improve bitumen's characteristics [13-19]. All the aforementioned types of biomaterials are obtained from different source materials and processes although in some cases, different biomaterials can be obtained from the same process or starting material. For example, bio-oil can be obtained via pyrolysis but so can bio-char which can al-so be classified as a nanomaterial. Bio-char can also be categorized as organic waste but so can Waste cooking oil which can also be regarded as a bio-based oil. Fig 1 illustrates the classification of the different classes of biomaterials and their relativity to one another.

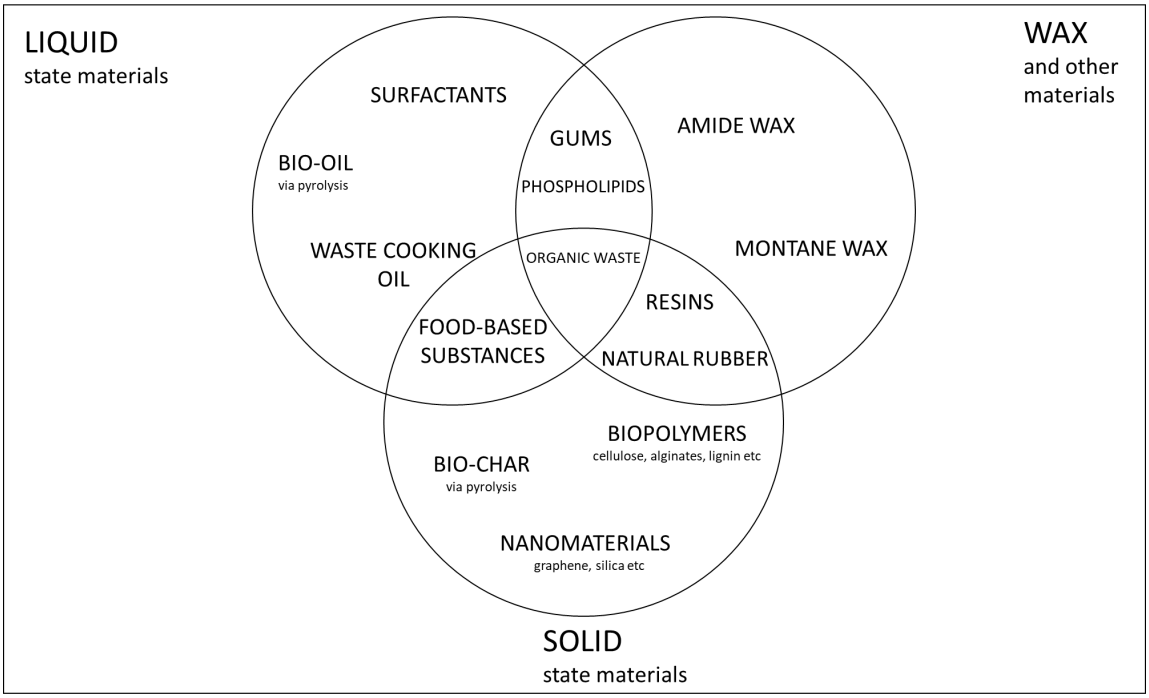

Figure 1. Biomaterials used as bitumen additives and their categorical relativity.

The different types of biomaterials have different mechanisms of action in bitumen and this can go a long way in characterizing different classes of biomaterials as additives for bitumen depending on their effect. Bio-oils for instance are used as bitumen fluxers by reducing the viscosity of the bitumen and in the long term, increase the stiffness of the bituminous asphalt pavement by a process called oxidative polymerization. Natural waxes, below their melting point, increase the stiffness and elasticity of bitumen while above their melting point, decrease the stiffness and increases bitumen's viscosity. Biopolymers such as polysaccharides and natural rubber modify bitumen by changing its visco-elastic behaviour by increasing bitumen's range of plasticity. Nanomaterials on the other hand, often improve the tensile strength of the asphalt conglomerate by forming strong intermolecular crosslinks in bitumen's matrix which in the long term translates to increased stiffness and tensile strength of the paved asphalt [9,14,20,21].

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Chapter 3

Materials

3.1. Bitumen, its role as an asphalt binder and its comparison with tar

In this project, several types of bitumen were used. The bitumens all had penetration grades of either 50/70 or 70/100. In a general context, bitumen is often confused with tar. These are two different materials obtained from different sources. Bitumen is more efficient and also environmentally friendly in comparison with tar. Tar is derived from coal rather than petroleum and has some key differences when compared to bitumen. For one, tar has a lower melting point than bitumen, so it softens and deforms more easily in hot climates. It also has poor water resistance and can decompose quickly when exposed to moisture. Another difference between bitumen and tar is their environmental impact. Both materials come from non-renewable sources, but tar production is generally considered more harmful to the environment than bitumen production. This is due to the fact that tar production often releases harmful gases and chemicals and also produces large amounts of waste [1,2].

Table 1: Principal differences between bitumen and tar [2]

BITUMEN			**OXIDIZED BITUMEN**	**TAR**
(Source)	*(Walcave,1971)*	*(Brandt,1985)*	*(Brandt,1985)*	*(Brandt, 1985)*
N° Samples	8	4	3	2
Phenanthrene (mg/Kg)	0.4÷3.5	1.7÷7.3	0.3÷2.4	$(19.8 \div 25.7) \cdot 10^3$
Chrysene (mg/Kg)	< 0.1÷8.9	0.5÷3.9	0.8÷1	$(11.2 \div 22.7) \cdot 10^3$
Benzo[a]Pyrene (mg/Kg)	ND÷2.5	0.2÷1.8	0.4÷0.5	$(11.4 \div 15.2) \cdot 10^3$
Benzo[ghi]Pyrilene (mg/Kg)	< 0.1÷4.6	1.7÷4.6	1.2÷2.0	$(3.43 \div 3.53) \cdot 10^3$
Max single IPA (mg/Kg)	39.0 (Perylene)	4.2 (Benzo[ghi]Perylene	2.4 (Phenantrene)	$76.0 \cdot 10^3$

According to a paper jointly published by the Asphalt Institute and Eurobitume in 2011, the current global consumption of bitumen is approximately 102 million tonnes per year, 85 % of which is used in various kind of asphalt pavements [3,4]. From a chemical point of view, the analysis of the molecular weight distribution shows that bitumen is a complex mixture of about 300-2000 chemical compounds (medium value 500-700) making it difficult to completely characterize it chemically. For this reason, bitumen is generally fractionated by more simple methodologies [5], which allow to identify two principal constituents:

- Asphaltenes (percentage in bitumen varies from 5-25%) are amorphous brown/black solids, insoluble in n-heptane and are composed of a complex mixtures of hydrocarbons, characterized by condensed aromatic compounds. Asphaltenes contain oxygen, nitrogen, sulphur and

heavy metals (V, Ni etc…) with long (up to 30 carbon atoms) aliphatic chains, pyrrolic and pyridinic rings as shown in (Fig. 1). Asphaltene particles have dimensions between 5-30 μm and a carbon-hydrogen ratio of about 1.

- Maltenes are divided into Resins and Oils, which are further classified as Saturated Oils and Aromatic Oils. This classification is called SARA (Saturate, Aromatic, Resin, Asphaltene). The relative abundance of the SARA fractions also correlate to the chemical composition of the bitumen regarding its internal structure and some of its macroscopic properties [6].

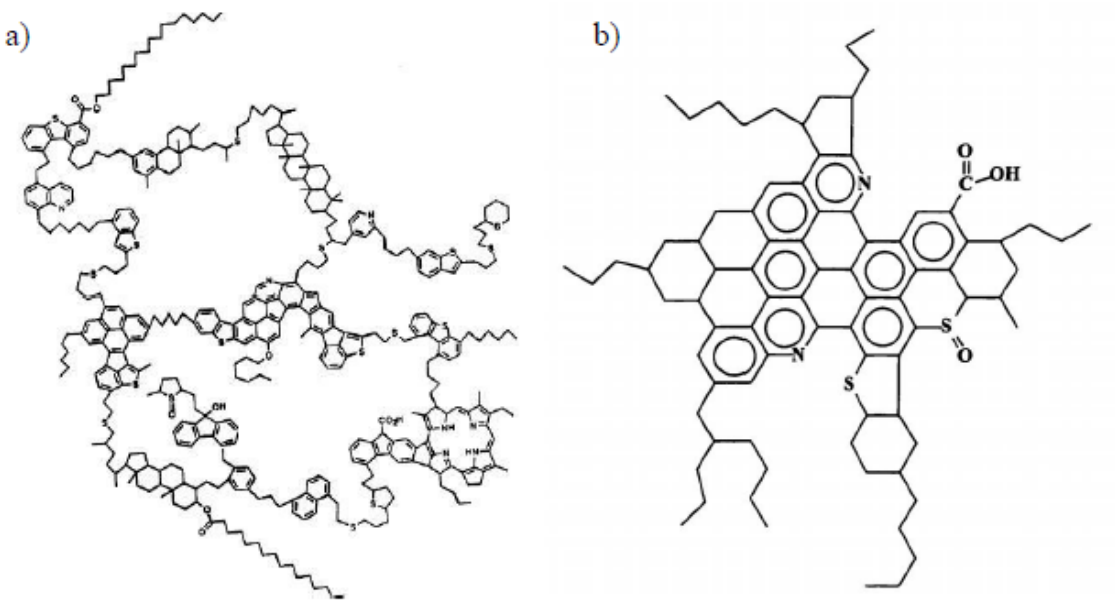

Figure 1: Asphaltene hypothetical structure: a) Archipelago structure: $C_{412}H_{509}O_9S_{17}N_7$ with H/C ratio 1.23 and molecular weight 6239 g/mol [11,12], b) Continent structure: $C_{84}H_{100}O_3S_2N_2$ with H/C ratio 1.19 and molecular weight 1276 g/mol [7,8].

3.2. **Warm Mix Asphalt**

In this study, the asphalt mixes produced were WMA mixes and the additives which have the potential to improve WMA technology were evaluated in order to bring this technology to the forefront in the asphalt industry thereby reducing the environmental impact of paving processes as conventional Hot Mix Asphalt will become increasingly obsolete.

Warm mix asphalt (WMA) is a relatively new technology that has gained popularity in recent years as a more sustainable and environmentally friendly alternative to traditional hot mix asphalt (HMA). WMA is manufactured at a lower temperature than HMA, usually 30-60 ° C lower, and has several advantages. One of the main benefits of WMA is the reduction of energy consumption and greenhouse gases emitted during its production. By producing asphalt at lower temperatures, WMA requires less energy to heat the material, resulting in lower carbon emissions and less dependence on fossil fuels. In addition, lower manufacturing temperatures reduce the amount of smoke and harmful fumes generated during the mixing process, improving air quality for workers and surrounding areas [9].

3.3. Reclaimed Asphalt Pavement

Reclaimed asphalt pavement (RAP) is the material obtained when old asphalt pavement is removed and milled into small particles. This material can be recycled and reused as a component of new asphalt mixes, lessening the need for virgin bitumen and aggregates thereby reducing the environmental impact associated with its production [10].

In this PhD project, the focus was on recycling the recovered bitumen binder using rejuvenators. This study involved testing the efficiency of several biomaterials as candidates for potential bitumen rejuvenating additives.

3.4. Bitumen Recycling Agents

Bitumen recycling agents are additives used to rejuvenate aged or oxidized bitumen, making it suitable for use in new asphalt mixes. They work by restoring the chemical and physical properties of the bitumen, improving its workability, adhesion, and durability, reducing the need for new virgin bitumen in asphalt mixes [11].

In this study, several recycling agents were used. One of these recycling agents was a mix of plant esters, another was a blend of amine derivatives and another was a blend of phosphate isomers. A few bio-oils were also used with some of these bio-oils being by-products of the pyrolysis of biomass. Bio-char, which is another by-product of this pyrolysis of biomass was also tested as a bitumen rejuvenator due to its high hydrocarbon content.

3.5. Bitumen Adhesion Promoters

Bitumen adhesion promoters are additives that are used to improve the affinity between bitumen and aggregate in asphalt mixes. They work by modifying the surface properties of the aggregate, making it more compatible with the bitumen and promoting adhesion between the two materials [12].

In the studies carried out during this PhD, several materials were tested as adhesion promoters. One of these substances is a food-based natural phenol, another one was a phospholipid-based additive (tested in both powder and liquid forms). A few organic waste-derived substances were also tested.

3.6. Bitumen Modifiers

Bitumen modifiers are additives used to improve the performance and durability of asphalt pavements. They change the chemical and physical properties of bitumen, improving the weak aspects of the bitumen binder thus making it more resistant to damage and degradation.

There are many different types of bitumen modifiers, each with their own properties and benefits. A common type is a polymer modifier, which includes a polymer mixed with bitumen to improve bitumen's elasticity and flexibility, reducing the risk of cracking and other pavement damage. Polymer modifiers can also improve pavement resistance to temperature changes and other environmental factors. Another type of bitumen modifier is antioxidants, which contain compounds that help prevent oxidation and aging of bitumen. This helps extend pavement life and reduces the need for frequent maintenance and renovation [13].

In this PhD project, several bitumen modifiers were used. One of them was a plant-derived gallic acid ester and another was a waste wax. By-products of biomass pyrolysis and also organic waste-derived substances were tested in the studies carried out during this project.

3.6.1. **Polymer-modified Bitumen**

Polymer-modified bitumen (PmB) is a type of bitumen that is modified with synthetic polymers to improve its performance and durability in asphalt pavements. PmB is typically used in applications with high traffic and stress where conventional asphalt binders might not perform as well [14].

PmB is obtained by mixing bitumen with a variety of polymers, such as ethylene vinyl acetate (EVA), styrene-butadiene-styrene (SBS), and styrene-isoprene-styrene (SIS), to create PMB. The resulting mixture is a highly elastic and flexible substance that is resistant to pavement distress, such as cracking and deformation [15].

Improving asphalt pavements' resistance to fatigue, temperature changes and other environmental factors is one of PMB's key advantages. This makes it ideal for use in high-stress applications such as airports, ports, and industrial areas.

Polymer-modified bitumen was studied extensively in several studies carried out in the course of the PhD programme.

3.7. **Bituminous Emulsions**

Bituminous emulsion, also referred to as asphalt emulsion is a liquid binder obtained by dispersing bitumen in water using an emulsifying agent. Tiny bitumen droplets (dispersed phase) which are oily in nature are suspended in water (dispersant phase). These normally immiscible liquids are stabilized by the emulsifying agent which is often a surfactant. The stable, homogenous mixture that is produced can be applied as a binder in various asphalt applications [16].

The versatility of bituminous emulsions is one of their main advantages. They can be used as a binder in a variety of asphalt applications, such as cold mix asphalt production, tack coating, chip sealing, and road surfacing. Since they emit fewer emissions and odours than conventional hot mix asphalt, bituminous emulsions can also be used in environmentally sensitive areas. The ability to apply bituminous emulsions at lower temperatures than conventional hot mix asphalt is another advantage. As a result, asphalt pavements may be produced and applied with less energy and emissions, improving their sustainability and environmental friendliness [17].

Bituminous emulsions are incredibly durable and are also resistant to aging and weathering. They ensure that asphalt pavements continue to perform well and last for a long time by offering excellent adhesion to a variety of aggregates and surfaces.

In a study carried out during this PhD programme, a bio-surfactant obtained from animal fat was tested as an emulsifier to stabilize bituminous emulsions.

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Chapter 4

Experimental Techniques

4.1. Dynamic Shear Rheology

Rheology can be defined as the study of the flow and deformation of materials with special emphasis on flow. Movement and flow of a liquid are not the same thing since a liquid can be moving and not be flowing at the same time. For example, water being carried in a bucket is moving but is not flowing. In flow, elements of the liquid are deforming and adjacent points in the liquid are moving relatively to each other [1]. Dynamic Shear Rheology specifically evaluates how materials respond to shear forces that vary over time.

Fluids deform in an irreversible manner when subjected to shear stress; in other words, they flow. Solids on the other hand deform elastically when subjected to a small shearing force and revert to their original shape when the applied force is removed. Soft matter exhibits behavior that falls somewhere in between. The majority of soft matter systems are viscoelastic, which means they exhibit both elastic (solid-like) and viscous (liquid-like) behavior. Viscoelastic materials' flow behavior and mechanical reaction to deformation can be measured, and the results can be analyzed in terms of their small-scale dynamics. Since soft materials are structured on length scales between the atomic and bulk scales, the mechanical properties of soft materials depend on the length scale that measurements are probing [2].

The basic principle of dynamic shear rheology is that when a material is subjected to an oscillatory shear stress, it will exhibit a complex response that can be described by two primary parameters: the storage modulus (G') and the loss modulus (G"). The storage modulus represents the material's ability to store energy, while the loss modulus represents the material's ability to dissipate energy. During a dynamic shear rheology test, a sample of the material is placed between two parallel plates, and a sinusoidal oscillatory force is applied to one of the plates. The resulting shear stress and strain are measured, and the G' and G" values are calculated from the resulting force and displacement data. The G' and G" values can be used to calculate other important rheological parameters, such as the complex modulus (G*), which represents the overall resistance of the material to deformation, and the phase angle (δ), which represents the degree of viscous or elastic behavior exhibited by the material [3].

The principle of shear rheology is straightforward; the material of interest (in this case, bitumen) is subjected to shear in a controlled way and its mechanical response to this shear is measured. Usually, one either applies a known shear stress and measures the strain, or one applies a controlled shear strain and measures the resulting shear stress. Figure 4.1 shows a schematic illustration of a fluid layer undergoing simple shear.

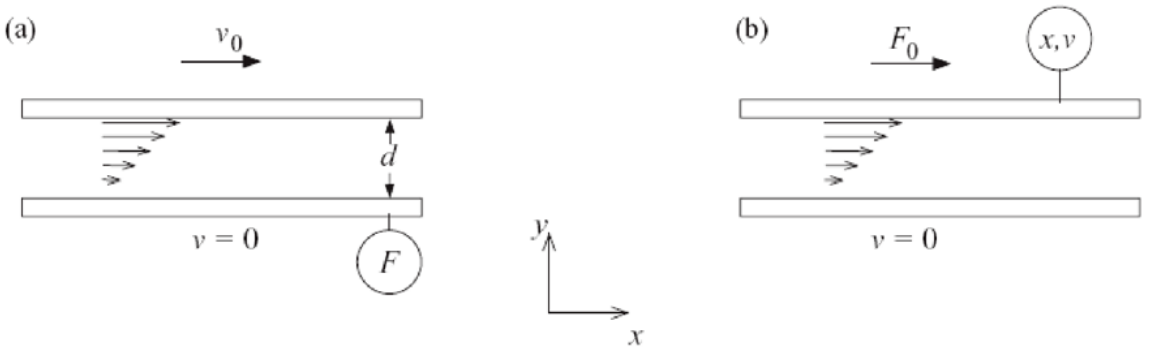

Figure 4.1: The distinction between strain and stress-controlled deformation

In figure 4.1(a), a fluid sample sandwiched between two plates is deformed in a strain-controlled measurement by moving the upper plate at a controlled velocity v0 while the bottom plate is kept stationary. A transducer, denoted by the circle, measures the force needed to hold the lower plate fixed. Figure 4.1(b) shows a stress-controlled measurement where the top plate is subjected to a controlled shear force, and the resulting velocity is recorded. In electronics, the distinction between voltage and current-controlled measurements is analogous to that between stress and strain-controlled measurements. A resistor has the same resistance whether it is measured using a voltage supply or a current supply, and in many instances, the same information can be obtained using either technique [4].

Typically, rheological measurements of bitumen samples are performed using a shear stress-controlled rheometer outfitted with a parallel plate geometry (gap 2 mm, / = 25 mm) and a Peltier system (0.1°C) for temperature control. For material characterization, dynamic tests are used, which are performed under linear material behavior conditions where measured material functions are the only function of the microstructure and are independent of the amplitude of applied load [5,6]. Temperature sweep tests are carried out at 1 Hz, increasing the temperature from 25° C to 120° C at 1 °C/min while applying the correct stress values to ensure linear viscoelastic conditions (previously established by stress sweep tests) at all tested temperatures. These tests are intended to investigate the material phase transition from a visco-elastic solid to a viscous liquid.

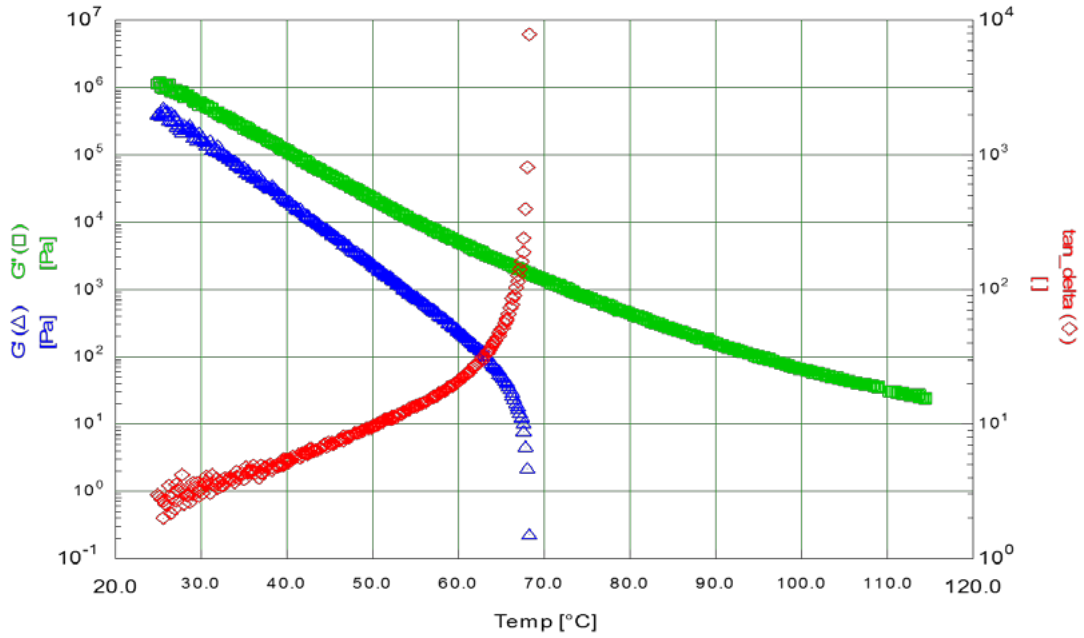

Figure 4.2: Temperature Sweep test of a bitumen sample.

4.2. Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a powerful analytical technique used in a variety of disciplines including chemistry, physics, biology, and medicine. It is based on the fundamental concept of the interaction between atomic nuclei and an external magnetic field. It detects the energy absorbed by changes in the nuclear spin state. NMR can be used to analyze a wide range of samples, including liquids, solids, and gases, and can provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules with no alteration of the sample's structure. It is particularly useful in the analysis of organic compounds because the chemical structure

and functional groups of these compounds can be determined via the NMR signals from the hydrogen and carbon nuclei.

The application of NMR has expanded beyond chemical and physical analysis to become a crucial tool in medicine, where it is used in magnetic resonance imaging (MRI) to visualize the body's internal organs. In MRI, the patient is placed in a strong magnetic field and exposed to radiofrequency pulses, allowing images of the body's internal structures to be generated based on the NMR signals emitted by hydrogen atoms in water molecules.

Generally, NMR is a versatile and powerful analytical technique that allows scientists to study the properties of materials at the atomic level. Its ability to provide detailed information about molecular structure and dynamics has led to significant advances in many areas of science and medicine.

4.2.1. **Basic principles of NMR**

The basic principle of NMR is that certain atomic nuclei, such as those of hydrogen and carbon, have a property called spin, which causes them to behave like tiny magnets. When these nuclei are placed in a strong magnetic field, they will align themselves either with or against the direction of the field, depending on their spin orientation. If a radiofrequency pulse is applied to the sample, the spins of the atomic nuclei will be perturbed, causing them to precess around the direction of the magnetic field. As they precess, they emit a detectable signal, which can be measured and analyzed to provide information about the chemical structure and properties of the sample.

The NMR signal is characterized by two parameters: the chemical shift and the spin-spin relaxation time. The chemical shift is related to the electron density surrounding the atomic nucleus and can be used to identify the type of atom that is emitting the signal. The spin-spin relaxation time is a measure of the rate at which the precessing nuclei lose their energy and return to their original orientation [7].

It is well known from elementary NMR theory [8] that a nucleus of spin I has 2I+1 energy levels, equally spaced with a separation.

$$\Delta E = \mu H_0 / I \qquad \mathbf{3.1}$$

where H_o is the applied magnetic field, and μ, the nuclear magnetic moment, is given by

$$\mu = \frac{\gamma \hbar I}{2\pi} \qquad \mathbf{3.2}$$

Here γ is the magnetogyric ratio, a constant for a given nucleus, and h is Planck's constant. From the usual Bohr relation, the frequency of radiation that induces a transition between adjacent levels is

$$\nu_0 = \frac{\Delta E}{h} = \gamma H_0 / 2\pi \qquad \mathbf{3.3}$$

At equilibrium, nuclei are distributed among the energy levels according to a Boltzmann distribution. Following any process that disrupts this distribution (e.g., moving the sample into or

out of the magnetic field, or absorption of rf energy), the nuclear spin system returns to equilibrium with its surroundings (the "lattice") by a first-order relaxation process characterized by a time T_1, the spin- lattice relaxation time. To account for processes that cause the nuclear spins to come to equilibrium with each other, a second time T_2, the spin-spin relaxation time, is defined so that

$$\nu_{1/2} \approx 1/T_2 \qquad \mathbf{3.4}$$

with $\nu_{1/2}$ being a spectrum line of full width at half maximum intensity. If the magnetic field is not perfectly homogeneous, nuclei in different parts of the sample experience slightly different values of the field, hence by equation 3.3 resonate at slightly different frequencies. This leads to a contribution to the line width due to inhomogeneity (ΔH_o) of

$$\nu_{\frac{1}{2}}(inhom) = \gamma \Delta H_0/2\pi \qquad \mathbf{3.5}$$

So we can define a time T_2^* in terms of the observed line width as

$$\nu_{\frac{1}{2}}(obsd) = 1/\pi T_2^* \qquad \mathbf{3.6}$$

Thus T_2^*includes contributions from both natural line width and magnetic field inhomogeneity :

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \left(\frac{\gamma \Delta H_0}{2}\right) \qquad \mathbf{3.7}$$

It is easily shown by classical mechanics that the torque exerted on a magnetic moment by a magnetic field inclined at any angle θ relative to the moment (Figure 4.3) causes the nuclear magnetic moment to precess about the direction of the field with a frequency given by the well-known Larmor equation

$$\nu_0 = -\gamma H_0/2\pi \qquad \mathbf{3.8}$$

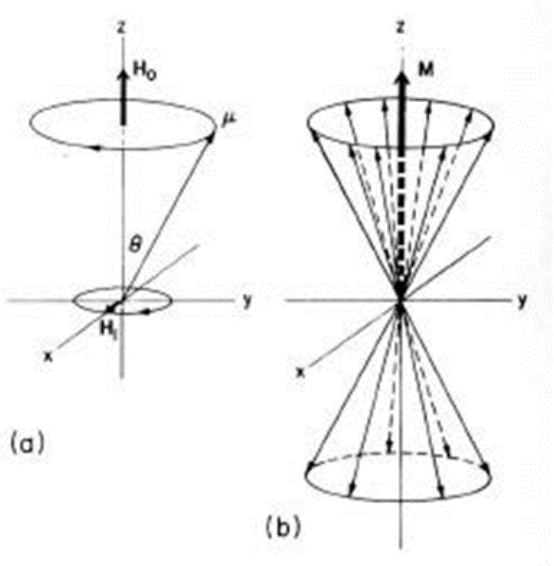

Figure 4.3 (**a**) Precession of a magnetic moment μ about a fixed magnetic field H_0. The radio frequency field H_1 rotates in the xy plane. (**b**) Precession of an ensemble of identical magnetic moments of nuclei with I = 1/2, the net macroscopic magnetization is oriented along H_0 (the z axis) and has the equilibrium value M_0.

4.3. Atomic Force Microscopy

Atomic force microscopy (AFM) is a powerful imaging technique used in materials science, biology, and nanotechnology to visualize the surface topography and mechanical properties of materials at the nanometer scale. It was invented in 1986 [9] and originated with the invention of the scanning tunneling microscope in 1982 by Binning and Rohrer [10,11]. Atomic force microscopy (AFM) is a type of scanning probe microscopy that allows for the imaging and characterization of surfaces at the nanoscale level. It works by scanning a sharp probe, usually made of silicon or diamond, over the surface of a sample and measuring the interactions between the probe and the sample.

In addition to imaging, AFM can also be used to measure the mechanical properties of materials, including their elasticity, adhesion, friction and stiffness. This is achieved by exerting a force to the sample using the probe, and measuring the cantilever's deflection as a result. This allows researchers to study the mechanical behavior of materials at the nanometer scale, which is crucial in the development of new materials and devices. AFM has revolutionized the field of nanotechnology, allowing researchers to study and manipulate materials at the atomic and molecular scale. Its ability to provide high-resolution images and measure mechanical properties at the nanometer scale has led to significant advances in many areas of science and technology, including materials science, biology, and electronics.

Overall, AFM is a powerful tool for studying the properties of materials at the nanoscale level. Its ability to provide high-resolution images and measure a variety of physical and mechanical properties has led to significant advances in many areas of science and technology.

4.3.1. Basic Concepts

The basic principle of AFM is based on the interaction between the probe and the sample. The probe is mounted on a flexible cantilever that is deflected by the forces acting on it as it scans over the sample surface. These forces include van der Waals forces, electrostatic forces, and chemical bonding forces, which depend on the sample's surface topography and composition. As the probe scans over the sample, it is moved up and down in response to these forces, and the deflection of the cantilever is measured using a laser or other optical technique. The resulting data is used to generate a three-dimensional image of the sample's surface topography, with sub-nanometer resolution.

Atomic force microscopy (AFM) belongs to a family of techniques dedicated to nanoscale surface characterization based in the concepts developed by Binning and Roher [9 – 11]for the scanning tunneling microscope (STM). Basically AFM entails the attainment of topographic images making probe scans over a surface, in a surface plane, x-y, while the distance between the surface and the probe, is being controlled [12,13]. The obtained topography image corresponds to the measured height values, z(x,y), for a given area, A, defined by a window scan size L. Each height value is associated to a pair of surface coordinates,(x,y), and the image may is described by a matrix with N lines and M columns which corresponds to the surface (x,y) points being the matrix elements the height z(x,y). The validity and accuracy of surface proprieties achieved via AFM are greatly influenced by both the measuring features as tip, cantilever, scan feature, and image data analysis procedure.

During the topography image acquisition with an atomic force microscope (AFM), the interaction between the tip and the surface is dependent on the distance between both. When the interatomic distance is large, the attractive force between the tip and the surface is weak. As the tip is approaching further the attraction increases until the atoms are so close together that the electron

clouds start to repel each other electrostatically. This signifies that the interaction force goes to zero at a distance of about few angstroms. Generally the topographies are obtained maintaining the interactions magnitude constant during the tip scanning, in both direct contact (contact) and intermittent contact (tapping) modes. In the contact mode, the tip wearing comes as a result of abrasive and adhesive contact with the surface which can lead to both tip contamination and surface damage. During the measurement in non contact mode deformations can also occur contributing for elastic wear out. Therefore, the interactions between tip and surfaces may cause image artifacts and even surface damage [14,15].

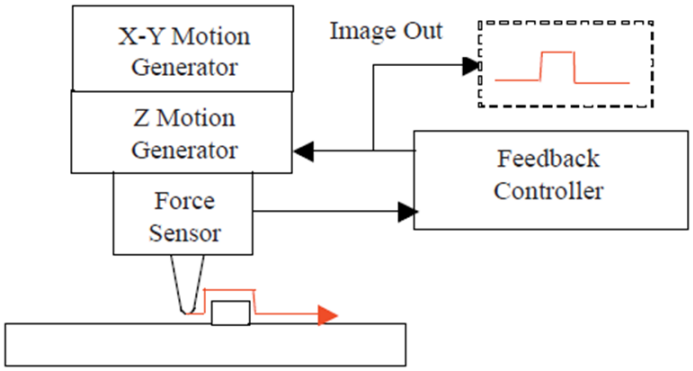

Figure 4.4: Representation of the underlying mechanism of the AFM technique

4.4. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique that is used to measure the heat flow associated with changes in the physical and chemical properties of materials as they are heated or cooled. The method is based on measuring the temperature difference that occurs as a sample and a reference material are put through a carefully controlled thermal program.

The fundamental principle behind DSC is that a small amount of reference material with a known heat capacity is placed in a separate reference pan, and the sample material is placed in the sample pan. After that, the pans are sealed and put inside of a furnace where the temperature is gradually increased or decreased over a specified range. As the temperature of the system changes, the heat flow associated with the physical and chemical changes in the sample material is measured by comparing the heat flow to the reference material. A differential thermocouple, which measures the temperature difference between the sample and the reference pans, is used to make this comparison [16].

DSC can be used to study a variety of physical and chemical changes in materials, such as melting, crystallization, phase transitions, chemical reactions and mesomorphic transition temperatures and the corresponding enthalpy and entropy changes. It is also used to characterize and quantify other effects that evidence changes in latent heat or heat capacity. A major advantage of this technique is its simplicity and ability to be applied over a diverse range of samples (solids, gels and even powder form) [17]. This analytical technique is an effective tool for characterizing the physical properties of resins, polymers, waxes, etc. It is a somewhat universal method that does not entail very sophisticated technical know-how due to its relative simplicity in comparison to several other techniques. In addition to this, the energy characteristics (heat capacity C P and its integral over temperature T—enthalpy H), which are measured via calorimetry, have a clear relatable physical meaning. Via DSC, scientists and researchers learn about the thermal and kinetic properties of

materials, such as melting point, enthalpy, heat capacity, and reaction rate, by examining the heat flow associated with these changes [18,19].

DSC is a versatile and widely used analytical technique, and it has applications in many fields, including materials science, chemistry, and engineering. It is particularly useful for studying the thermal properties of polymers and other complex materials, as well as for characterizing the thermal stability and reactivity of pharmaceuticals and other chemicals. In general, differential scanning calorimetry is a useful tool for learning about the thermal and kinetic characteristics of materials. It is an invaluable tool for research and development in many fields because of its capacity to measure the heat flow associated with changes in material properties, which provides crucial information about the behavior and properties of materials.

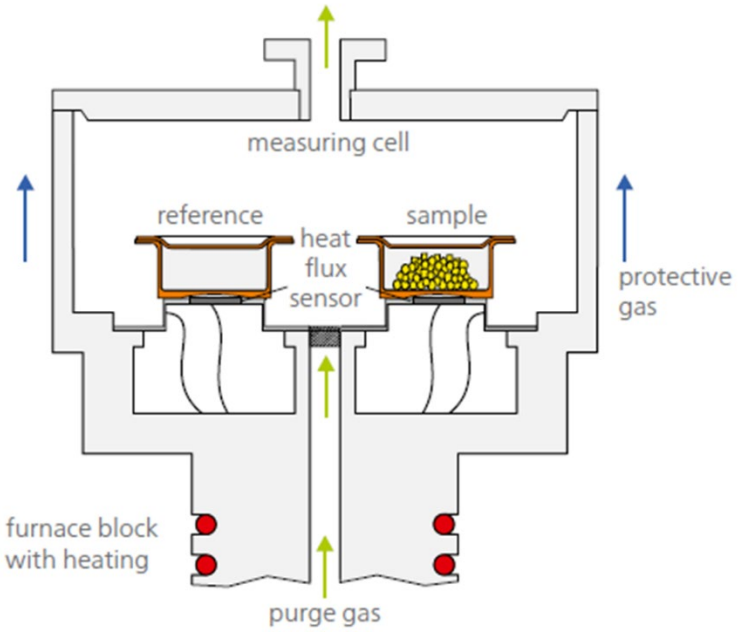

Figure 4.5: Block diagram of DSC mechanism

4.5. Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a powerful high resolution imaging technique used to study the surface morphology and composition of materials. SEM employs a focused beam of electrons to scan the surface of a sample, generating a high-resolution image that provides information about its topography and composition. Even though SEM only displays surface images of a material and provides no internal information, it is still regarded as a powerful tool that can be used in characterizing the crystallographic, magnetic, and electrical characteristics of the sample, as well as in determining whether the particle's morphology has changed after modifying the surface of the sample with other molecules [20,21].

High-energy electrons are shot at the sample in a SEM, and the emitted electrons and X-rays are then analyzed. These emitted electrons and X-rays provide details about a material's topography, morphology, composition, grain orientation, crystallographic information, etc. Morphology describes the size and shape of an object, whereas topography describes the surface characteristics, or "how it looks," such as its texture, smoothness, or roughness. Similar to how crystallography refers to the arrangement of atoms within a material, composition refers to the elements and compounds that make

up a material. The best tool for producing a finely detailed visual image of a particle with a spatial resolution of 1nm is the scanning electron microscope (SEM) [21 – 23].

SEM is widely used in many fields of science and engineering, including materials science, biology, and geology. In materials science, SEM is used to study the microstructure and morphology of materials, including metals, ceramics, and polymers. In biology, SEM is used to study the structure of cells and tissues, as well as the surfaces of organisms such as bacteria and viruses. In geology, SEM is used to study the surface features of rocks and minerals. In general, scanning electron microscopy is a powerful tool for studying the structure and composition of materials. Its ability to provide high-resolution images at the nanoscale level and analyze the composition of materials makes it an invaluable technique for researchers and scientists in many fields.

4.5.1. **Basic Principle**

The basic principle of SEM is that a beam of electrons is focused onto the surface of a sample, and the electrons interact with the atoms in the sample, generating a variety of signals. These signals are then detected and used to create an image of the sample surface. The basic requirement for SEM to operate under a vacuum is to avoid interactions of electrons with gas molecules in order to obtain high resolution. The SEM instrument is based on the principle that the primary electrons released from the source provide energy to the atomic electrons of the specimen, which can then release as the secondary electrons (SEs). An image can be formed by collecting these secondary electrons from each point of the specimen. In addition, heating or applying high energy in the range of 1–40 keV accelerates the primary electrons generated and emitted from the electron gun [20,22]. The focused and constrained monochromatic beam of these emitted electrons has a diameter of 100 nm or less.

Magnetic field lenses and metal slits inside a vacuumed column focus and constrain these emitted electrons to a monochromatic beam (to a diameter of 100 nm or less). Scanning coils scan the confined primary electrons in a raster pattern across the sample surface [20,24]. The primary electron beam will interact in a variety of ways with the sample's near-surface region up to a certain depth once it contacts the sample surface [22]. Significant amounts of kinetic energy are being lost by the impinging electrons inside the specimens as a result of their interactions with the specimens, which produce a variety of signals. In the sample, it scattered both elastically and inelastically. The atomic number, atom concentration, and incoming electron energy (accelerating voltage) of the analysed sample all affect the scattering of electrons and interaction volume. The interaction volume and scattering process will increase with an increase in electron energy (accelerating voltage), and they will decrease with an increase in the atomic number and concentration of the element. Similar to this, the angle of incidence of the electron beam is crucial to the process of scattering and interaction volume. Therefore, the main determinants of the volume inside the specimen in which interactions take place are the electron beam's angle of incidence, the material's atomic number, and the accelerating voltage. Higher atomic number materials absorb or block more electrons, resulting in smaller interaction volumes. Similar to this, applying high voltages will produce electrons with high energy, which will allow them to travel further inside the sample and produce a larger interaction volume. Similar to this, the interaction volume will decrease with increasing angle of incidence (further from normal).

Due to the Coulomb (electric charge) field interaction of incoming electrons with the specimen nucleus and electrons, it will consequently emit a variety of signals, including secondary electrons (SEs), backscattered electrons (BSEs), photons (X-rays used for elemental analysis), and visible light (cathodoluminescence - CL) [24,25]. Electron collectors (detectors) collect the

signals, which the computer then manipulates to create the needed image. Different details about the sample could be seen depending on the detected signal (secondary electrons, backscattered electrons, or X-rays) [20]. The backscattered and secondary electrons are the two electrons that are frequently used to create sample images. However, backscattered electrons are used to illustrate the contrasts in the composition of multiphase samples (i.e. for quick phase judgment), whereas secondary electrons are thought to be the most significant electrons for indicating sample morphology and topography. Similarly, incident electrons' rigid collisions with electrons present in the orbitals of sample atoms produce X-rays. The electrons are then excited to higher energy levels, and when they return to lower energy levels, depending on the differences in the energies of different elements, they emit X-rays with a specific wavelength. After an electron beam impinged on each element, the result was the generation of a distinctive X-ray. As the generation of X-rays does not result in any specimen volume loss, SEM is non-destructive; as a result, the same material can be repeatedly examined (Fig. 4.4).

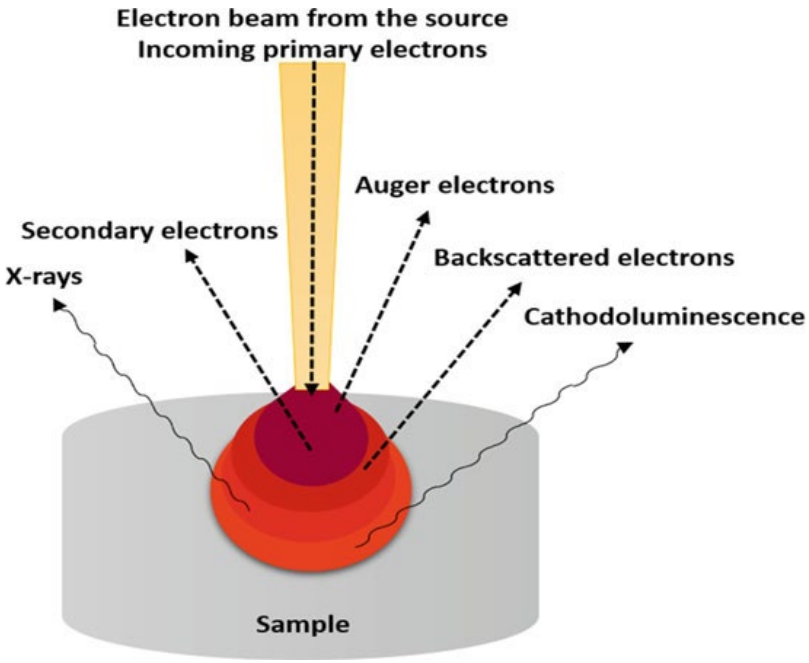

Figure 4.6: The interaction of electron beam with specimen and the signal emitted from the sample

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Chapter 5

RESULTS – Bitumen Recycling Agents

5.1. Recycling of bitumen in asphalt via the use of rejuvenators

Bitumen recycling in asphalt is a process that involves the use of rejuvenators to restore the aged bitumen's original properties thereby bringing the bitumen to a state similar to its first-use, virgin state. This rejuvenated bitumen can then be used in combination with virgin bitumen for new paving operations. Bitumen is an important component of asphalt mixes and it plays a crucial role in the durability and performance of asphalt pavement. Over time, bitumen can become oxidized and lose its original properties due to exposure to sunlight, air, water and other atmospheric agents.

Rejuvenators are substances that can restore the original properties of aged bitumen by reducing its viscosity, increasing its ductility but most importantly chemically interacting with the components of the aged bitumen, supplementing and replenishing the fractions in which it is deficient. The use of rejuvenators can help reduce the amount of virgin bitumen needed in asphalt production and can also reduce the cost of asphalt production. The use of rejuvenators can improve asphalt pavement quality, including increased durability, improved resistance to cracking and rutting, and enhanced flexibility. Additionally, the use of rejuvenators can help reduce the environmental impact of asphalt production by reducing the amount of waste generated and the amount of energy needed to produce new bitumen.

There are different types of rejuvenators, including petroleum-based and bio-based products. Petroleum-based rejuvenators are generally made from crude oil, while bio-based rejuvenators are made from renewable resources such as plant oils. Both types of rejuvenators can be effective in restoring the properties of aged bitumen, and the choice of rejuvenator depends on the specificities of its application and environmental considerations. It is worthy to note that the rejuvenators used in the studies carried out in the ambit of this PhD project are bio-based. The use of rejuvenators in asphalt production can bring about numerous benefits, including reduced costs, increased durability and environmental sustainability. By using rejuvenators, asphalt producers can recycle aged bitumen and reduce their reliance on virgin materials, leading to a more sustainable and efficient asphalt production process.

5.2. Results Part 1

"Reclaimed Asphalt Recycling Agents: looking into the blueprint of their mechanisms of action"

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Introduction

1.1. Reusing and/or recycling and sustainability

Perhaps there is no other technique than reusing and/or recycling Reclaimed Asphalt Pavement (RAP) that is more practical for reducing the carbon equivalent footprint in the asphalt pavement industry. In fact, it has been considered one of the most applicable strategies respecting the principles of sustainability and climate mitigations concerns. According to existing literature, even the replacement of just 30% of new aggregates with RAP allows for a 14% reduction in energy consumption, and 20% in carbon emissions [1]. Many similar studies have shown the same benefits which are dependent on several factors including the plant type and bituminous binder used. Nonetheless, the benefits of reusing and/or recycling RA are not just limited to the emissions. Additionally, on one hand, it significantly reduces construction costs and on the other hand, it reduces the need for non-renewable resources. In other words, an ideal circular economy could be achieved via asphalt recycling.

1.2. Rejuvenating agents vs. flux oils

In spite of the 40 years of history of asphalt pavement recycling, the main concern in the properties of using RAP in Hot Mix Asphalt (HMA) is the characteristics of its binder, which is highly dependent on the choice of a proper recycling agent [2]. Within existing literature, when more than 30% of RAP is incorporated in new asphalt concrete production, the use of a recycling agent is highly recommended to ensure the compatibility and the required performance properties [3]. For this purpose, different recycling agents have been introduced to the asphalt pavement industry aimed at promoting the practice. However, what should be taken into the account is that recycling agents have different capabilities and regeneration mechanisms to address the deficiencies of aged binders [2]. While some of these products are just capable of reducing the viscosity of aged binder, some others can actually recover the physical, mechanical features and restore some of its chemical properties to different extents, and are the so-called real rejuvenators [4-6]. The European Asphalt Pavement Association, EAPA [7] defines the terms as follows:

"*Asphalt Re-use / Recycling agent: product used in the manufacturing of asphalt mixes containing reclaimed asphalt to act on the aged bituminous binder and help to meet the requirements/specifications of binder and asphalt mixes."* and *"The term "Rejuvenator" has been often used to refer to some of these products. ...for example, while some products affect only rheological properties (e.g., viscosity, penetration or softening point, others can also act on the chemical composition and properties of the aged binder"*

Other studies such as those conducted by Bajaj et. al [8] and Belgian Research Road Centre, BRRC [9] have provided more details on asphalt re-use/recycling agents and their mechanisms of action. According to the latter, the mechanism of action of these additives could be one or more of the followings:

A) Plasticiser effect/lower viscosity. Agents used to replenish aged bitumen are physically in the form of an oil and their addition always leads to a lower viscosity of the aged bitumen. The viscosity of the recycling agent and the new binder must be such that the whole of the regenerating product + the old bitumen + the new bitumen eventually reaches the proper viscosity in the mix. This effect can be considered as a softening of the aged bitumen. At the same time, a lubricating effect or reduction of friction (lubrication) can also occur, because via its wetting power (wettability), the addition of a liquid product improves the workability of the aggregates in the asphalt.
B) Compensation effect in the chemical composition (maltene/asphaltene ratio). Regenerants from petrochemicals are rich in aromatics and thus restore the balance of the chemical composition (SARA fractions) of an aged bituminous binder by enriching the fraction of bitumen's main constituents and restoring the asphaltene/maltene balance.
C) Dispersing agent effect. Some asphalt re-use/recycling agents act as dispersants and are therefore able to break the interactions/associations between the asphaltenes that are present in large quantities (following oxidation). Their action can in this case, be considered as a "*remobilization*" of an aged binder.

The aforementioned mechanisms of action are differentiated by using the terms softening agents for plasticizers (A above) and asphalt re-use/recycling agents for additives which also affect the chemical composition (B above) and/or the structure of the bituminous matrix (C above).

1.3. State-of-the- knowledge

As discussed above, recycling agents could work in very diverse ways that may determine their effectiveness in the long-term performance of recycled asphalt mixtures. In fact, bearing in mind the importance of multiple recyclability of asphalt mixtures, differentiating these additives becomes more crucial. However, the proper methods to be applied is still a subject under question. In order to fill the current knowledge gaps, several research works have introduced different techniques and procedures that could be used for categorizing the recycling agents.

Currently, in conventional recycling practice, the most common mix design and optimizing procedure involves testing the physical properties either by traditional penetration, softening point, and viscosity or by Dynamic Shear Rheological (DSR) analysis. Applying these testing methods, to date, several different blending charts and design flowcharts have been developed for optimizing the dosage of the recycling agents [10]. Nevertheless, their efficiency in an accurate mix design and the resulting recycled asphalt durability is under scepticism. Limited temperature range of control and multi-lateral mechanism of recycling are some of the missing points of such blending charts found within existing literature [11]. Consequently, researchers have studied and proposed complementary testing methods to control the recycling action from different aspects. From these methods perhaps, Fourier-transform infrared spectroscopy (FTIR), Atomic Force Microscopy (AFM), Differential Scanning Calorimetry (DSC), SARA fraction analysis are the most applied ones. These methods have been discussed in many research works and regardless of some insignificant discrepancies, they have been found to be useful techniques for investigating the mechanism of recycling from chemical, thermogravimetric, and microscopic aspects. The following sections summarize some of the main findings of the many research works published in this context.

Microscopic analysis including light microscopy and AFM has been used in several research works. Among these two methods, the latter has been more frequently applied for investigating the effects of additives on the chemical properties [12] and there is a consensus on the findings. Based on these research works, regardless of what the recognizable elements within AFM images may correspond to which chemical constituent, different recycling agents impact aged bitumen's morphology in different modes. This could be divided into two general modes; In the first, the recycling agent breaks the agglomerations of the Catana phase (bee structures) and reduces the intensity of the para and peri phase. In this state, the morphology resembles the virgin (non-aged) state. In the second group, a new morphology is shaped. It neither resembles the origin state nor the aged state. In some references [13-15], this mechanism of action has been used for categorizing the rejuvenators from those of flux oils (softeners). From another point of view, AFM has also been used to investigate the level of stiffness and roughness of the Catana phase of the bituminous samples. Within existing literature, aging increases the stiffness of these elements, and the recycling agents may or may not decrease the level of stiffness.

In addition to AFM, light microscopy has been also used in few research works but not independently. Technically, the light microscope and its objective lenses are not capable of high-resolution imaging required for the microscopic study of a material of bitumen's nature. The authors of this paper have applied the technique investigating the melting point of the extracted asphaltenes of aged and recycled bituminous samples [16]. The results showed that the melting point of the asphaltenes extracted from some of the bituminous samples containing recycling agents is higher than others and resembles the melting point of the asphaltene extracted from the reference aged bitumen. This could be considered as evidence of how diverse recycling agents could act differently.

Thermoanalytical techniques such as Differential Scanning Calorimetry (DSC) have also been often used to study the action of asphalt recycling agents on the glass transition (T_g). The temperature at which an amorphous polymer material turns into a viscous liquid or rubbery form when heated is known as the glass transition temperature (T_g). The method has been applied to investigate both bituminous binders and extracted asphaltenes in different studies. In literature, it has been shown that the T_g of some of the recycled blends containing recycling agent is much lower than that of the corresponding aged binders without recycled materials [17-18]. Considering the latter, DSC has been found to be an efficient technique for investigating the recycling action mechanism from a thermoanalytical point of view [15]. In view of this, the asphaltene samples containing a rejuvenator showed similar T_g to their reference bitumen and those containing flux oils showed higher.

1.4. Objectives

Despite the wide range of research works and studies which have investigated different types of recycling agents, just a few of them have concentrated on the microscopic and chemical impact of recycling agents on the aged bituminous binders. Accordingly, the authors aim at investigating such important impacts using microscopic and chemical techniques, highlighting the intricacies involved. It is worth mentioning that the objective of this study is not comparing the level of performance of different re-use/recycling agents, but the mechanism of their action on an aged bituminous binder.

2. Materials

For the purpose of this study, two different paving grade bitumens and two recycling agents were used. Table 1 summarizes some of the given properties of the tested bitumens both provided from

Italian refineries. A preliminary study and measurement of some of the bitumen's main properties was carried out and is presented in the next sections.

Table 1. Some of the given characteristics of the base virgin 70/100 bitumen.

Characteristic	Unit	Bitumen		Method
		70/100	50/70	
Penetration @25°C	dmm	70 – 100	50 – 70	EN 1426:2015
Softening point	°C	43 – 51	46 – 54	EN 1427:2015
Dynamic viscosity @60°C	Pa.s	≥ 90	≥ 145	EN 13702:2018
Dynamic viscosity @135°C	Pa.s	≥ 0.23	≥ 0.50	EN 13702:2018
Flash point	°C	Min 250	Min 230	EN ISO 2592:2017
Fraass Breaking point	°C	Max -10	Max -9	EN 12593:2015

As for the recycling agents, considering the preceding test results of the first phase of this research, where 7 markedly available different recycling agents were studied [5 & 13], two recycling agents of varying nature were selected and tested. Table 2 summarizes some of the properties of the recycling agents. Both additives were investigated on an anonymous basis in this study. The additives were added in a proportion of 6% (on weight of the aged bituminous sample). It is worth mentioning that the choice of the dosage was based on the findings of the aforementioned phase one of this research, where three different dosages were studied and the optimum one was selected.

Table 2. Some of the given properties of the recycling agents.

Characteristic	Unit	Recycling agent 1 (R1)	Recycling agent 2 (R2)
Aspect	-	Liquid	Liquid
Colour	-	Yellow	Yellow
Viscosity	cP	25 – 50	20 – 30
Pour point	°C	≤-5	≤0
Chemical nature	-	Mix of amino derivatives	Blend of vegetable esters

3. Methods

3.1. Testing materials and aging

In view of the objectives of this study, as the first step, after characterization of the two virgin bitumens (non-aged state), the aged bitumen samples were produced to be used and tested in the next steps. The aging of the samples was also repeated two more times after the incorporation of the recycling agents in one-time aged bitumen thus simulating multiple recycling actions. As for the aging of the samples in the first round, both RTFO short term-aging and PAV long-term aging were carried out based on European standards EN 12607-1 and EN 14769, respectively. The subsequent aging cycles were carried out using solely PAV. Table 3 summarizes the testing steps and the applied IDs of the samples in this study.

Table 3. Testing steps and the applied IDs

Testing step	Testing bitumen	
1	70/100	50/70
2	RTFO+PAV 70/100	RTFO+PAV 50/70
3	(RTFO+PAV 70/100) + R*i*	(RTFO+PAV 50/70) + R*i*
4	(RTFO+PAV 70/100 + R*i*) + PAV	(RTFO+PAV 50/70 + R*i*) + PAV
5	(RTFO+PAV 70/100 + R*i* + PAV) + R*i*	(RTFO+PAV 50/70 + R*i* + PAV) + R*i*
6	(RTFO+PAV 70/100 + R*i* + PAV + R*i*) + PAV	(RTFO+PAV 50/70 + R*i* + PAV + R*i*) + PAV
Note: R*i* refers to Recycling agent 1 and 2		

3.2. Sample Preparation

Both recycling agents are liquid in nature. Each of the recycling agents was individually mixed with hot bitumen (about 150 °C) in a ratio of 6% wt/wt of the binder. This was done by heating up 100g of bitumen to 150 °C and then adding 6g of the recycling agent (R*i*) to the sample while the whole sample was being continuously stirred with a high-speed shear mixer set between 500-700 rpm. These conditions were maintained for 20 minutes after which the resulting modified bitumen was sampled in drops on greaseproof paper and used for further analysis.

3.3. Testing methods

The testing plan of this study consisted of conventional bitumen testing i.e., softening point and penetration measurement, rheological analysis by means of Dynamic Shear Rheology (DSR), Atomic Force Microscopy (AFM) to study the morphological impacts, deasphaltenization (asphaltene extraction), melting point measurements, and Thermoanalytical testing by means of Differential Scanning Calorimetry (DSC). Where applicable, European standards were considered during the tests and analyses. More details are provided within each specific section.

3.3.1. Dynamic Shear Rheology

Rheological Analysis was carried out on all samples using a stress-controlled Dynamic Stress Rheometer (SR-5000, Rheometric Scientific, Piscataway, NJ, USA) equipped with a parallel plate geometry having a diameter of 25mm, using a gap of 2mm between the probing tool and the parallel Peltier plate. The frequency was set at 1 Hz and the stress at 100 Pa. A Temperature Sweep (TS) which is practically a thermal ramp commonly known as time cure test was carried out in a temperature range of 25 °C to 120 °C with a heating rate of 1 °C per minute thus giving it the name "time cure". This test was performed to determine the temperature at which the bitumen loses it elastic modulus and changes from its initial semi-solid state to a liquid state. The transition temperature, which is equivalent to the tan delta (loss modulus) of the sample is the point where bitumen loses its elasticity and changes from a viscoelastic solid to a viscous liquid. All rheometric measurements were carried out in the viscoelastic regime. More details on this technique are described in a previous study [12].

3.3.2. Atomic Force Microscopy

Atomic Force Microscopy (AFM) analysis was performed using a Bruker Nanoscope VIII microscope model. For this morphological investigation, the tapping mode of the microscope was used and its cantilever oscillations were regulated close to its resonance frequency (150 Hz). Cantilevers with elastic constants of 5 N/m and 42 N/m were used. The cantilever tip touches the sample periodically due to the up-down oscillation of the cantilever. As the tip approaches the sample surface, a vibration of the cantilever occurs. The tested sample's morphological features determine the magnitude of this vibration as a result of the fact that the phase angle shift of the cantilever vibration signifies energy dissipation in the tip-sample ensemble. Phase and topography images were taken contemporarily. The acquired images were developed and elaborated using the instrument-branded software.

3.3.3. Differential Scanning Calorimetry

Differential Scanning Calorimetric measurements were carried out on the asphaltenes, which were extracted from the bitumen samples used in this study. The method of asphaltene extraction known as deasphaltenization is described in [19]. The calorimetric measurements were performed using a SETARAM 131 calorimeter and all tests were carried out under constant nitrogen flow. The instrument was calibrated using a sample of Indium of known weight and enthalpy values. For the asphaltene samples used in this study, 20 – 30 mg of each sample was weighed into SETARAM

aluminium crucibles. The crucibles were capped and sealed using a mechanical press. The following test procedure was carried out on each asphaltene sample:

- Isotherm at 25 °C for 20 mins;
- Thermal ramp from 25 °C to 250 °C at 20 °C/min;
- Cooling cycle from 250 °C to 25 °C at 20 °C/min;
- Isotherm at 25 °C for 20 mins;
- Thermal ramp from 25 °C to 250 °C at 20 °C/min

It is important to note that the first thermal ramp and cooling cycle were carried out in order to ensure a uniform thermal state of the various samples. The first thermal ramp showed various endothermal and exothermal peaks according to the initial state of each sample which is difficult to control via the precipitation process used to extract the asphaltenes from the bitumen. The first cooling cycle at a constant cooling rate of 20 °C per minute was done to ensure that all samples were set under identical starting conditions. The first ramp and cooling cycle ensured that the calorimetric profile obtained from the second thermal ramp displayed only glass temperature (T_g) transitions which correlate to the nature of the samples and are easily comparable from one sample to another. As a result of this methodological peculiarity, only the calorimetric curves obtained from the second thermal ramp are shown and analysed in this study.

3.3.4. Light Microscopy of Asphaltenes

The asphaltene samples were examined using a Prior Scientific Instruments MP3500K microscope coupled with a Eurotherm 246 thermoregulator which regulated the temperature of a heating panel placed on the stage of the microscope. The microscope was also equipped with a Canon EOS 4000D camera to capture real time photos of images observed under the microscope. This setup made it possible to microscopically observe in real time the behaviour of the asphaltenes with a gradual increase in temperature and then determine the melting point of the asphaltene samples.

The asphaltene samples were placed in a double microscope glass slide (sandwich model) and were observed under the microscope. A manual temperature ramp was carried out with an initial temperature of 130 °C with a periodic temperature increase rate of 5 °C. After each 5 °C increase, the asphaltenes were left to stay for 1 – 2 minutes to bring about uniformity and homogenous heating throughout the whole sample for each sample before the photos were taken.

4. Results and analysis

4.1. Mechanical properties

4.1.1. Conventional physical tests

At the first stage of this study, the changed physical/rheological properties of the aged bitumen was assessed by means of conventional bitumen testing methods. According to the results summarized in the table 4, as expected, every cycle of aging increased the stiffness of the bitumen and each recycling action recovered somehow the rheological properties. Based on the results, it can also be inferred that all of the tested recycling agents were capable of recovering the fundamental physical properties of the aged bitumen and no significant difference was recorded between the obtained results. In other words, at this stage, both recycling agents could be classified as fluxing (softening) agents.

Table 4. Physical properties of all samples

Sample		Penetration (dmm)	Softening point (°C)	Dynamic viscosity (Pa.s)	
No.	**ID**	**25°C**	**-**	**100°C**	**135°C**
1	70/100	76	44.8	11.4	1.2
2	RTFO+PAV 70/100	51	57.5	38.8	2.6
3	(RTFO+PAV 70/100) × 2nd PAV	38	66.5	68.5	4.0
4	(RTFO+PAV 70/100) × 3rd PAV	28	75.8	141.6	5.7
5	(RTFO+PAV 70/100) + R1	74	46.0	7.1	0.9
6	(RTFO+PAV 70/100) + R2	75	44.2	6.4	0.8
7	(RTFO+PAV 70/100 + R1) + PAV	70	52.8	12.5	1.6
8	(RTFO+PAV 70/100 + R2) + PAV	74	44.6	11.8	1.3
9	(RTFO+PAV 70/100 + R1 + PAV) + R1	72	43.3	9.8	1.1
10	(RTFO+PAV 70/100 + R2 + PAV) + R2	80	41.8	8.0	0.8
11	(RTFO+PAV 70/100 + R1 + PAV + R1) + PAV	78	41.4	7.3	0.8
12	(RTFO+PAV 70/100 + R2 + PAV + R2) + PAV	68	52.6	11.5	1.1
Sample		**Penetration (dmm)**	**Softening point (°C)**	**Dynamic viscosity (Pa.s)**	
No.	**ID**	**25°C**	**-**	**100°C**	**135°C**
1	50/70	64	46.8	24.5	2.6
2	RTFO+PAV 50/70	46	62.8	50.6	3.4
3	(RTFO+PAV 50/70) × 2nd PAV	34	72.2	100.4	6.1
4	(RTFO+PAV 50/70) × 3rd PAV	26	80.4	217.1	8.8
5	(RTFO+PAV 50/70) + R1	68	47.2	23.4	3.0
6	(RTFO+PAV 50/70) + R2	70	46.4	22.9	2.9
7	(RTFO+PAV 50/70+ R1) + PAV	62	56.8	30.6	3.3
8	(RTFO+PAV 50/70+ R2) + PAV	60	56.6	30.7	3.5
9	(RTFO+PAV 50/70+ R1 + PAV) + R1	61	57.2	23.3	2.4
10	(RTFO+PAV 50/70+ R2 + PAV) + R2	68	55.4	21.8	2.2
11	(RTFO+PAV 50/70+ R1 + PAV + R1) + PAV	52	59.4	25.5	2.6
12	(RTFO+PAV 50/70+ R2 + PAV + R2) + PAV	58	58.2	23.2	2.1

4.1.2. DSR analysis

Bitumen is a viscoelastic substance having both a viscous and elastic modulus and in light of this, the transition temperature is the point at which bitumen loses its elastic modulus thereby transitioning into a liquid state. This transition temperature is proportional to the loss tangent (tan delta). Tan delta is the relationship between the viscous modulus (G") and the elastic modulus (G') i.e., G"/G'. The tan delta profile of all samples is shown in Figure 1. Bitumen upon aging becomes stiffer and more rigid thereby increasing its transition temperature. During such temperature changes, the binder exhibits behaviour ranging from a glassy material (at lower temperature) to a viscoelastic/non-Newtonian fluid (at higher temperature). The range of temperature change which is of interest in bitumen rheology is the transition between viscoelastic solid to viscoelastic fluid [20]. It can be seen that the tan delta of neat bitumen increases with progressive aging steps i.e., with each cycle of aging, the transition temperature keeps increasing thus signifying an increase in stiffness of the bitumen samples upon aging.

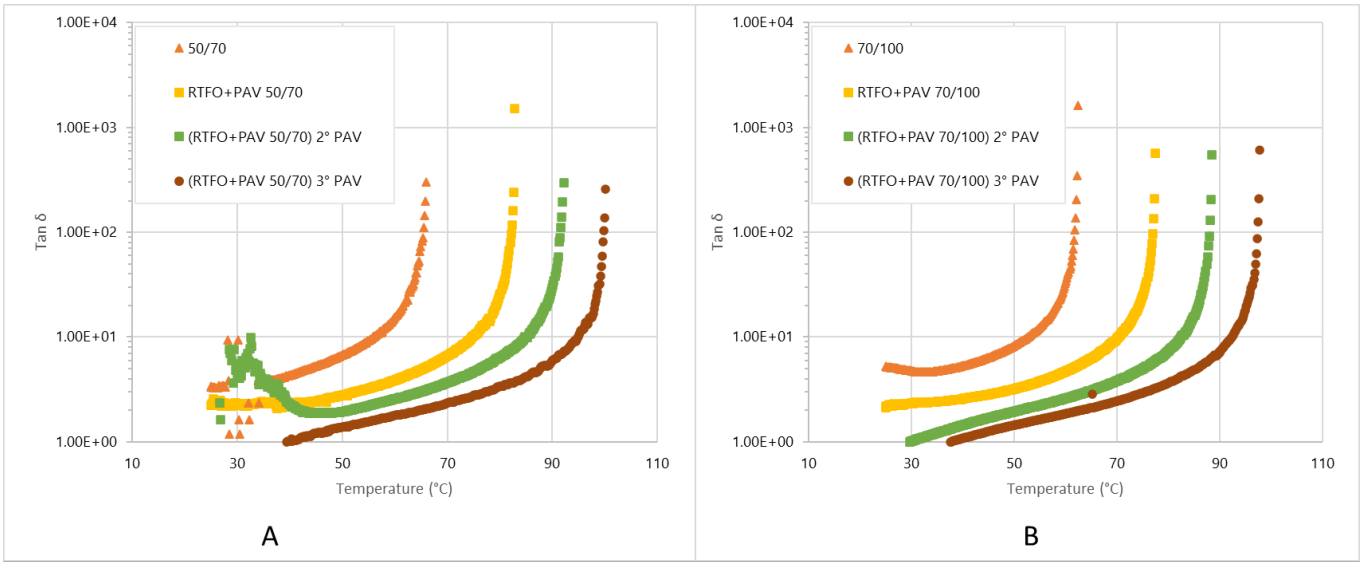

Figure 1: Time Cure Test – Semi log plot of Temperature Sweep tests for neat, aged and re-aged (a) 50/70 (b) 70/100 bitumen

For the bitumen having a penetration grade of 50/70, when the aged bitumen was modified with recycling agent R1, its transition temperature decreased to a value very similar to that of neat unaged bitumen as can be seen in Fig 2. Upon aging of this R1-modified sample, the transition temperature increased again but was still relatively lower compared to the aged sample which doesn't contain any recycling agent. This could mean that the R1 recycling agent in the modified sample reduced the susceptibility of the bitumen sample to oxidative aging. The sample which was aged after being modified was modified a second time with R1 recycling agent and its transition temperature returned once again to a value very similar to that of neat unaged bitumen. This newly modified sample was once again aged and it was observed that its transition temperature increased again but was relatively lower than any of the previously aged bitumen samples. This is in line with the trend observed after the first cycle of aging and recycling.

The same results were obtained after the rheological measurements carried out on the 70/100 bitumen except for the fact that the sample obtained after the final aging cycle and two cycles of aging and modification had its transition temperature very similar to that of the starting bitumen as can be seen in Fig 2b. This similarity in the transition temperatures of the starting bitumen and the three-

time aged bitumen could be as a result of the fact that in the three-time aged bitumen, two doses of R1 recycling agent are present in the sample thus making the bitumen resistant to oxidative aging.

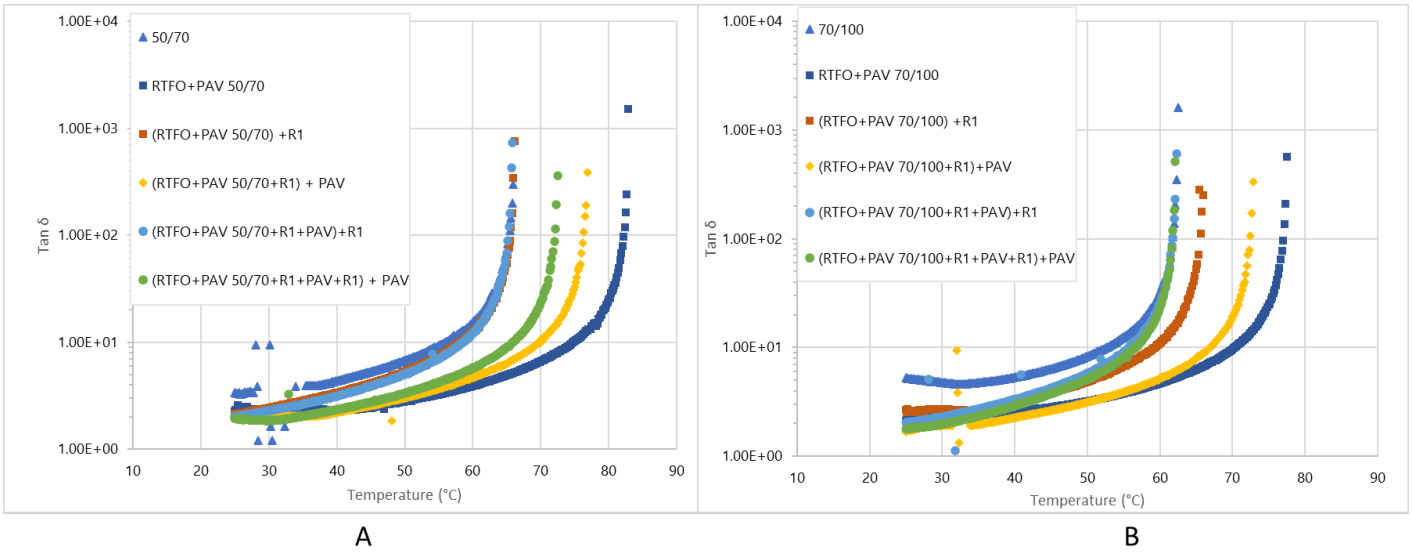

Figure 2: Time Cure Test – Semi log plot of Temperature Sweep tests for neat, aged, R1-modified and re-aged samples for (a) 50/70 (b) 70/100 bitumen

Logically, softer bitumen becomes less stiff after aging and so the higher penetration grade of the 70/100 bitumen could also contribute to this aging-resistant phenomenon. This could be due to its relative softness compared to the 50/70 bitumen and so after being doubly modified, it becomes so soft that its mechanical properties become similar to that of neat unaged bitumen. In general, R1 recycling agent proves to be very effective in both types of bitumen from a rheological point of view.

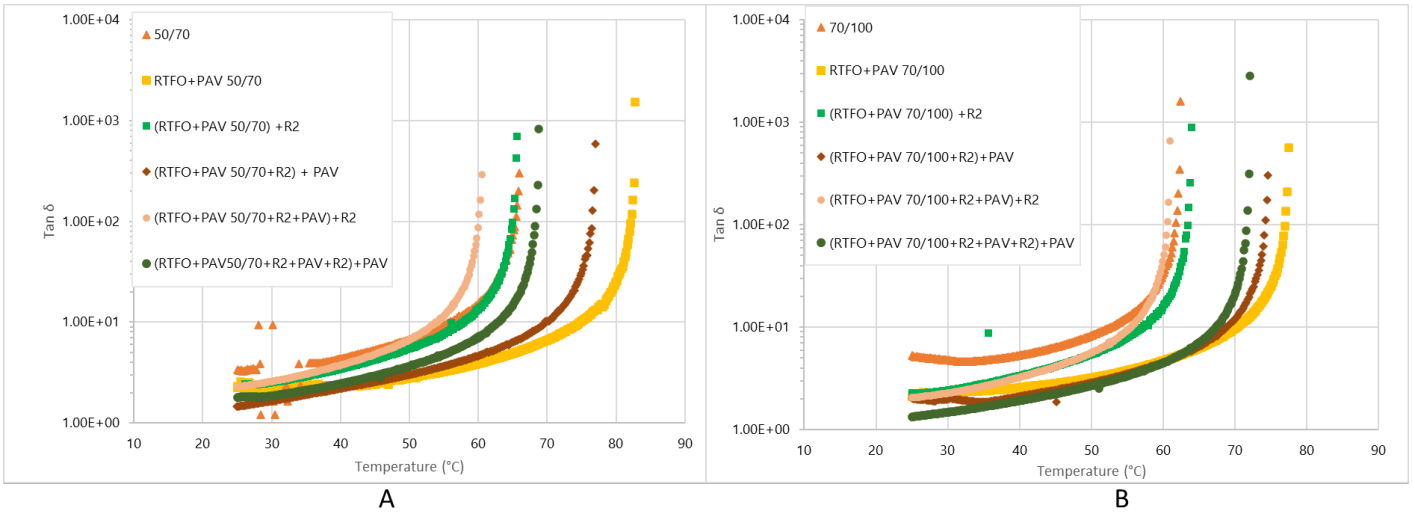

Figure 3: Time Cure Test – Semi log plot of Temperature Sweep tests for neat, aged, R2-modified and re-aged samples for (a) 50/70 (b) 70/100 bitumen

As shown in Figure 3a, the R2 recycling agent, when used to modify the aged 50/70 bitumen sample, restored the transition temperature of the bitumen to that of virgin bitumen. After the second aging cycle, the transition temperature increased again as expected but upon modification of this

newly aged sample with R2 recycling agent, a noteworthy trend is observed; the transition temperature of the sample becomes even lower than that of the unaged neat bitumen. After aging of this two-time R2-recycled bitumen sample, the transition temperature increased relatively slightly. In fact, its transition temperature was close to that of virgin neat bitumen. The same trend occurs with the 70/100 bitumen which was subjected to the same conditions as the 50/70 bitumen as can be observed in Fig 3b. From a rheological point of view, this phenomenon could be because R2 recycling agent might have an additional softening effect on the bitumen thus fluxing it and reducing its viscosity.

4.2. Atomic Force Microscopy (AFM)

Atomic Force Microscopy is a non-invasive technique that reveals the surface morphology of bitumen and it is a useful tool which allows the topographic characterization of bitumen's surface at a higher resolution than conventional light microscopy. One major advantage of this technique is that AFM bitumen samples require little to no preparation before microscopic analysis unlike electron microscopy techniques. Via AFM, four phases can be identified:

i. Catana phase comprised of so-called bee structures that look like undulated wavy structures with a morphology of alternating swelling and depressions.
ii. Peri phase which surrounds the bee structures.
iii. Para phase which is dominant, flat in nature and is next to the peri phase.
iv. Sal phase which in combination with the para phase consists of aromatics and saturates and these comprise the smooth matrix.

These four phases are often said to correspond to bitumen's SARA fractions although there is no consensus on this hypothesis [19]. Several studies and literature reviews suggest different interpretations of these four phases identified in AFM images [21-26]. The most commonly used interpretation is the one in which the bee structures are said to correspond to the asphaltenes (some researchers refer to it as the crystallized paraffin of bitumen) with resins (peri phase) being the regions surrounding the bee structures. Aromatics and saturates are said to correspond to the smooth matrix (Para and Sal phases) observed in AFM images. Regardless of the different interpretations, information obtained from AFM images are very useful in providing an understanding of the intricacies of bitumen's inner morphology. One thing that is however largely agreed upon however is that oxidative aging increases asphaltene concentration in the bitumen matrix which is responsible for the characteristic rigidity and cracking of aged bitumen [5,16,25]

As can be seen from Figure 4, the non-aged samples have bee structures (clear domain with stripes) believed to be the asphaltenes suspended in the darker domain which is believed to be the maltenic fraction. The asphaltenes of the non-aged samples are generally small in size. In both types of bitumen, it can be seen that the bee structures increased in size after aging due to the fact that they incorporated oxygen during the oxidative aging process. Some interconnection between the bee structures is also observed. This is indicative of cluster formation of asphaltenes in the colloidal matrix leading to stiffness of the bitumen in general. With more aging cycles (2^{nd} PAV and 3^{rd} PAV), the asphaltenes increase in size although there is no significant increase in asphaltene size between the second aging cycle (2^{nd} PAV) and the third aging cycle (3^{rd} PAV).

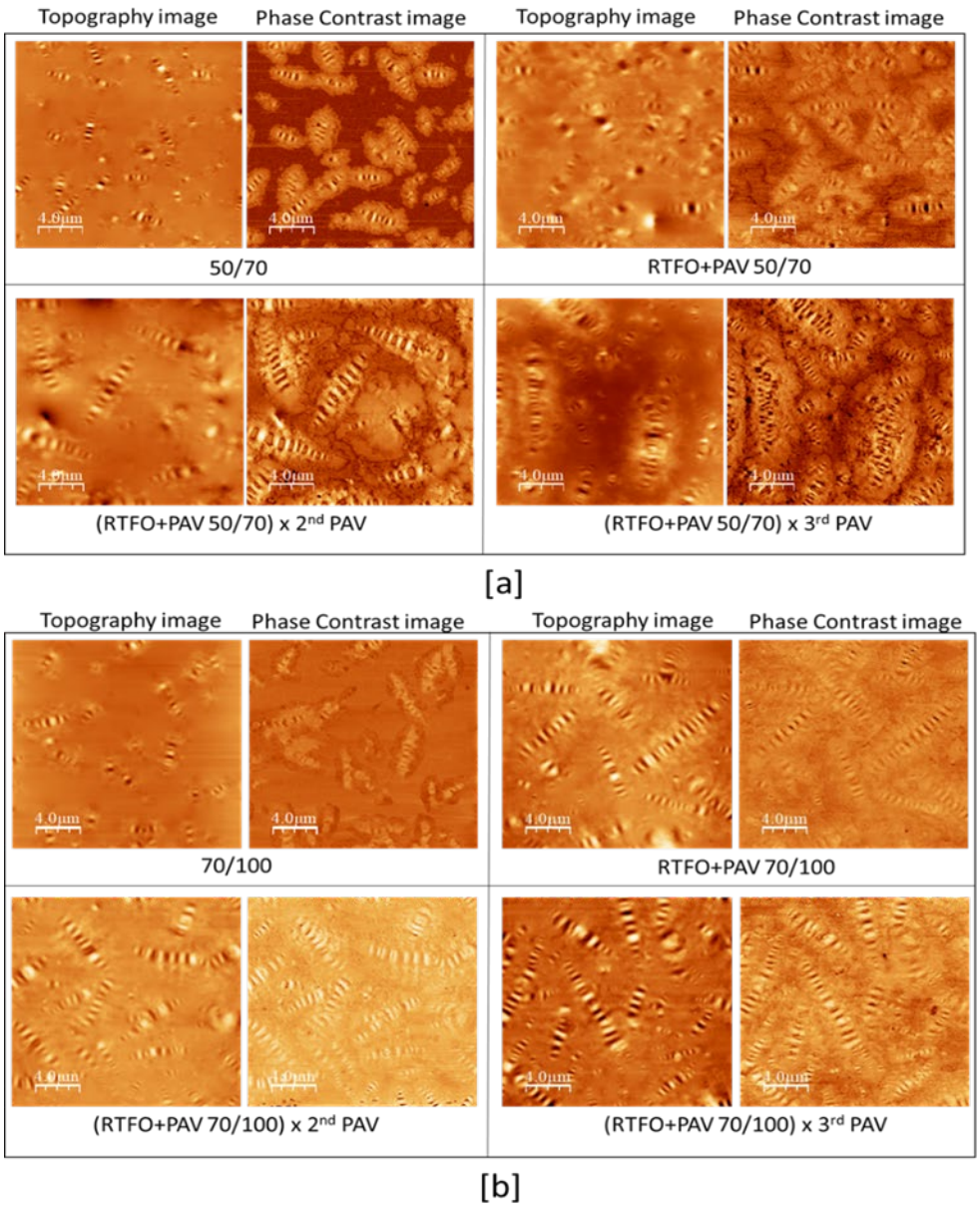

Figure 4: AFM images of the reference unaged and aged (a) 50/70 and (b) 70/100 bitumen samples

In figure 5, it is observed that in both bitumens, the bee structure size of the R1-modified sample has reduced and has become similar to that of the non-aged sample (see Figure 4). Upon aging this R1 modified sample again, the size of the bee structures increases only a little.

The images in the top right corners of figures 5a and 5b show the R1-modified samples of both bitumens which underwent a second aging cycle. These samples were modified with the R1 recycling agent again and they showed bee structures that reduced to sizes similar to those of the non-aged sample.

After this, these newly recycled samples were modified with R1 recycling agent again and the bee structures once again increased in size and in the case of the 50/70 bitumen (lower right, Figure 5a), these bee structures were observed to have formed a crust of interconnected disfigured structures. For the 70/100 bitumen, the bee structures are observed to be even bigger than those of the sample with only two aging cycles (lower right, Figure 5b). In both bitumens, the repeated restoration of the domain size of the bee structures demonstrates the efficiency of the R1 recycling agent in reversing the effects of oxidative aging on aged bitumen.

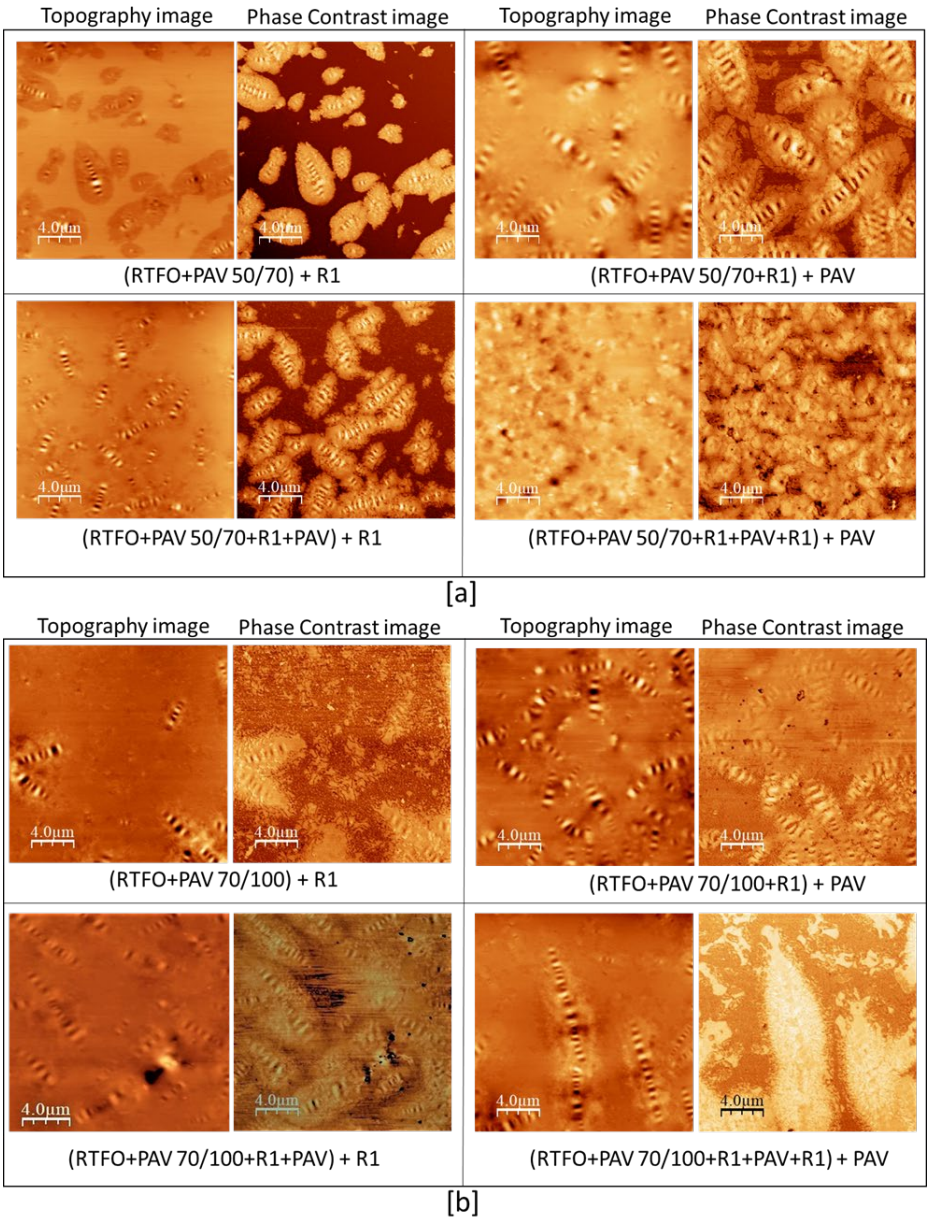

Figure 5: AFM images of the bitumen samples containing recycling agent 1

On the other hand, the R2 recycling agent is found to function differently compared its R1 counterpart. Shown in figure 6, upon addition of the R2 recycling agent to the first-time aged bitumen, a significant increase in the Para and Sal phases is observed. This suggests an increase in the maltenic fraction of the bitumen. This recycled bitumen sample was aged again and as expected, the Para and Sal phases decreased in magnitude and upon the addition of the R2 recycling agent, the Para and Sal phases increase again. The sample was aged once again and this final aging step as could be expected, reduced the size of the Para and Sal phases which can be said to correspond to the maltenic fraction consisting of oils and waxes and are responsible for the softness of bitumen. This could mean that the R2 recycling agent augments the maltenic fraction and this explains the consequent restoration of the soft texture of the bitumen after it has been modified with the R2 recycling agent.

It is worthy to note that throughout all the R2-recycling and aging cycles, the bee structures still maintain the interconnections conferred on them by the aging process. This suggests the presence of asphaltene clusters which are characteristic of aged bitumen even though the samples contain a certain percentage of R2 recycling agent. Also, while the size of the bee structures reduced upon

addition of R2, these bee structures were still relatively larger than those of the R1 modified bitumen samples. This could mean that R2 doesn't interact chemically with the bitumen and so does not influence the state of the bee structures. These clues point toward the notion that R2 recycling agent does not have a real rejuvenation effect on the bitumen but rather it merely softens the aged bitumen by increasing the maltene content of the bitumen.

Overall, the AFM data suggest that R1 is effective in restoring the asphaltene-maltene ratio in aged bitumen while R2 acts mainly on the maltenic fraction to soften the aged bitumen.

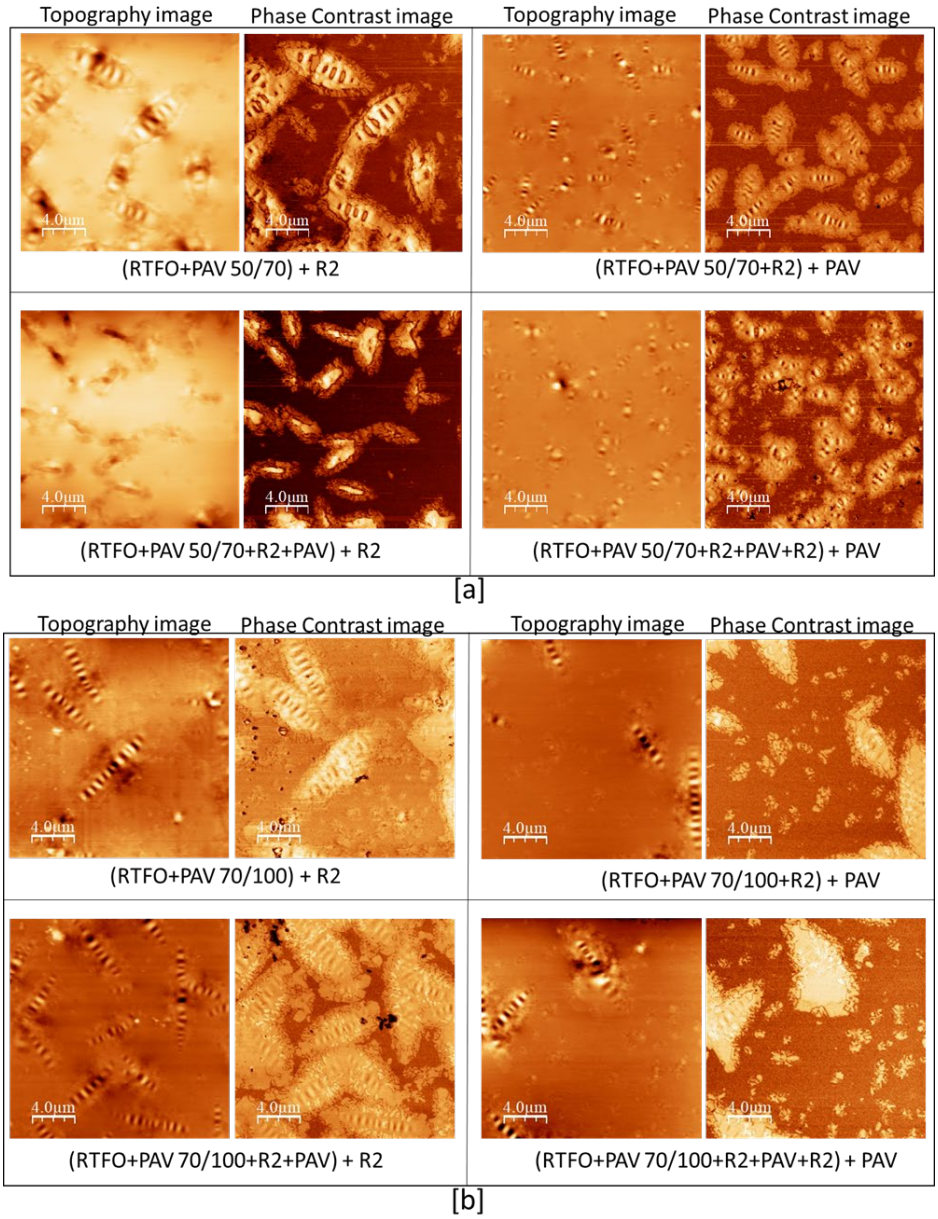

Figure 6: AFM images of the bitumen samples containing the recycling agent 2

4.3. Differential Scanning Calorimetry (DSC)

This technique was carried out to investigate the thermal behaviour of asphaltenes in unaged, aged and recycled bitumen samples. This could give indications on the mechanism of action of the recycling agents. Carrying out calorimetric measurements of the asphaltenes is a good way to investigate the mechanisms of aging and rejuvenation of aged bitumens as this can make us understand if the properties of a bitumen modified with recycling agents has been restored or not.

This method distinguishes the effects of recycling agents by detecting the glass transition (T_g) of the samples after continuous aging and recycling. In this context, the T_g is the temperature at which the asphaltene particles transform from a crystalline state to an amorphous material. The more aged, a bitumen sample is, the higher this temperature. This was done based on the hypothesis that upon aging of bitumen, the asphaltene molecules in bitumen increase in size by incorporating oxides and form clusters thereby stiffening the bitumen making it susceptible to cracking and breaking [27-30]. The calorimetric measurements were carried out on the asphaltenes because it is the fraction that confers hardness on bitumen and is a major component which makes bitumen a viscoelastic material. Upon oxidation of bitumen, the percentage of asphaltene molecules in bitumen increases at the expense of the maltenic fraction consisting of oils, waxes and resins. This makes it logical to reason that understanding the thermal properties of asphaltenes is pivotal in the investigation of the mechanisms that govern the aging, rejuvenation and recycling of bitumen in asphalt pavements [16]. In the case where it is demonstrated that aged bitumen has been rejuvenated, it can therefore be said that the asphaltenes present in the bitumen in one way or another have had their thermal properties restored.

Figure 7 shows the step-wise aging of the bitumen samples of the two bitumen types of different penetration grades used in this study. In both bitumens, it is observed that with each aging cycle, the T_g continually increases. However, after the first aging cycle, subsequent aging cycles did not bring about an increase in T_g proportional to that brought about by the first aging cycle.

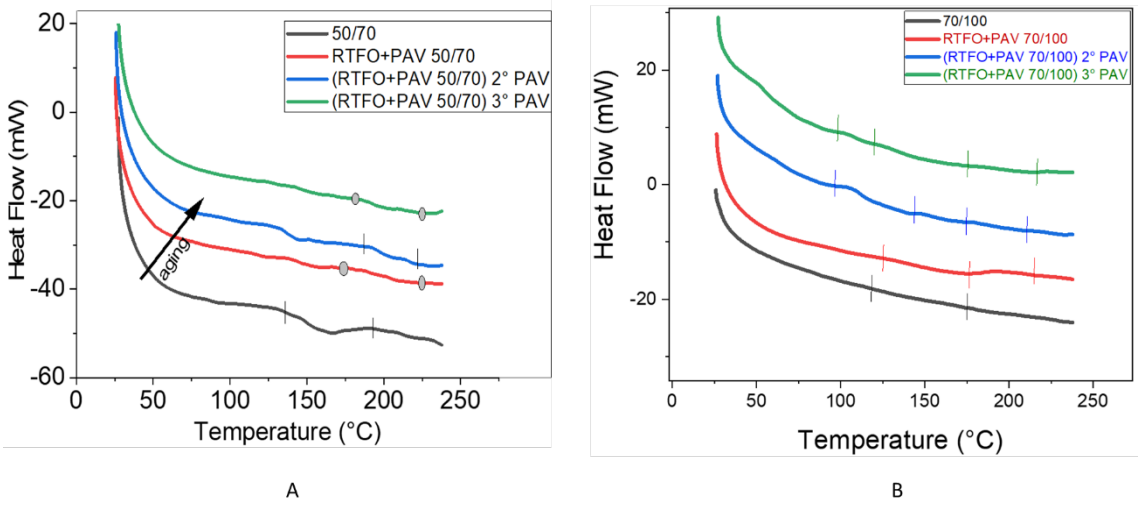

Figure 7: DSC profiles of the asphaltenes of virgin, single aged, double aged and triple aged (a) 50/70 bitumen and (b) 70/100 bitumen.

It is important to note that for the 70/100 bitumen, there are more inflection points (indicated by the bars on each curve) compared to the 50/70 bitumen. This occurs in situations where during aging, some asphaltene particles form clusters and get more oxidized than the other particles in the inner part of the clusters by shielding them from the oxidative aging process. Consequently, the internal asphaltenes are not significantly affected by the aging process (therefore they show T_g values similar to those recorded for non-aged bitumen) because they are protected by those located in the external part of the cluster while towards the exterior (of the cluster) the asphaltenes are more subjected to the oxidation process as they are more exposed and therefore more T_g values are recorded and they drift more and more towards higher temperatures. In general, the double and triple aged samples still have higher T_g temperatures than the virgin and single aged samples.

As can be seen in figure 8a, the T_g of the aged bitumen is higher than that of the unaged bitumen as expected. When R1 recycling agent was used to modify 50/70 bitumen, it was observed

that it brought back the T_g value to a range similar to that of the unaged bitumen. Upon aging of this recycled bitumen sample, the T_g shifts again towards higher values. It is however important to note that the T_g of this newly aged sample is relatively lower than that of the sample aged the first time. This recycled double aged sample was modified once again with R1 recycling agent and it was observed that the T_g shifts slightly towards lower values. However, two inflection points were observed for this sample and the same cluster notion speculated to be responsible for that phenomenon is most likely responsible in this case as well. Finally, this double aged, double recycled sample was again aged and as expected, the T_g shifted towards higher values. In fact, the T_g of this sample is more or less the same as that of the neat aged bitumen.

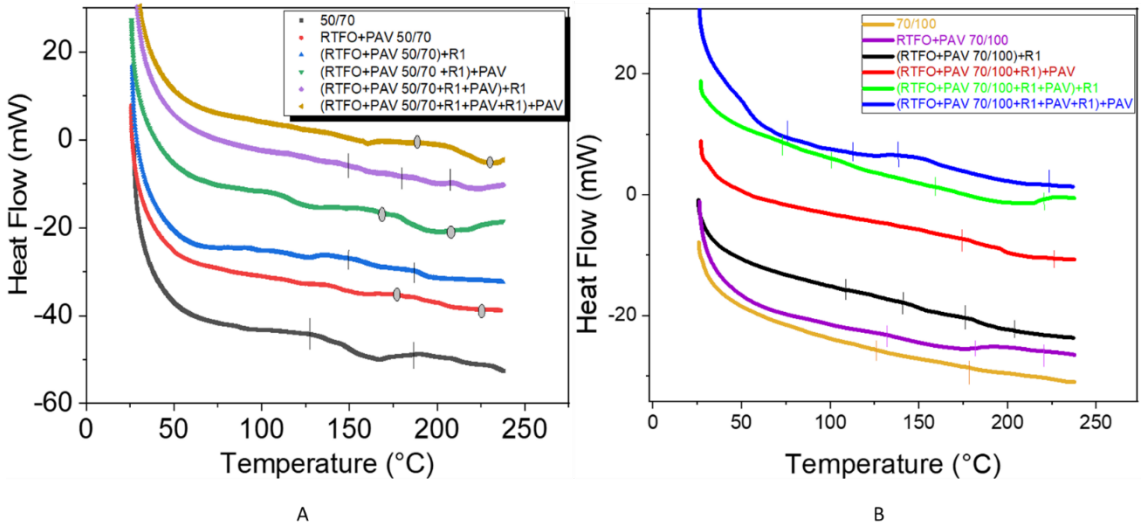

Figure 8: DSC profiles of neat, aged and R1-recycled (a) 50/70 and (b) 70/100 bitumen.

Figure 8b shows the results recorded for the 70/100 bitumen in which multiple inflection points are observed for each sample. The notion of cluster formation which is responsible for the varying degrees of oxidation of different asphaltene particles in the same sample is largely observed in this bitumen. Nonetheless, the same T_g shifting trend observed in the 50/70 bitumen was also observed in this bitumen.

The aged neat bitumen upon aging showed higher T_g values although it two inflection points are noticed. This aged sample was modified with R1 recycling agent and the T_g reduced shifting towards lower values even though multiple inflection points were observed. This recycled sample was aged and as expected the T_g value increased again, this time showing only one inflection point. This signifies that during the aging process of this sample, the level of oxidation was evenly distributed throughout the asphaltene particles. This aged sample was recycled again by the addition of R1 recycling agent. Although inflection points showing lower T_g values were observed, one inflection point with a T_g slightly lower but similar to that of the preceding sample is present. This could mean that the R1 recycling agent was able to restore the T_g of the asphaltenes but at this stage of multiple aging cycles, due to the excessive formation of clusters, R1 was not able to reach all the asphaltene particles present in the cluster thus showing inflection points. This recycled sample was subjected to one final cycle of aging and a bigger inflection point was observed and the T_g was slightly higher than that of the preceding recycled sample.

The aging and recycling cycles carried out on the 50/70 and 70/100 bitumens were repeated using the R2 recycling agent. For the 50/70 bitumen (Figure 9a), after the first modification with the R2 recycling agent, the T_g decreased showing an inflection point at a temperature lower than that of the aged sample. This R2-recycled sample was aged and as expected the T_g increased. This aged

sample was modified again with R2 recycling agent and interestingly, the T_g had no significant difference from that of the preceding aged sample. This R2-recycled sample was aged again but the inflection point observed for this sample was very similar to that of the previously recycled sample showing similar T_g values between the last recycled and aged samples.

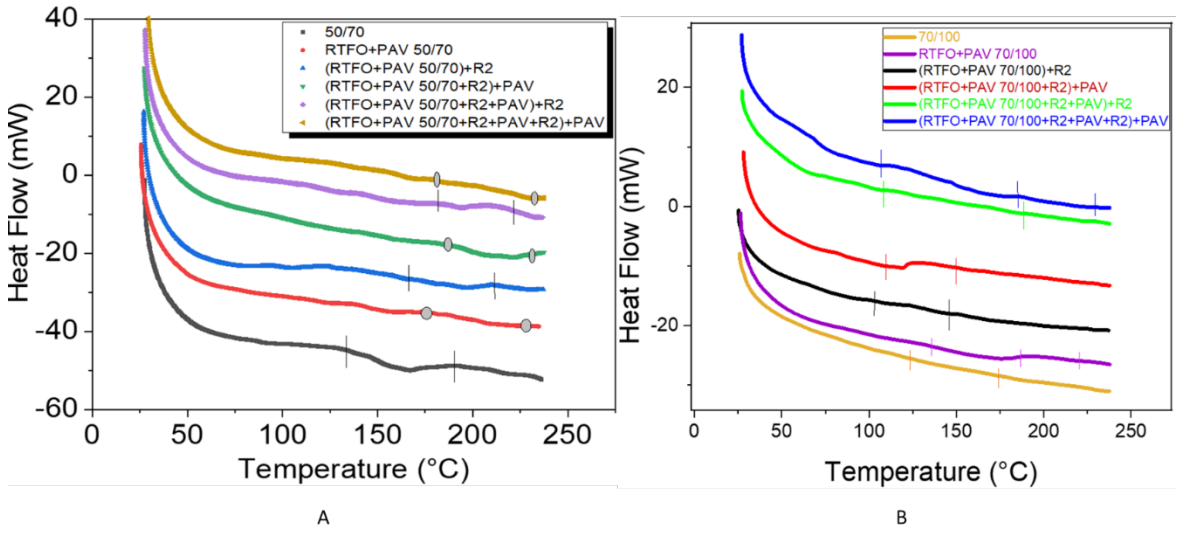

Figure 9: DSC profiles of neat, aged and R2-recycled (a) 50/70 and (b) 70/100 bitumen.

For the 70/100 bitumen (figure 9b), after the first modification with the R2 recycling agent, an inflection point indicating a T_g lower than that of the aged sample was observed. Upon aging of this recycled sample, the inflection point did not significantly increase or decrease. This aged sample was modified again with R2 and no significant change in the T_g was observed. The inflection point was double the size of the recycled sample but both samples (recycled and aged) had almost the same starting T_g temperature value. This sample was aged and two inflection points were seen although no significant change in the T_g is observed. In this 70/100 bitumen, only two samples had multiple inflection points which could mean that the aging process was uniform throughout the bitumen and not so many clusters were formed.

Overall, in both bitumens used, the R1 recycling agent was able to restore the properties of the aged bitumen in a constant manner even after several aging cycles. This suggests that R1 recycling agent was able to interact chemically with the components of the aged bitumen, reversing the effects of the oxidative aging. On the other hand, the R2 recycling agent was able to reverse the effect of aging and restore the properties of the bitumen only after the first cycle of aging. It can be said that the recycling agent was not able to reverse the effects of the aging process after a certain degree of aging. This could suggest that the R2 recycling agent does not chemically interact with the bitumen but rather only modifies its mechanical properties. These results suggest that R2 is not capable of interacting with the components of the bitumen on a chemical level to restore the properties of the aged binder.

4.4. Asphaltene melting point

The concept behind this technique is relatively simple; bitumen upon aging becomes rigid as a result of the nature of the asphaltene fraction. This rigid bitumen even at high temperature becomes more viscous than virgin bitumen. Since the asphaltenes are the solid part of bitumen and the major part that is susceptible to oxidation, they become more heat resistant and melt at higher temperatures compared to those of unaged bitumen. The melting point of asphaltene is the temperature at which it changes from a crystalline state to an amorphous state. Figure 10 shows the images of the asphaltenes

of the reference samples and the temperatures at which they are solid and melted respectively. In the upper right part of Figure 10, the solid crystalline and melted forms are enlarged to highlight the melting phenomenon of the asphaltene clusters of one sample with a step-wise increase in temperature. The same rounding phenomenon also occurs in the other melted samples shown in Figures 10, 11 and 12.

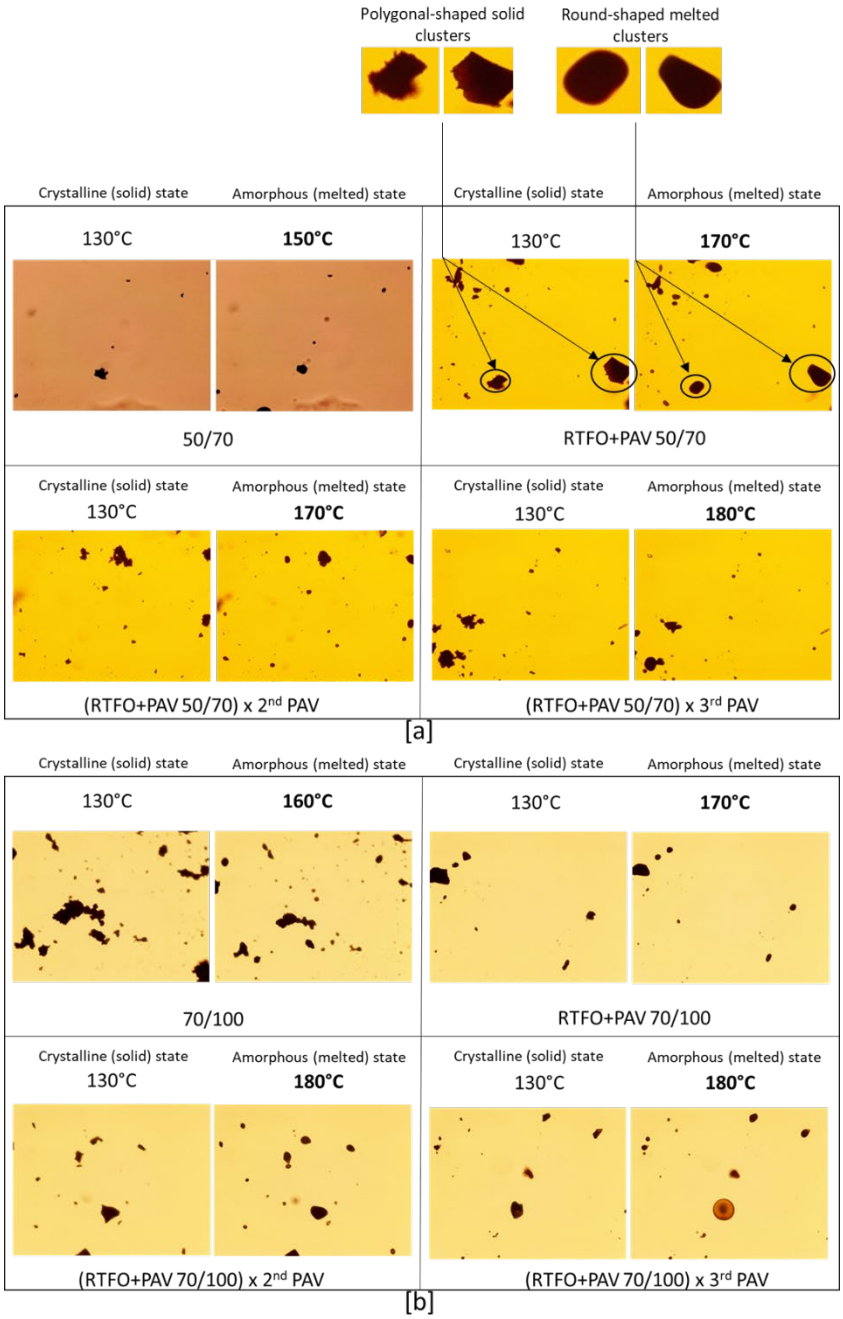

Figure 10: Light Microscopy images of asphaltene melting points of virgin and aged (a) 50/70 and (b) 70/100 bitumen

Based on Figure 10, it can be observed that the melting point temperature of the aged samples increase with each aging cycle i.e., the more aged the sample is, the higher its asphaltene melting point. Figure 11 shows how the asphaltene melting point decreases to values similar to that of virgin state in both types of bitumen upon adding R1 recycling agent to RTFO+PAV aged bitumen. This melting point slightly increases again when this newly recycled bitumen is subjected to another PAV aging cycle. The melting point, however, decreases again when R1 recycling agent is added a second

time and finally increases again when subjected to a third PAV aging cycle. From this point of view, it can be said that the R1 recycling agent is an effective rejuvenator as it restores the thermal properties of the aged asphaltenes to those of unaged virgin 50/70 and 70/100 bitumens.

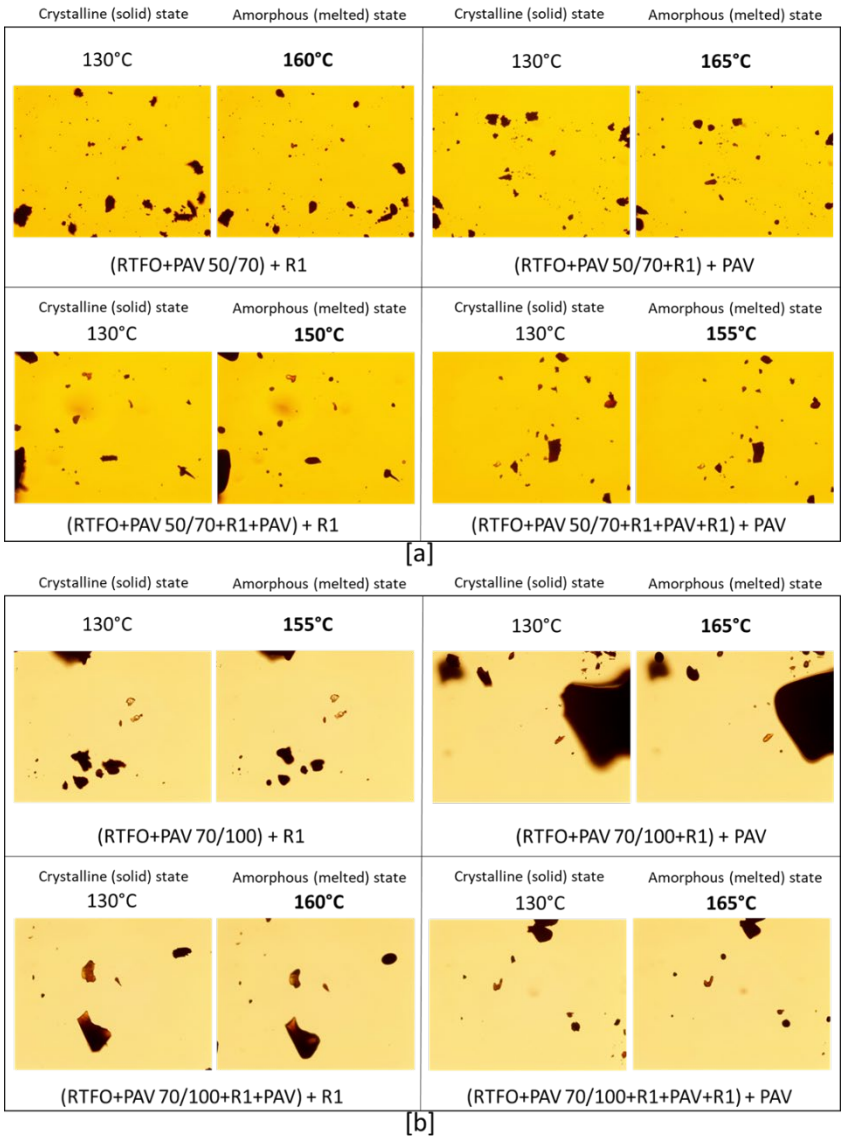

Figure 11: Light microscopy images of asphaltene melting points of R1-modified and aged (a) 50/70 and (b) 70/100 bitumen

On the other hand, in Figure 12, it is observed that in both bitumens, the R2 recycling agent was able to bring the melting point of the aged asphaltenes to values closer to that of unaged asphaltenes during the first recycling cycle. However, slightly different results were observed for the second recycling cycle. For the 50/70 sample, the second recycling cycle restored the melting point to what was observed after the first recycling cycle which was 5°C higher than that of the unaged virgin sample. Meanwhile, regarding the 70/100 sample, the second recycling cycle made no difference and was not able to reduce the asphaltene melting point after the second aging cycle and so the melting point of the double-recycled sample remained at 180°C. This could be indicative of the fact that the R2 recycling agent does not chemically act on the asphaltenes as suggested by the other techniques used in this study.

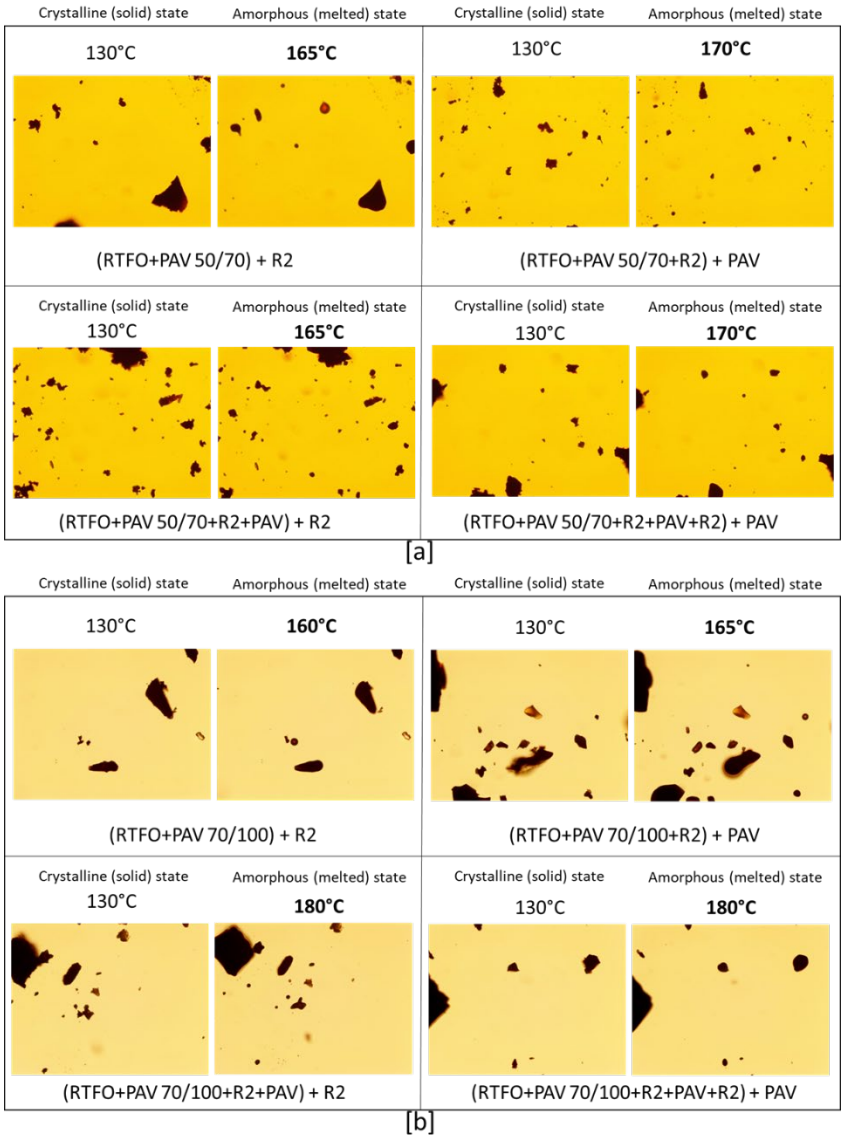

Figure 12: Light Microscopy images of asphaltene melting points of R2-modified and aged (a) 50/70 and (b) 70/100 bitumen

Overall, these results obtained via this light microscopy of asphaltenes technique corroborates the data obtained from the DSC measurements. This makes perfect sense since both techniques are based on measuring the thermal properties of the asphaltenes of the different bitumens under study.

On a general note, R1 recycling agent which performs better in this study is a blend of compounds containing specific amino groups while R2 recycling agent is made up of esters of plant origin. Amino derivatives interact with the oxidized part of the bitumen (asphaltenes) "replacing" them thus restoring the structural chemical properties. This "replacement" or substitution occurs because asphaltenes are known to consist of condensed aromatic rings and heterocyclic compounds containing nitrogen or sulphur, while amine groups in general consist of 5-membered heterocyclic rings containing nitrogen. Plant esters also contain heterocyclic rings but they majorly contain carboxylic acids, alcohol and a few hydrocarbons which replace the hydroxides contained in a classic carboxylic acid. This could mean that the blend of plant esters dilutes the oxidized heterocyclic compounds of the asphaltenes with its own blend of carboxylic acids, heterocyclic rings and alcohol. Esters are well known to perform as high-grade synthetic lubricants in general and in this case, it can be said that their action is that of a dilution of oxidized asphaltenes and not of a true regeneration of heterocyclic or aromatic rings. This is not sufficient for a complete regeneration of the oxidized asphaltenes and

this could explain why amino derivatives function better than plant esters on aged bitumen in a regenerating sense.

5. Conclusion

This research work has investigated the efficiency and most importantly, the mechanism of action of two recycling agents on two different aged bitumens. Their rejuvenating capabilities were tested using a variety of techniques with the scope of identifying how these recycling agents restore bitumen's chemical properties which have been lost to several cycles of oxidative aging. A recycling agent can either be a rejuvenator or a fluxing agent; the difference lies in its mode of action on aged bitumen. An actual bitumen rejuvenator should be able to act chemically on the components of aged bitumen to restore the morphological and chemical properties besides recovering the physical aspects of the binder to the virgin state. This would guarantee the long-term performance and quality of recycled asphalt pavements. Contrarily, a fluxing agent is not capable of chemically influencing or restoring the lost properties of an aged bitumen and can only be used to reduce its viscosity in order to improve its workability in asphalt mixtures. The results obtained in this study generally suggest the R1 recycling agent to be a rejuvenator while R2 recycling agent which had a different mode of action and was not as effective as R1 can be classified as a fluxing agent.

The findings from the rheological, microscopic, and thermoanalytical studies carried out in this study point towards these conclusions:

- In line with the results obtained from the conventional testing methods, an increase in the stiffness of aged bitumens was observed via DSR analysis. R1 and R2 recycling agents were both able to reduce the stiffness of the aged bitumen samples. DSR is instrumental in evaluating the effectiveness of recycling agents but the nature of this technique (physical property-based) renders it incapable of distinguishing between a rejuvenating and a mere fluxing effect.
- AFM studies gave an insight into the morphology of virgin, aged and recycled bitumen. It was able to identify the effects of the recycling agents on the different components that make up bitumen. R1 was demonstrated to be effective in conferring a real rejuvenation effect especially on the asphaltene fraction of aged bitumen by disintegrating the asphaltene clusters formed during oxidation and also restoring the asphaltene-maltene balance of bitumen's colloidal system. R2, however, proved to be effective in supplementing the maltenic oily fraction thus merely fluxing the aged bitumen.
- DSC analysis revealed an increase in glass transition of aged bitumen. This was reversed after the application of the recycling agents. The recycling agents, however, had varying capabilities as R1 in all cycles was able to successfully reverse the T_g increase brought about by each and every aging cycle. R2 on the other hand, was no longer effective in reducing the T_g after the second aging cycle. R2-modified samples also brought about many inflection points in the DSC curve and this could be due to the fact that R2 could not disintegrate the asphaltene clusters brought about by repeated aging cycles.
- Light microscopy of asphaltene melting point corroborated the data obtained from DSC analysis. The melting point of the asphaltenes of R1-containing samples were very similar to that of virgin bitumen. R2 was somewhat effective in restoring the melting point of 50/70 aged bitumen to that of virgin bitumen. The same could not be said for 70/100 bitumen as R2 showed ineffective in restoring the thermal properties of the 70/100 aged bitumen.

Although the findings of this study show that both recycling agents were able to improve the physico-chemical properties of aged bitumen, only the R1 recycling agent can be considered to be an actual rejuvenator. R2 can be classified as a viscosity modifier i.e., a fluxing agent. It is, however,

worth mentioning that both R1 and R2 recycling agents also have the potential to be effective anti-aging agents due to the fact that after their addition to aged bitumen, the effects of the subsequent aging cycles were less pronounced. Above all, the techniques used in this study have also proven to be efficient in differentiating a rejuvenating effect from a fluxing effect. This was demonstrated by the fact that DSC and melting point analysis provided indications on how the thermal properties of asphaltenes influence the state of aged bitumen. AFM studies also shed light on the morphological changes between virgin and aged bitumen. Going forward, these techniques can be very instrumental in revealing what is not fully understood about bitumen and oxidative aging.

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5.3. Results Part 2

"Rejuvenating Agents vs Fluxing Agents: their respective mechanisms of action on bitumen subjected to multiple aging cycles"

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1. Introduction

Carbon reduction commitments after the UN Climate Change Conference (COP26) 2021 and Paris summit, have sensitized governments on the environmental concerns more than ever. As one of the main carbon-affiliated sectors, within the road industry, several technologies have been proposed to reduce the carbon equivalent of asphalt pavement construction and maintenance interventions [1,2]. None of these technologies and initiatives is more practical and generally accepted in the road industry than the recycling of Reclaimed Asphalt (RA). Although, in terms of material functionality, recycling RA has been improved over the past few decades, few limitations still remain. For instance, it has been shown that when RA is incorporated in a high ratio in an asphalt mix, producing quality recycled asphalt is dependent on the correct choice of the type, dosage, and application method of the recycling agent [3].

To date many different design flowcharts or blending charts have been proposed to optimize the dosage of the recycling agents mostly considering just physical properties determined by conventional binder tests i.e., viscosity, penetration, softening point, and etc. However, recent research shows that the mechanism of a complete rejuvenation is not a unilateral but a multi-lateral action [4]. Different recycling agents have unique and varying potential to address the deficiencies of aged binders to different extents [5,6]. In other words, it can be said that all of the additives that are being used for recycling purpose could be considered as recycling agents, however, not all of them are rejuvenating agents. To investigate the multi-lateral mechanism of recycling, in addition to physical and mechanical property characterization, which is usually the primary step, several techniques have been introduced in research and practice. Depending on the type of the technique, they can be divided into microscopic, physico-chemical, chemical techniques and so on. Among these techniques, microscopic analysis such as Atomic Force Microscopy (AFM) that provides knowledge on the microstructural properties is a widely popular approach. Regardless of what the different features in AFM images correlate to, there is a consensus on the fact that while some recycling agents damage the chemical morphology of aged bitumen, there are some others that could restore it [2,7]. This restoration could be either by dispersing the so-called bee structures and reducing their size or regenerating the dominant para phase [8,9]. This may or may not be observable during conventional bitumen tests [10, 11]. Compared to AFM, light microscopy has been less applied in this context. This is due to the technical inadequacy of light microscopy for bitumen observation purposes. However, the authors have successfully used this technique in previous studies to investigate the asphaltene thermal properties including the melting point. The technique is based on the fact that during the oxidation of bitumen, the asphaltene clusters, tend to increase in size and texture as explained by the Yen-Mullins model. Based on the results, while the addition of one of the recycling agents reduced the melting point of the asphaltenes to values close to the reference value, the others did not [12].

Investigation of the chemical composition of virgin and aged bitumen such as SARA analysis is a technique frequently used for investigating recycling agents and differentiating rejuvenators from those of flux oils (softeners). A real bitumen rejuvenation mechanism involves the rejuvenator influencing changes in the colloidal matrix of aged bitumen which restores the asphaltene-maltene ratio to a state similar to that of virgin bitumen [13]. Recycling agents especially fluxing oils may reduce the viscosity and modulus of the overall bitumen through lowering the viscosity of the continuous solvent phase, but may have little effect on the intermolecular agglomeration and self-assembly of the polar micelles [15]. Despite the sensitivity of the method, it has been recognized as a valid approach for investigating bitumen aging in general [2,5,9,17].

2. Materials and methods

2.1. **Materials**

For the purpose of this study, a 70/100 paving grade bitumen was used. Table 1 represents some of the given physical properties of the bitumen. The additives were two recycling agents in liquid form and for the purposes of this study were called R1 and R2. Table 2 summarizes some of the properties of the recycling agents. The additives were added in a proportion of 6% to the aged samples (by weight of bitumen). It is worth mentioning that the choice of the dosage was based on the preliminary stages of this research [3,9] where different dosages were investigated and 6% was found as the optimum dosage for the recycling agents.

Table 1. Some of the given characteristics of the base virgin 70/100 bitumen.

Characteristic	Unit	Value	Method
Penetration @25°C	dmm	70 – 100	EN 1426:2015
Softening point	°C	43-51	EN 1427:2015
Dynamic viscosity @135°C	Pa.s	≥ 0.23	EN 13702:2018
Flash point	°C	Min 250	EN ISO 2592:2017
Fraass Breaking point	°C	Max -10	EN 12593:2015

Table 2. Some of the given properties of the recycling agents.

Characteristic	Unit	Recycling agent 1 (R1)	Recycling agent 2 (R2)
Aspect	-	Liquid	Liquid
Colour	-	Yellow	Yellow
Viscosity	cP	25 – 50	20 – 30
Pour point	°C	≤-5	≤0
Chemical nature	-	Mix of amino derivatives	Blend of vegetable esters

2.2. **Sample preparation**

In order to add the recycling agents to the aged bitumen sample, the bitumen was first heated to a temperature of 150 ± 5°C. The recycling agent was then added and mixed with the bitumen using a high speed shear mixer set to 500-700 rpm in order to obtain a homogenous mixture. It should be noted that although for the first round of the aging, both short-term and long-term aging were applied by means of Rolling Thin Film Oven (RTFO) and Pressure Aging Vessel (PAV) respectively, in the second round, the samples were only subjected to PAV aging. Multiple PAV aging was done in order strongly oxidize the bitumen and simulate real life duress to which asphalt pavements are normally subjected. Based on the consecutive steps listed below, the performances of the recycling agents were

evaluated by testing the samples using techniques explained further in each specific section. The testing plan and applied ID for the samples are as follows:

Table 3. Testing steps and the corresponding samples

Testing step	Testing bitumen
1	Virgin bitumen
2	RTFO+PAV bitumen
3	(RTFO+PAV bitumen) + R*i*
4	(RTFO+PAV bitumen + R*i*) + PAV
5	(RTFO+PAV bitumen + R*i* + PAV) + R*i*
6	(RTFO+PAV bitumen + R*i* + PAV + R*i*) + PAV

Where; R_i refers to Recycling agent 1 and 2.

2.3. **Asphaltene extraction (deasphaltenization)**

The asphaltenes were extracted from bitumen by exploiting their differential solubility. The protocol carried out has also been used for a previous study [12] and is a slight modification of ASTM standard protocol D2007-80 of asphaltene extraction [14]. A specific amount of bitumen was weighed into a tube and then dissolved in equal part Chloroform i.e. for example 1g of bitumen in 1ml of CCl_4. Upon complete dissolution of the bitumen in the solvent, 40 times its volume of n-pentane was added and the tube was vortexed to homogenize the solution. The asphaltenes started to precipitate in the solution because n-pentane is a differential solvent of bitumen. The tube was sealed with a stopper and parafilm and kept in a dark chamber for 24 hours. The solution was then filtered using a pre-weighed Whatman 1002-090 filter paper with a diameter and pore size of 90mm and 8µm respectively. The asphaltenes remained on the filter paper which was then put in the oven at 60 °C for 2 hours in order to allow evaporation of the n-pentane solvent. The filter paper was then weighed again to determine the percentage of asphaltenes obtained from the specific quantity of bitumen weighed as this percentage varies from one bitumen to another. The asphaltenes were then collected and analyzed. The whole deasphaltenization process was carried out at room temperature.

2.4. **Rheological Analysis**

Dynamic Shear Rheological analysis was carried out on the samples using a Dynamic Shear rheometer (SR-5000, Rheometric Scientific, Piscataway, NJ, USA) equipped with a parallel plate geometry with a diameter of 25mm. The mechanical properties of bitumen were measured by carrying out a Temperature Sweep (TS) commonly known as a time cure test. This involves subjecting the bitumen sample to slowly increasing temperatures until the bitumen loses its elastic modulus and only its viscous modulus remains. This was done to determine the transition temperature of bitumen. This transition temperature is the temperature at which bitumen transitions from viscoelastic solid to viscoelastic non-Newtonian fluid [16]. The time cure test was performed using the following parameters:

- Temperature: 25 – 120 °C (increasing at the rate of 1 °C per min)
- Stress: 100 Pa
- Parallel plate geometry: 25 mm diameter with a 2mm gap
- Frequency: 1 Hz

2.5. **Atomic Force Microscopy**

Atomic Force Microscopy (AFM) studies were carried out using a Bruker Nanoscope VIII microscope which was set to tapping mode. The oscillations of the cantilever were regulated close to its resonance frequency of 150 kHz. As a result of the upwards and downwards oscillation of the cantilever, its tip interacts sporadically with the surface of the sample. This interaction between the sample surface and the cantilever tip brings about vibration of the cantilever. The morphological features of the tested sample determine the magnitude of the vibrations which is influenced by the phase angle shift of the of the cantilever tip when it vibrates signifying energy dissipation in the tip-sample ensemble. Cantilevers with elastic constants of 5 N/m and 42 N/m were used for the measurements. Phase and topography images were taken contemporarily.

2.6. **Light Microscopy of Asphaltene melting point**

Light microscopy of asphaltenes was carried out using a Prior Scientific Instruments MP3500K light microscope equipped with a Canon EOS 4000D camera to capture real-time pictures of images observed under the microscope. This microscope setup was coupled with a Eurotherm 246 temperature regulator connected to a heating panel placed on the stage of the microscope. The extracted asphaltene samples were placed in a double microscope glass slide (sandwich model) and then the glass slide was placed on the heating panel on the stage of the microscope. A temperature ramp was applied with a starting temperature of 120 °C and a heating rate of 5 °C per minute. For every 5 °C increase in temperature, the samples were kept for 1–2 min to ensure uniformity and homogenous heating through the sample. The glass slide containing the asphaltenes was observed under the microscope at a magnification of 20X and images were captured in real time.

3. Results and discussion

3.1. Rheological properties

In the first stage of this research, as an essential procedure, the effectiveness of the recycling agents in recovering the changed physical/rheological properties of the aged bitumen was assessed by means of conventional bitumen testing methods. According to the results which are summarized in the table 3, as expected, every cycle of aging increased the stiffness of the bitumen and each recycling action brought about the recovery of the mechanical properties of the aged bitumen. Based on the results, it can be also inferred that all of the tested recycling agents were capable of recovering the fundamental physical properties of the aged bitumen and no significant difference was recorded between the obtained results. In other words, at this stage, both recycling agents could be classified as fluxing (softening) agents.

Table 4. The physical / rheological properties of test bitumen with and without the recycling agents.

Sample	**Penetration (dmm)**	**Softening point (°C)**	**Dynamic viscosity (Pa.s)**	
ID	25°C	-	100°C	135°C
Virgin bitumen	76	44.8	11.4	1.2
RTFO+PAV Bitumen	51	57.5	38.8	2.6

(RTFO+PAV Bitumen) × 2nd PAV	38	66.5	68.5	4.0
(RTFO+PAV Bitumen) × 3rd PAV	28	75.8	141.6	5.7
(RTFO+PAV Bitumen) + R1	74	46.0	--	--
(RTFO+PAV Bitumen) + R2	75	44.2	6.4	0.8
(RTFO+PAV Bitumen + R1) + PAV	70	52.8	--	--
(RTFO+PAV Bitumen + R2) + PAV	74	44.6	--	--
(RTFO+PAV Bitumen + R1 + PAV) + R1	72	43.3	--	--
(RTFO+PAV Bitumen + R2 + PAV) + R2	80	41.8	8.0	0.8
(RTFO+PAV Bitumen + R1 + PAV + R1) + PAV	78	41.4	7.3	0.8
(RTFO+PAV Bitumen + R2 + PAV + R2) + PAV	68	52.6	11.5	1.1

Bitumen, upon aging becomes stiffer and more rigid thereby increasing its transition temperature. In this study, from the rheological point of view, the complex modulus G* which is bitumen's overall resistance to deformation is evaluated in relation to the loss tangent (tan delta). Tan delta is the relationship between the storage (viscous) modulus (G'') and the loss (elastic) modulus (G') of the material. G* is a direct measure of the rigidity of bitumen's soft solid structure when exposed to stresses below the yield stress and this makes it a good indicator of the flexibility or stiffness of bitumen. With increasing temperature, G' decreases at a faster rate than G'' and so a crossover temperature occurs. This temperature is the temperature that was earlier referred to as the transition temperature [17]. The DSR profiles shown below depict G* in relation to the crossover temperatures of the samples. Higher transition temperature values imply greater stiffness of a sample.

The reference samples for this study were virgin bitumen and 3 other samples which have been subjected to multiple aging. This on one hand was done in order to simulate the realistic multiple aging cycles and on the other hand to compare them to the samples containing recycling agents which were also aged multiple times. As can be seen in figure 1, with each increasing aging cycle, the transition temperature which corresponds to the loss tangent, increases significantly.

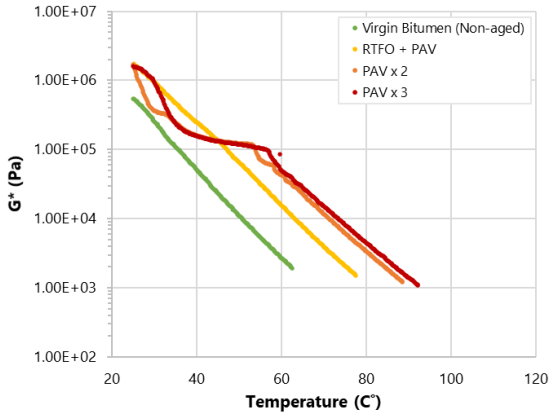

Figure 1. Complex modulus G* versus temperature of reference samples.

Figure 2 shows that both recycling agents are effective and have been able to recover the physical properties by reducing the stiffness of the aged binder. It is interesting to note that R1 even after two

aging cycles was able to restore the bitumen almost exactly to its initial unaged state. The R1 modified sample remained the same even after another subsequent final aging cycle. According to Figure 2, R2 was also able to reduce the stiffness of the aged bitumen even though it didn't do this as effectively as R1. It is also important to observe that the sample that was recycled with a second dose of R2 became softer than the virgin bitumen whereas the corresponding R1 sample was strikingly similar to the virgin bitumen when considering the transition temperature as well. This suggests that R1 has a higher effective recycling potential compared with R2 recycling agent due to the high effectiveness and specificity of R1 recycling agent in recovering the aged bitumen samples' original properties. This rheological analysis is very useful and indicative of the mechanical properties of the bitumen binder but it may not be enough to distinguish a rejuvenating from a fluxing effect of recycling agents.

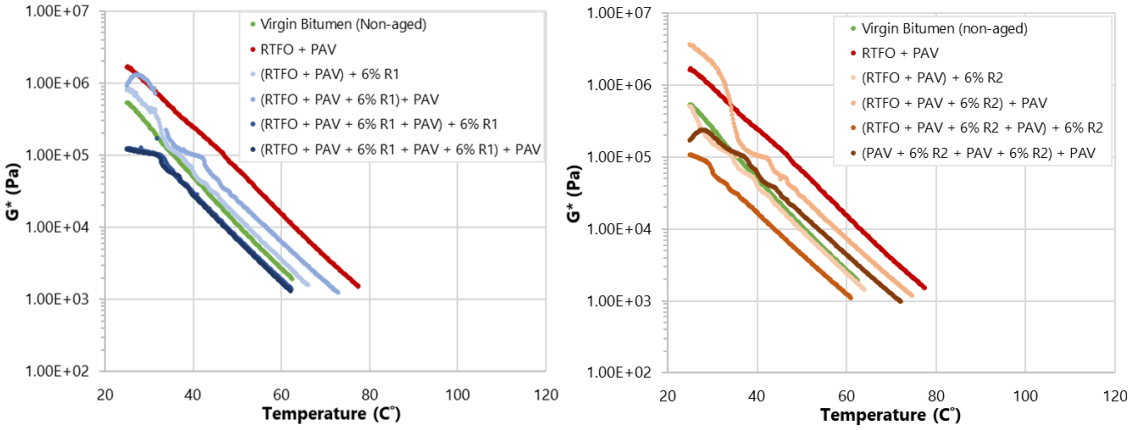

Figure 2. Complex modulus G* versus temperature of R1 and R2 modified samples.

3.2. Morphological properties

Within existing literature, AFM has been found to be a useful technique which can be used to study bitumen's inner structure as it allows the topographic characterization of surfaces at resolutions not available with light microscopy. It is also more practical and straightforward than Scanning Electron Microscopy (SEM) because AFM samples require minimal preparation. Using AFM technique for the purpose of studying bitumen's inner structure, four phases are usually observed in the images; Catana phase (consisting of bee structure), Peri phase, Para phase and Sal phase [2].

i. Catana phase is made up of so-called bee structures which resemble undulated wavy structures having a morphology of alternating swelling and depressions.
ii. Peri phase is the domain surrounding the bee structures.
iii. Para phase is dominant in bitumen's matrix, flat in nature, surrounding the peri phase.
iv. Sal phase in combination with the para phase consists of aromatics and saturates and these constitute the smooth matrix.

Evidence from literature review of AFM studies carried out on bitumen suggests that several interpretations of AFM images exist among researchers. The bee structures are speculated to be connected to bitumen's asphaltenic composition with resins being the regions surrounding the bee structures. Aromatics and saturates are said to correspond to the smooth matrix (Para and Sal phases)

observed in AFM images [18-21]. Regardless of differences in opinion regarding interpretation, AFM studies do provide a good deal of useful information and are instrumental in understanding the intricacies of bitumen's inner structure.

As can be seen from figure 3, the aging of the bitumen brought about an enlargement and roughening of the Catana phase. This can be explained by the incorporation of oxygen by the asphaltenes during aging and this translates to an increase in stiffness and rigidity of the bitumen since the bee structures got larger in size [22]. The para phase which probably represents the maltenic fraction of bitumen is also diminished with aging. The addition of R1 recycling agent is shown to reduce the size of the asphaltenes and also restore the maltenic fraction thus making it similar to non-aged bitumen. These aforementioned changes in bitumen's morphology were repeatedly observed with subsequent aging and addition of R1 recycling agent. The bee structures increased in size due to their incorporation of oxides via oxidative aging and also formed clusters. These clusters are usually due to asphaltene aggregation making the aged bitumen stiff and fragile and thus susceptible to cracking [23]. The first addition of the R1 recycling agent reversed this increase in bee structure size and then the second aging cycle increased the bee structure size again. The second cycle of R1-modification of the aged bitumen brought about once again a reduction in the size of the bee structures and the third aging cycle slightly increased the bee structure size even though the effect of the third cycle of aging on the recycled bitumen was not really pronounced likely due to the significant amount of R1 recycling agent present in the sample. This shows the effectiveness of R1 in restoring the balance of the ratio of the different fractions of aged bitumen, reversing the effects of multiple aging cycles.

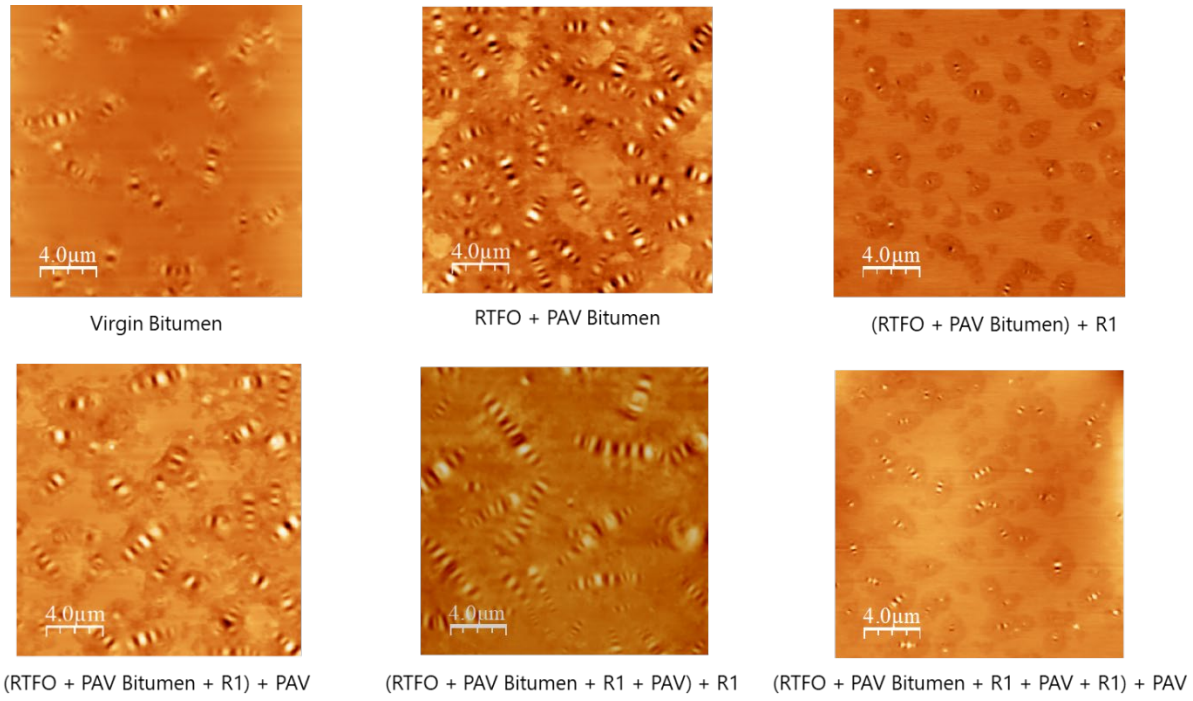

Figure 3. AFM Images of Virgin, Aged and R1 modified samples.

In figure 4 on the other hand, it was observed that upon the first addition of R2 recycling agent to the aged bitumen, the agglomeration of bee structures observed in the aged sample was de-clustered in such a way that a few clusters still exist but these small clusters seem to be dissolved clusters resulting from a bigger cluster. When this recycled sample was aged for the second time, the peri

phase surrounding the de-clustered bee structures became more pronounced. This indicates an augmentation of the peri phase which was most likely brought about by the first addition of the recycling agent. Since the peri, para and sal phases are more related to the maltenic fraction of bitumen [24-28], it is very likely that R2 functions to augment the maltenic fraction of aged bitumen. The second addition of the R2 recycling agent shows a further dilution of the bee structures in the smooth matrix as they are more separated but are less abundant in the aged bitumen's matrix. The third aging cycle shows few bee structures dispersed in the smooth sal phase indicating a mere fluxing and softening of the bitumen rather than a real rejuvenation as observed in the case of R1 recycling agent. The addition of R2 recycling agent significantly augments the maltenic fraction (para phase). The asphaltenes maintain the size they gained after aging and are dispersed in an abundant maltenic matrix.

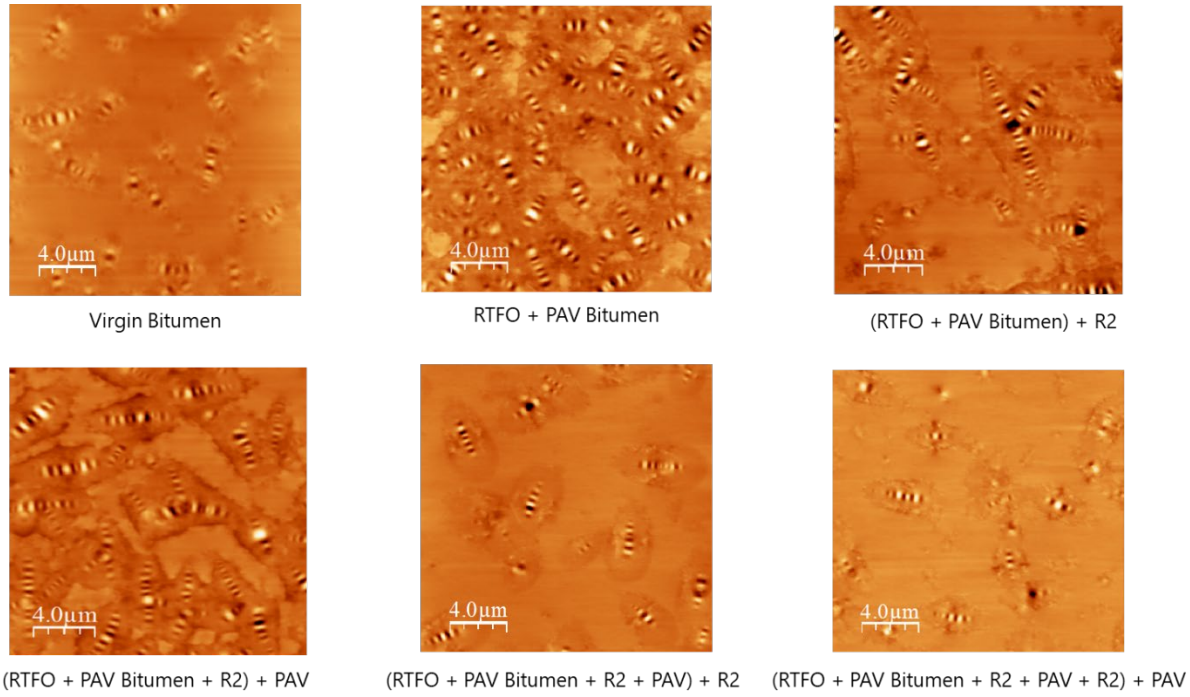

Figure 4. AFM Images of Virgin, Aged and R2 modified samples.

In the virgin bitumen sample, the bee structures (Catana phase) surrounded by the Peri phase are distinctly positioned showing that they are dispersed in the Para. Oxidative aging disrupts this colloidal system and causes an increase in size coupled with a clumping together of the bee structures [29]. Technically, a rejuvenator should work by restoring the morphological structure of the aged bitumen to that which was described for virgin bitumen. Instead, a fluxing/softening agent functions like an oil and thus interacts with the Peri, Para and Sal phases leaving the bee structures morphology unchanged in the colloidal matrix. Based on the information provided by AFM analysis, R1 recycling agent could interact with the bitumen's components on a chemical level, reversing the effects of oxidative aging thus rejuvenating it. R2 recycling agent on the other hand, could only augment the maltenic fraction and did not significantly interact with the bee structures and their morphology. This could mean that it merely fluxes the bitumen by reducing its viscosity.

3.3. Light Microscopy of Asphaltene melting point

This is a microscopy technique which also utilizes the use of a light microscope with the concept of basic calorimetry. It involves monitoring the response of asphaltene particles to a gradual increase in temperature and this response can be observed in real time under the microscope. Even though this technique is a qualitative method, its validity and accuracy has been verified using Differential Scanning Calorimetry as shown in previous studies [2, 12, 17]. This microscopy technique is a sort of real-time observation of the transition from one state to another that Differential Scanning Calorimetry usually measures. Bitumen after aging exhibits an increase in rigidity in its solid form and viscosity in its liquid form. Since the asphaltenes are the fraction of bitumen susceptible to oxidative aging [22,27], it's only logical to investigate the response of asphaltenes to an increase in temperature. Aged asphaltenes become more heat resistant and melt at higher temperatures compared to unaged virgin bitumen [23,29]. The melting point of an asphaltene is the temperature at which it transitions from a crystalline to an amorphous state. The images in Figure 5 show the asphaltenes of each sample and the temperatures at which they transition from crystalline to amorphous.

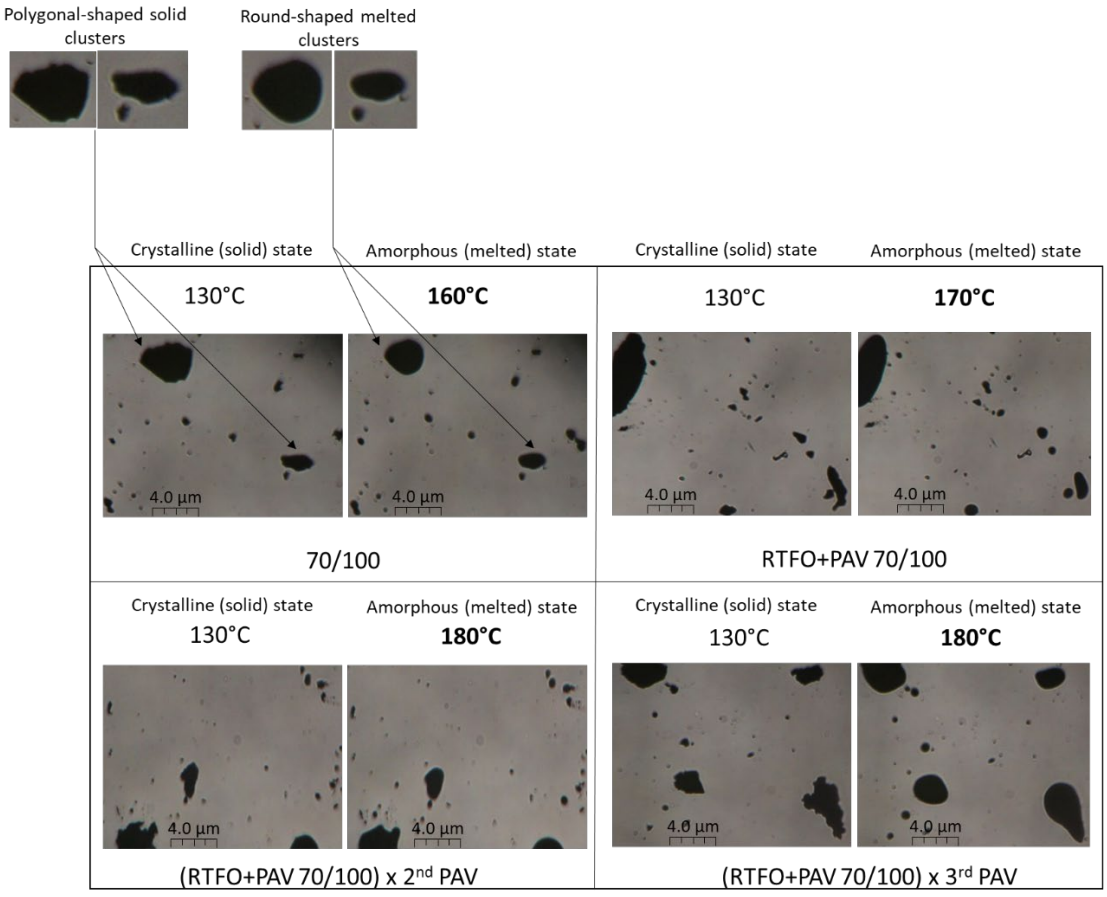

Figure 5: Light microscopy images of asphaltene melting point of virgin and aged 70/100 bitumen

In Figure 5, it can be observed that with each cycle of aging, the melting point of the asphaltenes of the virgin bitumen continues to increase. The highest melting point was observed in the sample which underwent three PAV aging cycles. Upon addition of the R1 recycling agent to the

bitumen which was aged once, it can be observed from Figure 6 that the melting point of the asphaltenes of the recycled bitumen reduced from 170 °C to 155°C which is even 5 degrees lower than the virgin bitumen. This shows the capacity of R1 recycling agent to restore the thermal properties of the asphaltenes of aged bitumen. Upon aging of this recycled sample, the melting point of the asphaltenes increased; this time, to 165 °C which is 5 degrees higher than the melting point of the virgin bitumen asphaltene sample. This aged bitumen was modified again with R1 recycling agent and the melting point decreased to 160 °C (the same melting point as the virgin bitumen asphaltene sample). A final aging cycle was carried out on the two-time recycled bitumen and it was observed that the asphaltene melting point increased once again to 165 °C. This could mean that the R1 recycling agent is capable of interacting chemically with the asphaltenes of the aged bitumen thereby restoring their properties which were lost to oxidative aging.

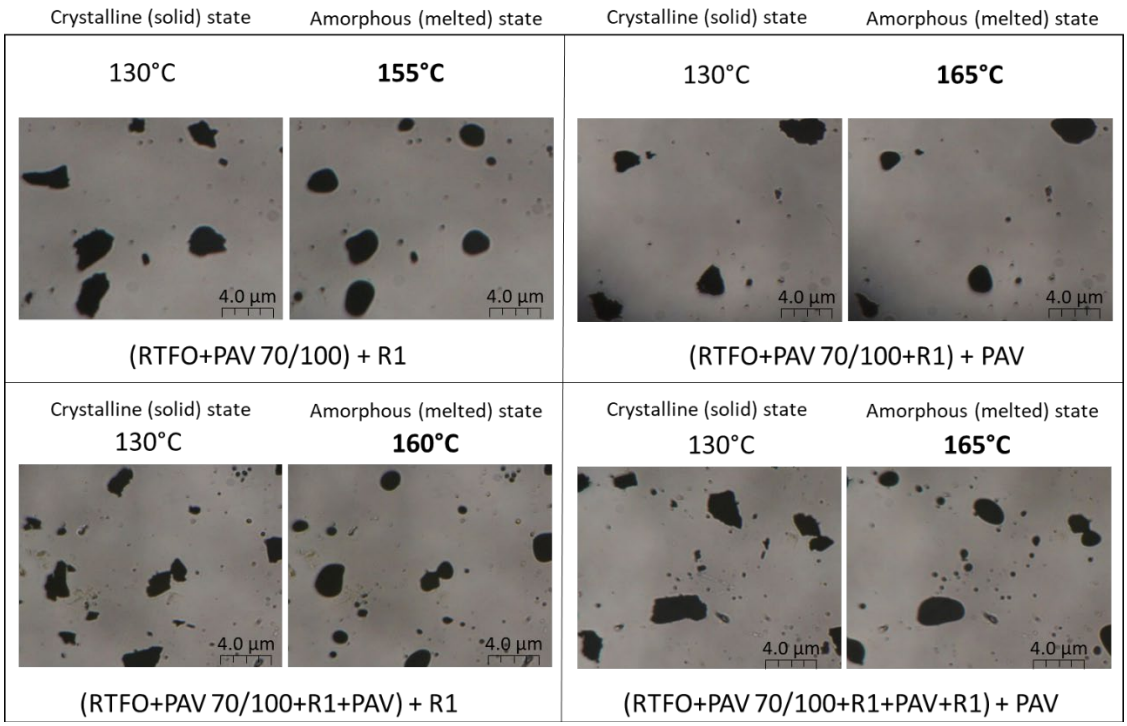

Figure 6: Light microscopy images of asphaltene melting point of R1-modified and aged 70/100 bitumen

On the other hand, in the case of R2 recycling agent, when it was added to the bitumen sample that was aged once, the melting point of the asphaltenes reduced from 170 °C to 160 °C as can be seen in Figure 7. This recycled sample was aged again and the melting point of the asphaltenes increased to 165 °C. This two-time aged sample was modified again with R2 and the melting point of the asphaltenes was even higher (180 °C – which was the same melting point of the neat bitumen which was aged twice). This means that the second modification of the bitumen with R2 recycling agent was not effective and even worsened the effects of aging on the asphaltenes thermal properties. This two-time recycled bitumen was aged for the third time and the asphaltene melting point remained the same at 180 °C. It can thus be said that R2 recycling agent after the first recycling process did not in any way improve the bitumen sample. This could be because R2 is a mere fluxing agent which softens the bitumen and reduces its viscosity. It does not really interact chemically with the aged bitumen to restore its virgin properties, Fluxing agents only augment the maltenic fraction of bitumen

thus reducing its viscosity and improving its flow. No real changes in the chemical structure of aged bitumen are usually observed when a fluxing agent is used to modify bitumen [2, 17].

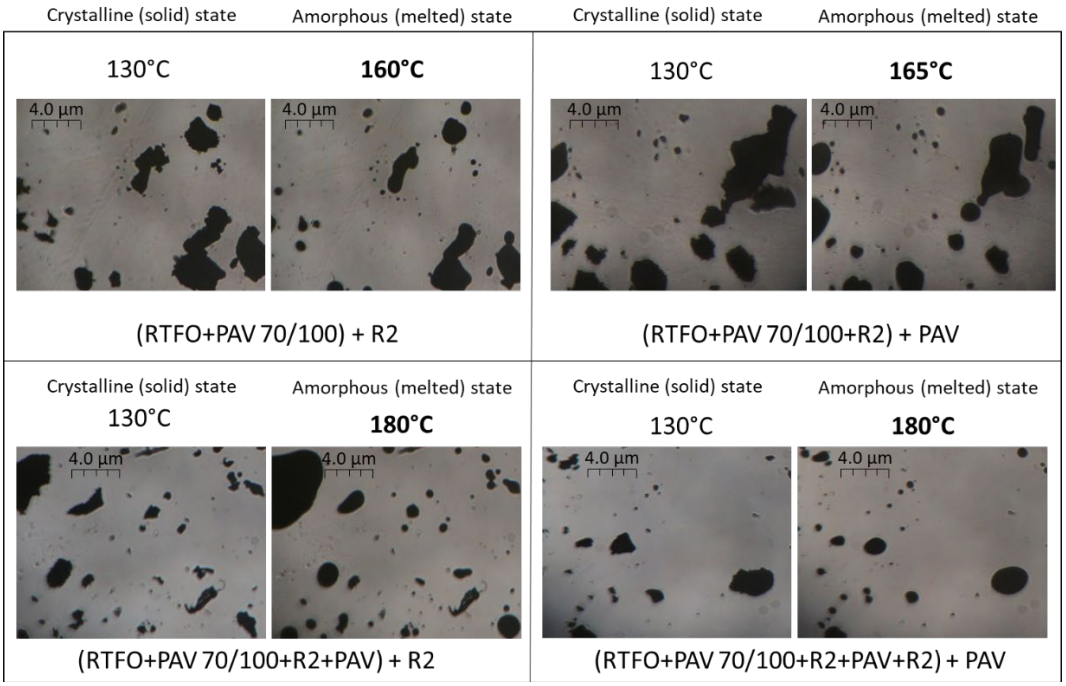

Figure 7: Light microscopy images of asphaltene melting point of R2-modified and aged 70/100 bitumen

The melting point value for each sample is reported in Figure 8 which shows a histogram with the asphaltene melting point temperatures of all the bitumen samples investigated in this study. In general, this simple microscopy technique was found to be very instrumental in distinguishing a rejuvenating from a mere fluxing effect.

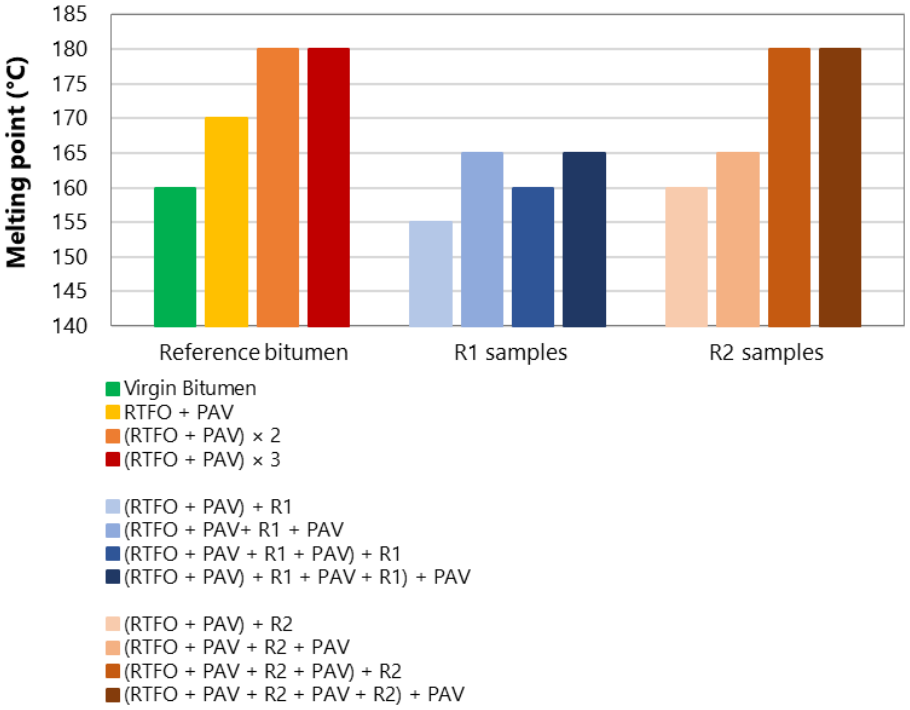

Figure 8. Melting point values of the asphaltenes extracted from each sample.

3.4. Rejuvenating effect versus Fluxing effect: Action Mechanism of recycling agents

Generally speaking, this study shows how differently the two recycling agents function. The techniques applied in this study were able to provide indications on the effects of these recycling agents on aged bitumen thereby enabling the characterization of their mechanisms of action. A real rejuvenator is capable of restoring the chemical compounds which were lost during aging and also breaking down the oxides which have been formed with the hydrocarbons and sulphides which make up bitumen's composition [30-34]. The R1 recycling agent which the results suggest is a real rejuvenator is made up of a blend of compounds composed of amino groups as can be seen in table 2. It is very plausible that the amino derivatives interact with the part of the bitumen which was oxidized (the asphaltenes) thereby reconstructing their chemical structure and reversing the asphaltene aggregation phenomenon which brings about stiffness of aged bitumen. Asphaltenes are known to consist of condensed aromatic rings and heterocyclic compounds which contain nitrogen and sulphur and oxidative aging depletes these compounds and also triggers the formation of oxides such as sulfoxides which have been identified in aged bitumen [17]. The reconstruction of the chemical structure of aged bitumen by R1 recycling agent could be as a result of the fact that amine groups in general consist of 5-membered heterocyclic rings which contain nitrogen and these compounds could either replace the depleted compounds in aged bitumen or supplement the existing ones while also breaking down the dative bonds of the sulfoxide groups which are characteristically present in high quantities in aged bitumen. R2 recycling agent on the other hand is a mix of plant esters.

Given that the findings of this study suggest that R2 is not capable of interacting chemically with aged bitumen but rather establishes a physical interaction by augmenting the maltenic fraction, it can be said that is is a mere fluxing agent. R2 recycling agent is composed of plant esters and they also contain heterocyclic rings but they are predominantly composed of carboxylic acids, heterocyclic rings and alcohol. Esters are also well known to function as excellent lubricants and in this case, it can be said that the action of R2 on oxidized bitumen is the dilution of oxidized asphaltenes and not a real rejuvenation via regeneration of heterocyclic or aromatic rings. This mechanism of action of the R2 recycling agent is not sufficient for a real rejuvenation of aged bitumen and this could explain why R1 made up of amino derivatives is a better candidate at restoring the structural properties of aged bitumen compared to R2 which is made up of plant esters. Asphaltene aggregation is also characteristic of aged bitumen and this is brought about by the interaction between the polyaromatic cores of the asphaltene molecules. Van de Waal forces between the aliphatic side chains of the asphaltene molecules also contribute to this aggregation and clustering [35,36]. Since the AFM images show the de-clustering of the bee structures brought about by R1 in aged bitumen, it's possible that the tendency of alkyl groups to surround N atoms in amino group molecules increases the steric interference between the asphaltene molecules thus destabilizing the asphaltene clusters in aged bitumen [22]. Esters which constitute the R2 recycling agent are less likely to influence steric interference and more likely to promote Van der Waal forces between asphaltene molecules which sustain asphaltene aggregation [35]. These properties indicate why R1 seems to be an ideal rejuvenator and R2 seems to be a softener of aged bitumen as shown by the results of this study.

Conclusions

In this study, two recycling agents have been studied to investigate their rejuvenating capabilities on bitumen binder subjected to multiple aging cycles. Rejuvenating agents and fluxing agents have different mechanisms of action on aged bitumen. A rejuvenator should be able to interact chemically with the components of bitumen to restore its properties. It should be also able to recover its physical rheological properties to guarantee long-term performance of recycled asphalt mixture. A fluxing agent is capable of only physically interacting with the aged bitumen by augmenting its maltenic fraction thereby making it softer. Studies which distinguish between real rejuvenation and mere fluxing of aged bitumen will prove to be very important in the advancement of RAP technology. These studies could highlight pathways that will bring about an increase in the percentage of Reclaimed Asphalt that can be used in new road paving operations and in the long run, facilitate recycling, resource conservation thereby promoting a circular economy.

The DSR; AFM and Optical Microscopy findings in this study can be concluded thus:

- Dynamic Shear Rheology is fundamental in evaluating the mechanical properties of bitumen and it often corroborates the results obtained from bitumen conventional tests. In fact, in this research the conventional tests results were also consistent with those of the DSR analysis. However, other techniques such as Atomic Force Microscopy and Light Microscopy are very important in order to understand the mechanism that govern the changes in bitumen's properties upon aging and recycling of bitumen with rejuvenators or mere fluxing agents.
- The DSR results show that both recycling agents used in this study reduced the stiffness of the aged bitumen recovering its mechanical properties close to that of the reference virgin bitumen. This was observed via both complex modulus and the transition temperatures. As mentioned earlier, these results were consistent with those obtained from the conventional bitumen tests as expected.
- Via AFM, R1 recycling agent was observed to have restored the internal structural components of the aged bitumen bringing it back to a structure very similar to the reference virgin bitumen. R2 recycling agent was only able to augment the maltenic fraction of the aged bitumen merely softening it.
- Via deasphaltenization and light microscopy of asphaltenes, it is observed that R1 effectively recovered the properties of the corresponding bitumen by restoring its property of change of state in relation to temperature. This was not observed with R2 meaning that it has little to no effect on the asphaltenes of aged bitumen. Since aging is said to have a major effect on the properties of asphaltenes, it can be said that R2 in the real sense does not reverse the effects of oxidation.
- Adding up the test results of this study and comparing what they imply with what is written in scientific literature on this topic, recycling agent R1 can be said to be a rejuvenator while recycling agent R2 can be said to be a fluxing/softening agent. Accordingly, the introduced methods could be efficient techniques to differentiate the recycling agents into fluxing (softening) agent and rejuvenator.

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5.4. Results Part 3

"Additives on aged bitumen: what probe to distinguish between rejuvenating and fluxing effects"

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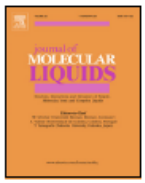

1. Introduction

The general problem affecting bitumen and asphalt concretes is their aging, a process giving ever increasing viscosity and stiffness with time thus implying losing of performances. Under ageing, bitumen molecules and their aggregates become less and less mobile to flow under the applied stress. So, cracking or fracture can take place [1] in the bulk material. Ageing is a complex mechanism, which can be considered as the overall result of several and somehow interconnected spontaneous processes, each of them characterized by its own timescale:

1. volatilization of light components in the maltene taking place even during asphalt construction [2,3];
2. oxidation of bitumen constituents by atmospheric oxygen. This gives oxidized molecules which being more polar can give enhanced self-assembly [4];
3. evaporation of low-molecular weight components: this causes not only a change of bitumen composition, but also an overall reduction light component (at least those with higher vapour pressure) [5];
4. chemical reactions causing polymerization and formation of a bigger structures within the bitumen (thixotropy) [6].

After ageing, the original physical properties of bitumen can be restored essentially in two main ways:

1. by simply restoring the original ductility/viscosity through addition of softening (usually called fluxing) agents like flux oil, lube stock, slurry oil, soy oil etc. [7,8];
2. by restoring the original chemistry of the pristine bitumen and its original inter-molecular structure [9]: this would imply a more sophisticated/complex action (rejuvenation) being able to push back the oxidations, agglomerations and self-assembly processes occurred during the whole aging.

Whatever the mechanisms, it must be stressed that, in general, the resources needed to modify the bitumens (costs, skills and technology involved) must be somehow justified. So, it can happen that cheaper additives, which can exert only a simple fluxing effect, can be sometimes preferred due to their low cost and accessibility. For example, in this ambit, recent trends based on the re-utilization of wastes to modify/restore bitumens in a circular economy approach, are drawing particular attention for environmental issues [10].

On the other hand, although probably the latter mechanism (rejuvenation) is more complex and harder to achieve, it can guarantee a better effect with more prolonged benefits at longer times [11].

For this reason recent research, both academic and industrial, are starting to consider the production of additives as real rejuvenators [12,13] with an obvious attention to environmental concerns [14] and, consequently, to the development of green additives [15]. Of course, different efforts are being made to distinguish between these two mechanisms [16]. In this study, the effects of two different additives on aged bitumen were investigated. One of these two additives (soy oil) being a bare fluxing agent, the other one (tritolyl polyphosphate isomers, TPI) behaving as real rejuvenator.

2. EXPERIMENTAL SECTION

2.1 Materials

The base bitumen was kindly supplied by Loprete Costruzioni Stradali (Italy) and was used as fresh standard. Its penetration grade (50/70) was measured by the usual standardized procedure [17], in which a standard needle is loaded with a weight of 100 g and the length traveled into the bitumen specimen is measured in tenths of a millimeter for a known time, at fixed temperature. TPI (Tritolyl Polyphosphate Isomers) was supplied by KimiCal s.r.l. (Rende (CS) – Italy) and soy oil by Loprete Costruzioni Stradali (Italy).

2.2 Sample preparation

A weighted amount of additive (1 g of additive in 20g of bitumen giving a final content of 4.76% wt/wt), was added separately to a fully flowing hot bitumen (150 ± 10 °C) and stirred at 500–700 rpm by a mechanical stirrer (IKA RW20, Königswinter, Germany) for 30 min at the same temperature to allow homogenization of the blend. Previous studies showed that such conditions assure the preparation of homogeneous samples: at lower rpm samples homogenization is not effective, while above 700 rpm the bitumen can become oxidized with consequent change in the rheological properties. This method is quite standard and also other authors use analogous procedure [18].

After mixing, the resulting bitumen was poured into a small sealed can and then stored in a dark chamber at 25 °C to retain the desired morphology. Due to the sensitivity of such kind of materials to the annealing time [19], and due to the comparative spirit of our work, we took care that all our samples had the same temperature cooling rate (5°C min-1) and annealing time (15min). A standard additive-free bitumen sample was used as reference, hereafter labelled as “ref”.

The bitumen samples were artificially aged by means of the Rolling Thin Film Oven Test (RTFOT) using a variation of the ASTM D1754 standard. In this respect a thermal treatment of 225 min at 163°C was used in ored to reproducer the behavior of a Recycled Pavement Asphalt (RAP)

2.3 Atomic Force Microscopy AFM

Atomic Force Microscopy (AFM) was carried out by a Nanoscope VIII, Bruker microscope operating in tapping mode (150kHz). When the tip is brought close to the surface, the vibration of the cantilever is influenced by the tip–sample interaction: shifts in the phase angle of vibration of the cantilever, implying energy dissipation in the tip-sample ensemble, are due to the specific mechanical properties of the sample. Cantilever with nominal tip radius of curvature 10nm were used. Both topographic and phase images were recorded and they usually match.

2.4 Rheology

The complex shear modulus G* = G' + i G'' [20] was measured in the regime of small amplitude oscillatory shear at 1Hz as a function of temperature (temperature controlled by a Peltier element, uncertainty ±0.1 °C) by dynamic stress-controlled rheometer (SR5, Rheometric Scientific, Piscataway, NJ, USA) equipped with a parallel plate geometry (gap 2 mm; diameter 25 mm for high temperature range and 8 mm for low temperature) in the regime of small-amplitude oscillatory shear [21]. Conditions were chosen after preliminary stress-sweep tests to guarantee linear viscoelastic conditions in all measurements.

The real and imaginary parts define the in-phase (storage, measure of the reversible elastic energy) and the out-of- phase (loss, irreversible viscous dissipation of the mechanical energy) moduli, respectively [22]. Rheology temperature-sweep tests from room temperature (RT, 25 °C) to high (up to 120°C) and to low (down to - 30°C) temperatures were performed monitoring the elastic modulus (G′) during each temperature ramp at a constant heating rate (1 °C/min) and at a frequency of 1 Hz.

2.5 Optical Microscopy

Samples were examined with a Leica DMLP polarising microscope equipped with a Leica DFC280 camera and a CalCTec (Italy) heating stage. Samples were inserted in a double microscope glass slide (sandwich model) and a temperature ramp was carried out with a starting temperature of 120 ° C and a heating rate of 5 ° C per minute. After any 5 ° C increase, photos were taken. After reaching the desired temperature at each point, the samples were left to stay for one minute to ensure total melting of the whole sample.

2.6 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared (FT-IR) analysis was carried out on the KBr asphaltene pellets samples in the mid-infrared area (4000–400 cm-1) with a Perkin Elmer Spectrum 100 FT-IR spectrometer.

3. RESULTS AND DISCUSSIONS

3.1 Rheological tests

Interesting information can be derived from the temperature dependence of G' and G'' for the studied samples. A clearly increasing trend is observed as a function of temperature in accordance with the typical bitumen behaviour. At a deeper sight, the trend shows two regions which correspond to two different regimes [23,24].

At low temperature, in fact, all samples exhibit a viscoelastic response typical of strong gel-like materials where G' > G'' but, when increasing temperature, G' decreases faster than G'' so a crossover temperature (Tcross, at which G' equals G'') takes place (see Fig. 1). So, for T > Tcross, samples typically behave as pseudoplastic fluids. Tcross is therefore to be considered as the transition temperature from a glassy elastic solid to a viscoelastic liquid. At this temperature, the sample changes from solid-like, with a mainly elastic response [25] but generally more susceptible to cracks [26], to viscoelastic, with a higher mechanical plasticity [27,28].

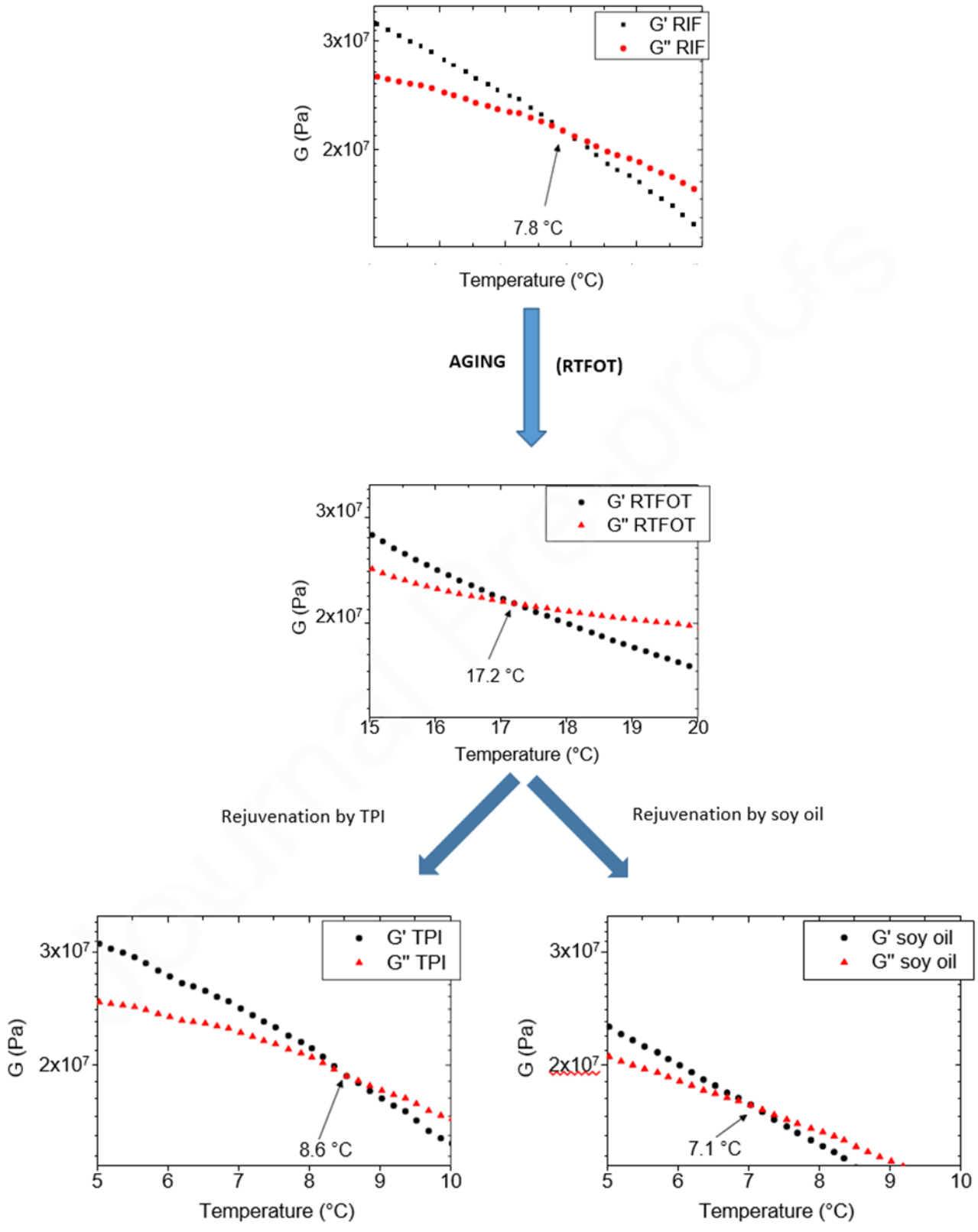

Fig.1. G’ and G’’ (at 1 Hz) as a function of temperature (lower temperatures) for the studied samples.

It can be seen that ageing shifts the T_{cross} value from 7.8 to 17.2 °C, as expected for a process making the material stiffer and more rigid. This is reasonably due to the oxidation of the aromatic components of the bitumen during the aging process. However, both additives can shift back Tcross quite efficiently, but it is worth of note that the effect exerted by soy oil is a bit more marked than TPI

When increasing temperatures, the material is progressively softened (see the typical behaviour of G' and G'' at high temperatures in Fig. 2). The value of G' at 50 °C (G' @ 50 °C) can be seen as an indicator of the rigidity of the material under usage conditions as made in previous papers [29,30]. The values of G' @ 50 °C are reported in the same Fig. 2: for these values the same considerations as those made for T_{cross} hold, i.e. the ageing shifts the G' @ 50 °C value from 1760 Pa s to 24500 Pa, as expected, and both additives can shift back the value quite efficiently (to 4220 and 3120 Pa for TPI and soy oil, respectively) with a more pronounced effect exerted by soy oil.

At even higher temperatures, a transition from a viscoelastic material to a viscous liquid can be observed. In fact, when temperature is further increased at a certain point G' drops (T_{melt}). From the microscopic point of view T_{melt} can be intended as the temperature at which the thermal motion is sufficiently high to completely destroy the intermolecular network. This means that, for temperatures higher than T_{melt}, no elastic response (storage of mechanical energy) is anymore present in the material under an applied stress; in few words, the bitumen behaves now as a Newtonian fluid. The values of T_{melt} are reported in the same Fig. 2; for these, the same considerations as Tcross hold: ageing causes an obvious increase of Tmelt (from 62 to 75 °C) which can be partially restored by addition of TPI or soy oil (shift back to 66 and 67 °C, respectively), with a scarce difference between the two additives.

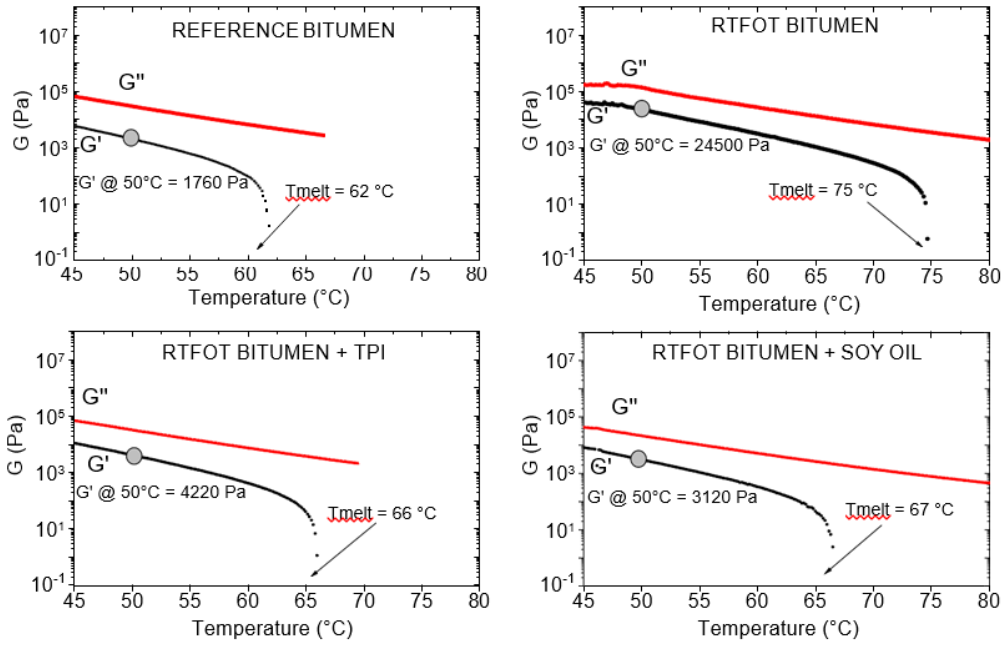

Fig.2. G' and G'' (at 1 Hz) as a function of temperature (higher temperatures) for the studied samples.

Therefore, as resulting from the rheological analyses, it seems it was not possible to clearly evaluate the effectiveness of the regenerating additive as it is not possible to differentiate the regeneration effect of the additive from the fluxing effect of the oil. This, in our opinion, can be due

to the fact that rheology is a bulk technique, synthetically probing the overall behavior of a material. Different microscopic structures can thus exhibit the same rheological behavior, although with subtle but important differences in some intermolecular interactions (polar inter-asphaltene interactions). In the specific, due to its microscopic structure, a bitumen can be described by the so-called weak-gel model, according to the theory of Bohlin [31] and Winter [32] which has been applied to several colloidal complex systems [33].

It is defined as a complex system characterized by a cooperative arrangement of flow units connected by weak physical interactions that cooperatively ensure the stability of the structure. In the analyzed samples, the asphaltene oxidation and the consequent self-assembly/aggregation of its units, as well as the loss of volatile maltene fractions, is counterbalanced, from the rheological point of view, by oil addition into the matrix (maltene). Residual differences between aged-and-additivated and pristine bitumens support this interpretation.

3.2 Light Microscopy

Fig. 3 reports the microscopy analysis of the asphaltenic fraction of the bitumen under increasing temperatures. These images have been recorded after the standard procedure for asphaltene isolation from bitumen, IP 143/01 [34] as recently implemented in ref [35].

It must be stressed that conventional methods for measuring melting point of organic solids, (heating sample in a capillary tube), rely on its physical state observation under relatively low heating rates, which prevents application to reactive materials such as asphaltenes. An alternative for qualitative observations of physical behavior is to rapidly heat tiny samples of asphaltenes, as described in [36] with in situ observation by a camera. The heating rate of 5 °C/min adopted in the present work was chosen following this criterion in accordance to the specificities of the instrumentation used.

The presence of micro-meter sized particles can be observed. The presence of aggregates larger than those usually observed in suspension [37], is ascribed to ripening/coalesce/agglomeration phenomena triggered by the progressive increase in nanoparticle concentration occurring during sample preparation (sample filtration and drying) [38]. It can be observed, in panel A, that the asphaltene clusters of the pristine (unaged) bitumen begin to melt around 150°C and are completely liquid at 160°C. This temperature range is in accordance with the fact that, as a complex mixture of components, asphaltenes generally do not display a distinct melting point. The melting temperature range found agrees with those found by other Authors. For example, Zhang et al [39] have indications, by visual observations, that softening and melting take place in their samples in the temperature range 150 - 230 °C.

The asphaltenes aggregates of aged bitumen (see Fig. 3 panel B) begin to melt at higher temperatures (around 165°C) and are completely liquid at 180°C. The increased temperature as compared to that of pristine bitumen is obviously due to the fact that asphaltenes are more oxidized and therefore are characterized by stronger intermolecular interactions, giving a tighter cluster with higher lattice energy.

It is interesting now to observe significant differences in the images of asphaltenes derived from the aged bitumen modified with soya oil or TPI. In fact, the asphaltenes derived from the bitumen with 4% TPI begin to melt at 155 °C and are completely liquid at 170 °C (see Fig. 3 panel C), showing a behaviour very similar to those derived from non- aged bitumen. Those derived from aged bitumen added with 4% soy oil, instead, show values similar to those recorded for asphaltenes of aged pristine bitumen (160-180°C, see panel D).

Thus, it can be claimed that the regenerating additive (TPI) has chemically interacted with the asphaltenic part of the bitumen, restoring it almost completely to its initial state. On the other hand,

it is clear that this is not true for soy oil, for which only a simple improvement of the flow in aged bitumen can be claimed (see rheological analysis), without any strict chemical interaction with asphaltenic part of the bitumen. It is confirmed, therefore, that the soy oil effect is to be individuated in the maltenic fraction, probably due to its mostly apolar structures allowing only apolar interactions. On the other hand, TPI, thanks to the phosphate group, allows more polar interactions, effectively binding the asphaltenes clusters. Due to the wide scenario of possible interactions among asphaltene and their clusters, a complex structural pattern, taking place at different length scales and characterized by different strengths with hierarchical structures [9], is present. Longer-range structures are expected to be hold up by weaker interactions, which can be broken simply by a temperature increase: small-angle neutron scattering experiments on asphaltenes, indeed, show that the large-scale asphaltene aggregates progressively disperse over a temperature range from 50 to 400 °C [40,41].

Moreover, due to the multiplicity of structures and interactions involved, it is hard to understand the exact localization of TPI-asphaltene interactions. For this, a theoretical approach based on computational chemistry, or ad-hoc experiments, are needed. Here, however, this aspect is not relevant, since what is important, for the purposes of this the research, is TPI stabilization effect towards the single asphaltene molecules, hindering their assembly and giving the overall decrease in melting point of their fraction. It can be concluded that optical microscopy, coupled with thermal treatment, directly probing the melting point of asphaltene clusters, is a good technique to distinguish a mere fluxing effect from a real rejuvenating effect. It is interesting to note that this technique focuses on the specific part of a bitumen (asphaltenes and their clusters/aggregates) directly involved in ageing, an aspect that can be, in our opinion, at the basis of the effectiveness of the technique.

Another interesting observation is that the exploitation of optical microscopy is a very simple approach which involves the use of scientific instrumentation present in almost all research laboratories and which has relatively low costs, both for maintenance and for purchase. This technique will allow the quality of the additives to be used as regenerants for bitumen to be assessed quickly and effectively. Furthermore, given the rapid sample preparation and test execution times, it will speed up the search for new regenerating additives and above all will allow the bodies responsible for quality control during the drafting of bituminous conglomerates (such as ANAS in Italy, NCAT and NAPA in U.S.A., etc.) for the construction of road pavements, an immediate verification of the final product (conglomerate) thus providing the possibility to intervene on the composition of the conglomerates in real time, avoiding future maintenance work.

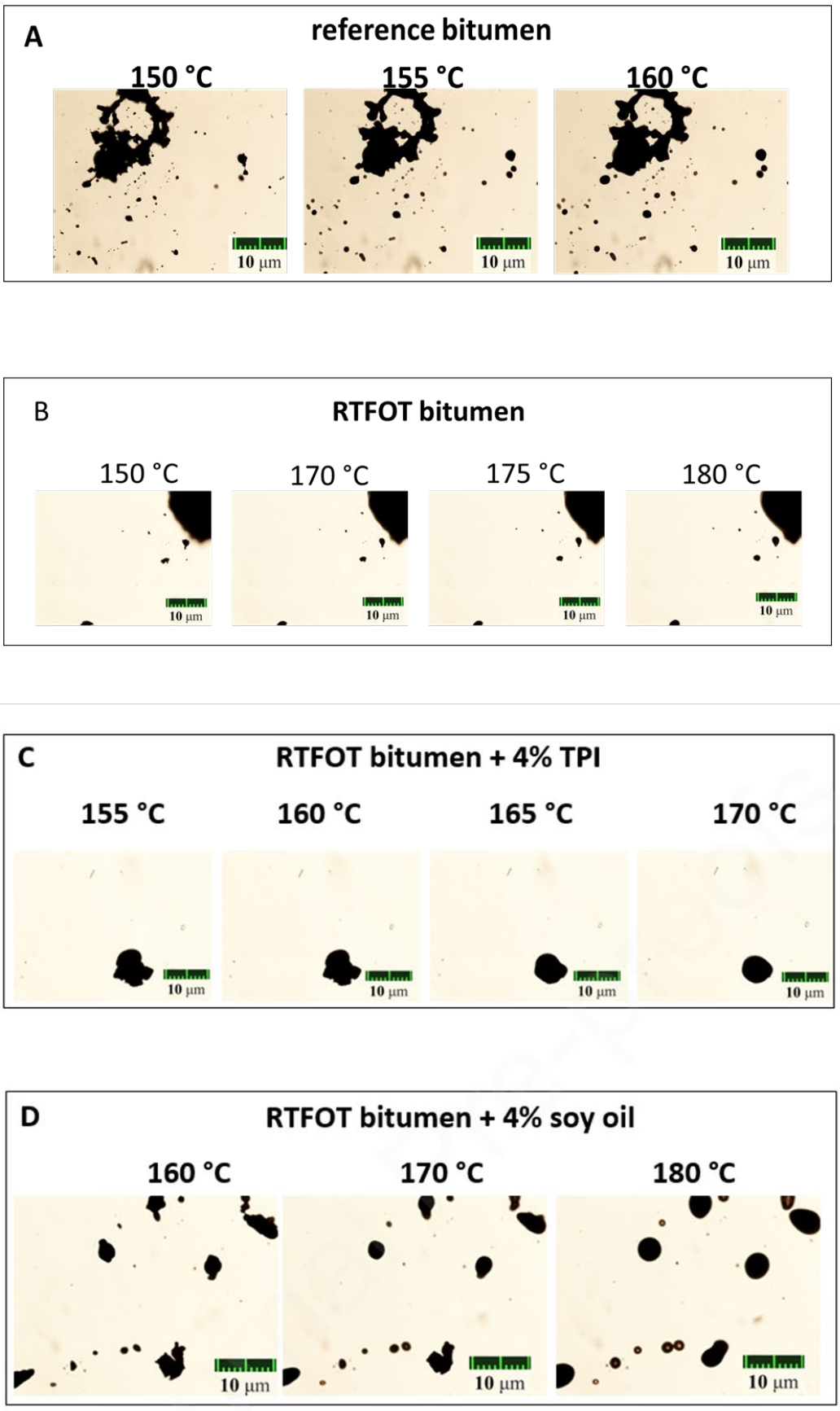

Fig. 3. Images from optical microscopy of the various samples at the temperatures shown.

3.3 Atomic Force Microscopy

Atomic Force Microscopy (AFM) has been proven to be suitable probe to study bitumens morphology at the microscopic level [42]. Furnishing the imaging of the mechanical characteristics of the observed parts [43] and giving information on the supramolecular self-assembly in this kind of material [44]. In Fig 4, the topography (first column) and phase (second column) images of the studied samples (different rows) are shown.

As it can be seen, the topography and phase images usually match. In the pristine bitumen, elongated clusters of 1-2 μm, with a rippled interior with sub-nanometers edges and dispersed in a quite uniform matrix, can be clearly seen. These aggregates can be safely considered to be made of asphaltene molecules organized in a hierarchical aggregation pattern and in accordance with previous structural observations [45]. This feature is quite well known in the literature, being dealt with as "bee structure" [46] and has been already observed in previous papers [19].

Although in aged bitumen, the domain sizes are similar as compared to those observed in pristine bitumens, the interconnection of the domains appears to be greater in the case of the aged bitumen. This justifies the increased viscosity and stiffness in this sample. In the soy oil and TPI – containing samples, the domains appear to be larger but in the case of the TPI, they seem to be less connected than in the soy oil case. In the phase images, it is observed that the soft part of the sample (dark part) covers a higher surface fraction in reference bitumen than in aged bitumen where the clear part (hard areas) prevails. This is due to the oxidation of the bitumen during the aging process. The right column of Fig. 4 reports the relative abundance (percentage) of the phase values. Two bands are clearly visible: one is centred at lower phase values and connected to the soft, maltenic, faction, and the other one is centred at higher phase values and connected to the harder, asphaltenic, part of the sample.

It is worth noting, first, that in the various samples the bands are centred at different phase angles, that means that the hardness itself of the two regions is different. In aged bitumen, indeed, the peaks are shifted to higher phase angles with respect to the pristine bitumen, meaning that both soft and hard regions are harder than the corresponding soft and hard regions of the reference bitumens. This can be somehow expected after an ageing process, since it causes an increase in the fraction of the hard region which hinders the dynamics of the remaining softer part obliging it to a tighter packing and consequently to a higher hardness. In the images relating to the samples with the addition of the regenerating additive TPI, an increase in the fraction of the soft areas is observed as well as a shift back to lower phase angles which resembles the images for non-aged bitumen. Samples with soy oil, instead, showed very similar images to those recorded for aged bitumen. A different visualization, obtained with the 3D reconstruction, is also reported (third column).

As a conclusion, AFM analysis seems to be able to distinguish the rejuvenating effect from a mere fluxing one. In fact, AFM probes a structural aspect directly connected to the polarity of the asphaltene molecules, therefore catching changes in the chemistry of the material under study. These effects can be justified considering for the chemical nature of the two additives: soy oil is essentially an apolar fluid, so it is expected that it will be localized within the more apolar part of the bitumen (maltene); on the other hand, TPI has a phosphate headgroup which can establish stronger (polar) interactions. The possibility to establish strong interaction of molecules possessing a phosphate group has been recently pointed out [47].

In these systems, the simultaneous presence of a polar phosphate group and an apolar molecular moiety, renders organic phosphates truly amphiphilic molecules, for which particular self-assembly is expected. In particular, a specific localization with the phosphate group strictly interacting with the asphaltene polar domains can be safely hypothesized, with the rest of the

molecules pointing towards the apolar (maltene) region, most probably interacting with nearby resins since these ones are located at the same asphaltene/maltene interfaces. However, it is to be considered essential that if several amphiphiles are close to each other they can give rise to peculiar self-assemblies [48] with unexpected emerging properties and dynamics [49, 50] up to the formation of ionic liquids [51]. Consequently, the characteristic effect of the TPI is due not only to its peculiar structure, but also to the combined action with the other stabilising amphiphiles naturally present in the bitumens.

The complex self-assembly of amphiphiles has been recently highlighted for specific applicative purposes in various applications of inorganic, organic and pharmaceutical fields [52–59] and this clearly shows the enormous potentialities of such strategy. So, in the specific, we strongly support research in this direction to easily find additives for bitumens with high added-value.

This methodology will also make it possible to establish, by means of sampling (coring) in situ and extraction of the binder, both the degree of aging of a road so as to be able to plan any maintenance interventions, and to verify, in cases where the road pavement has been built with a certain fraction of recycled material (Recycled Asphalt Pavement, RAP), the quality of the conglomerate and the successful regeneration of the bitumen can be ascribed to the RAP. In fact, the bodies proposed for quality control (such as ANAS in Italy, NCAT and NAPA in U.S.A., etc.) currently do not have laboratory methods capable of distinguishing whether an aged bitumen has actually been regenerated or simply softened so as to make it workable during the production of the conglomerate but not suitable for supporting the traffic loads of a road in when it will continue to have glassy properties due to oxidation of the binder. For example, in the ANAS Special Tender Specifications there are not the standards or methods to distinguishing whether an aged bitumen has actually been regenerated or simply softened but there are only standards or methods to evaluate the performance of the physical properties of the binder/conglomerate/road pavement [57].

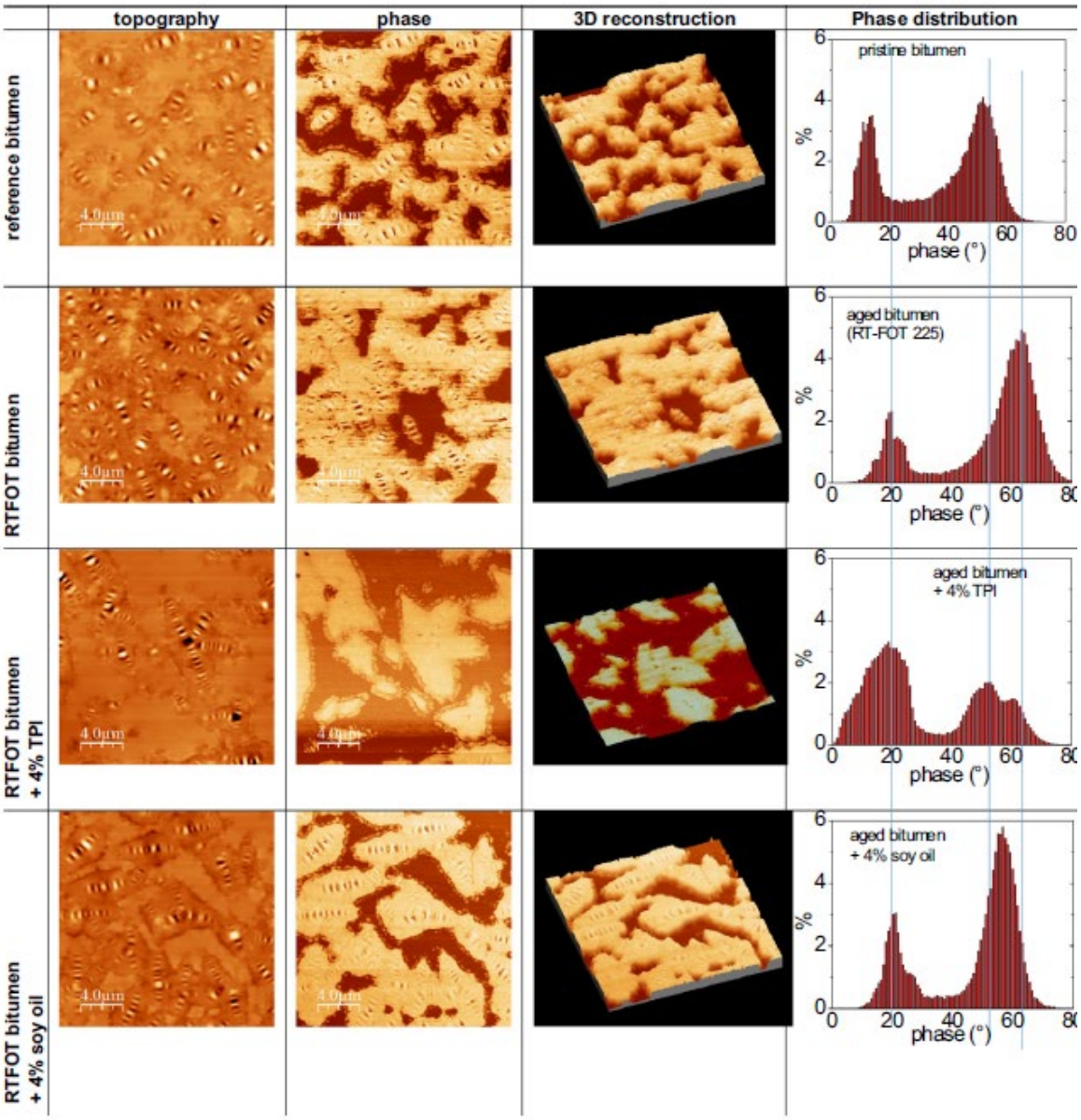

Fig. 4. AFM images of the studied sample. Each panel, reports in clockwise order, the topographic, the phase image and the 3D (black background) reconstruction

3.4 Infra-Red Spectroscopy (IR)

FTIR is a well-known method for investigating the chemical changes in bitumen due to aging as it probes different functional groups and molecular bonds [58].

As can be seen from perusal of Fig. 5, where the absorbance spectra of the studied samples are reported, marked differences can be highlighted. Of particular interest are:

1. the peak around 750 cm^{-1}, which can be assigned to the C-S stretching;
2. the peak around 1215, which can be assigned to the stretching of C-O-C in ethers and/or of S=O in sulfonic acids;
3. the peak occurring around 1460 cm^{-1} o the peaks related to the asymmetric vibration of CH_2 and CH_3 [59];
4. the multiplet in the 2750-3050 range (CH_2 and CH_3 symmetric and antisymmetric stretching) hereafter referred to as 3000 cm-1, for simplicity.

It should be emphasized that in the literature some peaks attributions are non-univocal and sometimes also questionable, probably due to the complexity of the material under investigation. So, in these cases, we referred to classical academic textbooks [60]. It is also important, for this investigation, to stress that the first two peaks are attributed to oxidized parts of asphaltenes, whereas the other two (peak # 3 and #4) are attributed to the hydro- carbonaceous part of the bitumen.

Since the IR spectra have been recorded on samples prepared by weighing the same amount of the respective bitumens, some qualitative comments from the visual inspection of the variations in peaks intensity can already be made. It can clearly be seen that ageing causes an increase of the peak at 750 and 1215 and a reduction of the other two signals. This is ascribed to the ageing, in which oxidation causes a chemical towards the formation of oxidized functional groups. Self-consistently, the addition of soy oil causes a moderate return of the intensity of each of these peaks to its pristine value. More markedly, TPI causes a return to values comparable to the pristine ones.

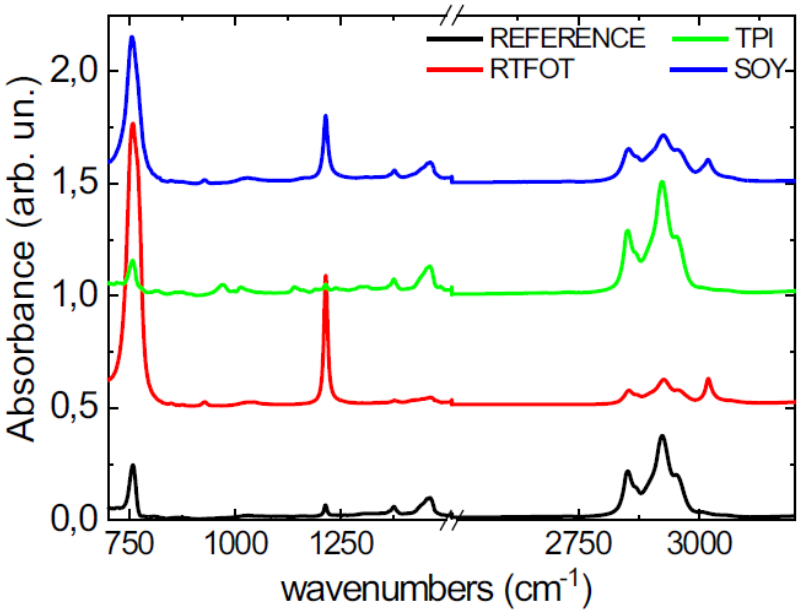

Fig. 5. IR spectra for the studied samples. Spectra are vertically shifted for clarity sake.

To make a more quantitative analysis, the ratio of the intensity of a peak (peak #1 or #2) attributed to an oxidized part of the material over the intensity of a peak (peak #3 or #4) attributed to a hydro-carbonaceous part was calculated. Being ratios of different peaks they would show relative intensities, a strategy adopted in the literature [61–63] to face the fact that the absolute intensity of an IR peak can be hardly be treated quantitatively.

The obtained ratios are reported in Table 1. In this table, the subscripted numbers report the wavenumbers of the peaks under consideration; for example, the I_{750}/I_{3000} ratio represents the intensity of the peak at 750 cm^{-1} over the intensity of the peak at 3000 cm^{-1}. Let's take into consideration any of them: it can be seen that this ratio markedly increases with aging as a result of the formation of oxidized functional groups at the expenses of C-H aliphatic groups. Soy oil is able to reduce the value but it is not able to restore it to its pristine value. On the other hand, TPI exerts a stronger effect pushing back the value to the pristine one, and even lower. Self- consistently, the same consideration can be made if all the other ratios are considered.

Table 1 Peak Intensity ratios discussed in the text

Sample	I_{760}/I_{1460}	I_{760}/I_{3000}	I_{1215}/I_{1460}	I_{1215}/I_{3000}
Reference bitumen	2.5	0.7	1.0	0.3
RTFOT bitumen	25.4	9.8	11.8	4.5
RTFOT bitumen + 4%TPI	1.1	0.3	0.4	0.1
RTFOT bitumen + 4%soy oil	6.9	3.1	3.2	1.4

This analysis clearly shows that the changes made by ageing can be partially cancelled by soy oil, but TPI shows a stronger power being able to restore the chemistry of pristine bitumen. FTIR seems, therefore, to be able to distinguish a rejuvenating additive from a mere fluxing agent. In fact, FTIR is able to probe the functional groups of the material under study, therefore catching changes in its chemistry. IR spectroscopy is already used in the road paving sector to identify the presence of some additives such as adhesion promoter within the bitumen used for bituminous conglomerates. Therefore, a methodology based on the use of an instrumentation already present in the various technical annexes, specifications, etc. made by the bodies responsible for the construction of road pavements, will facilitate its diffusion within the sector and will allow all laboratories involved in the quality control of bituminous conglomerates (such as ANAS, NCAT, NAPA, etc.) to be able to introduce further information, relating to the rejuvenation of bitumen, without having to make investments on equipment or qualified personnel.

Conclusions

Given the now well-established difference between a simple fluxing agent and a real rejuvenator to restore the mechanical properties of an aged bitumen to the pristine performances, we have investigated the capability of the techniques most common in bitumen analysis to distinguish between the two.

We have shown that oscillatory rheometry is not fit for this purpose, whereas optical and atomic force microscopies and infrared spectroscopy can be. The possibility to make this distinction with instrumentation available in common laboratories will introduce further information on to the rejuvenation of bitumen, allowing the quick and effective quality control of the additives to be used as regenerants for bitumen and without further investments on equipment or qualified personnel.

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5.5 Results Part 4

"Effects and mechanism of Rejuvenation of Field-Aged bitumen extracted from Reclaimed Asphalt Pavement"

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1. Introduction

In recent years, research in the asphalt sector has led towards the reuse of reclaimed asphalt pavement (RAP) for the production of recycled asphalt mixes to be used for new road paving operations. A major stumbling block of this initiative is that bitumen which is present in RAP has undergone aging making it stiff and brittle and thus is not ideal for use in new paving processes. In order for this RAP bitumen to be ideal for use in new road pavements, its mechanical properties have to be restored to a state closer to that of virgin bitumen. Road pavements, made up of micro-meter sized stone particles (aggregates) and bitumen (aggregates wt% ~95%), are naturally subject to aging phenomena which compromise their performance (Prosperi and Bocci, 2021; Loise et al., 2019). Bitumen is a hydrocarbon-rich, soft, black material composed of several components and is a by-product of petroleum industry processes. For this reason, its chemical composition is complex as it is composed of various substances and it's often necessary to utilize specific additives to improve its mechanical properties (Caputo et al,2018 ;2020). There are several factors that influence asphalt aging such as working temperature, storage and climatic conditions, etc.

Actually, the part susceptible to aging is the bitumen binder, which holds the asphalt conglomerate together and is responsible for the changes in the mechanical properties of the road pavement (Sirin et al., 2018). This change, due to an increase in the larger and heavier molecules of the bitumen, i.e. increase of the asphaltenic component, leads to cracking (Wang et al., 2020; Loise et al., 2021). Reclaimed asphalt pavement is obtained from the removal of aged road pavements: this contains about 4 – 6% of bitumen, as well as aggregates which are still in decent reusable condition (Xu et al., 2022; P. Caputo et al,2020).

There are several studies concerning bitumen aging and rejuvenation and most of these studies focus on the behaviour of bitumen modified with elastomeric or plastomeric polymers upon aging (Wang et al., 2019; Celauro et al., 2020; Feng et al., 2021; Sun et al., 2021; Cuciniello et al., 2021). Different products and substances have been used in recent years to mitigate the problem of bitumen aging. Several other studies also entail the use of nanomaterials as bitumen modifiers (Liu et al., 2017; Cheragian and Wistuba, 2020,2021; dell'Antonio Cadorin et al., 2021; Moretti et al., 2021; Han et al., 2021; Anwar et al., 2021). The bitumen obtained from RAP has a lower penetration and a higher

viscosity than that of virgin (non-aged) bitumen. In any case, the aging effect can be counteracted by treating RAP bitumen with rejuvenating agents which can not only reduce its stiffness, viscosity and brittleness, but also act on the internal structures by restoring the maltene/asphaltene balance (Loise et al., 2020). This paper aims at verifying the effectiveness of a rejuvenating agent tested on a bitumen obtained from RAP.

2. Materials and Methods

2.1. Materials and Sample Preparation

For this study, field-aged bitumen extracted from RAP was used. This aged bitumen was modified with a rejuvenating agent RRD supplied by Iterchimica S.p.A, Italy. The additive was added to the aged bitumen in a proportion of 6% (by weight of bitumen binder). In order to modify the aged binder, it was heated to a temperature of 150° C and the rejuvenator was added to the binder under constant stirring for about 30 minutes so as to obtain a homogenous sample. The two samples: Field Aged Bitumen (FAB) and Field Aged Bitumen containing the rejuvenating agent (FAB + RRD) were tested using techniques mentioned in section 2.2.

Table 1. Some of the given properties of RRD rejuvenating agent

Characteristic	RRD Additive	Method
Aspect	Liquid	-
Colour	Yellow	-
Viscosity (cP)	25-50	AOCS Ja 10-87
Pour point (° C)	⩽-5	ASTM D97
Chemical nature	Mix of amino derivatives	-

As can be seen in table 1, the rejuvenating agent is in liquid state can be easily mixed with bitumen binder under agitation and constant heating to provide a uniform dispersion in bitumen's colloidal matrix.

2.2. Techniques and testing methods

In this study, four techniques were used to evaluate the efficiency of the rejuvenating agent namely: Dynamic Shear Rheology (DSR), Differential Scanning Calorimetry (DSC), Atomic Force Microscopy (AFM) imaging and another imaging technique called asphaltene melting point using light microscopy.

Dynamic Shear Rheology

Rheological analysis was carried out on both samples using a Dynamic Stress Rheometer (SR-5000, Rheometric Scientific, Piscataway, NJ, USA) having a parallel plate geometry with 25mm diameter, using a 2mm gap. The frequency was set at 1 Hz and the stress at 100 Pa. A Temperature Sweep commonly known as time cure test was carried out on the samples from 25 °C -120 °C with a heating rate of 1 °C per minute. This time cure temperature ramp was performed to determine the temperature at which the bitumen transitions from its initial semi-solid state to a liquid state. All rheometric measurements were carried out in the viscoelastic regime.

Atomic Force Microscopy

Atomic Force Microscopy (AFM) analysis was carried out using a Nanoscope VIII Bruker Microscope. The microscope was set to tapping mode with cantilever oscillations regulated close to its resonance frequency (150 Hz). Phase and topography images were taken simultaneously. The images obtained were developed and elaborated using the instrument-branded software.

Differential Scanning Calorimetry

Calorimetric measurements were carried out on a SETARAM 131 instrument under constant nitrogen flux. A thermal ramp was carried out from 25 °C – 250 °C at a heating rate of 20 °C/min in order to determine the glass transition temperature of the asphaltenes. The calorimetry analysis was carried out on the asphaltene samples derived from the deasphaltenization process.

Light Microscopy of Asphaltenes

Light microscopy analysis of the asphaltenes was carried out using a Prior Scientific Instruments MP3500K microscope coupled with a Eurotherm 246 thermoregulator which was connected to a heating panel placed on the stage of the microscope. This made it possible to microscopically observe in real time the behaviour of the asphaltenes with a gradual increase in temperature and then determine the melting point of the asphaltenes. This light microscopy technique involves separating the asphaltene fraction from the bitumen (deasphaltenization) via precipitation using differential solvents [ASTM D4124-09, 2018] and then subjecting the asphaltenes to gradually increasing temperature while under light microscopy observation in order to determine the glass transition temperature T_g of the asphaltenes.

3. Results and Discussion

3.1. Dynamic Shear Rheology

Bitumen is a viscoelastic material having both a viscous and elastic response to mechanical stress. By increasing temperature, a transition is observed when the elastic modulus becomes negligible in comparison to the viscous one: in this condition bitumen thereby turns into a liquid state. This transition temperature is that at which the loss tangent (tan delta) shows a typical steep increase, as shown in Figure 1. That being stated, oxidative aging changes bitumen's micro structure due to the fact that the asphaltenes which represent the rigid fraction of bitumen, incorporate oxygen atoms and thereby are subjected to aggregation, forming bigger clusters. An increase in the size of the asphaltenes clusters in bitumen's matrix translates into an increased rigidity of the bitumen which makes the bitumen brittle and prone to cracking and breaking when it is in its solid state. This is the factor responsible for the cracking of old asphalt pavements. The increased rigidity of bitumen after aging is responsible for the higher transition temperatures observed during rheological studies of aged bitumen. The rheological measurements carried out showed that RRD rejuvenating agent was able to improve the bitumen mechanical properties, making it softer and thus reducing its transition temperature to values similar to those usually observed for unaged 50/70 bitumen as shown in Figure 1 (Loise et al., 2020).

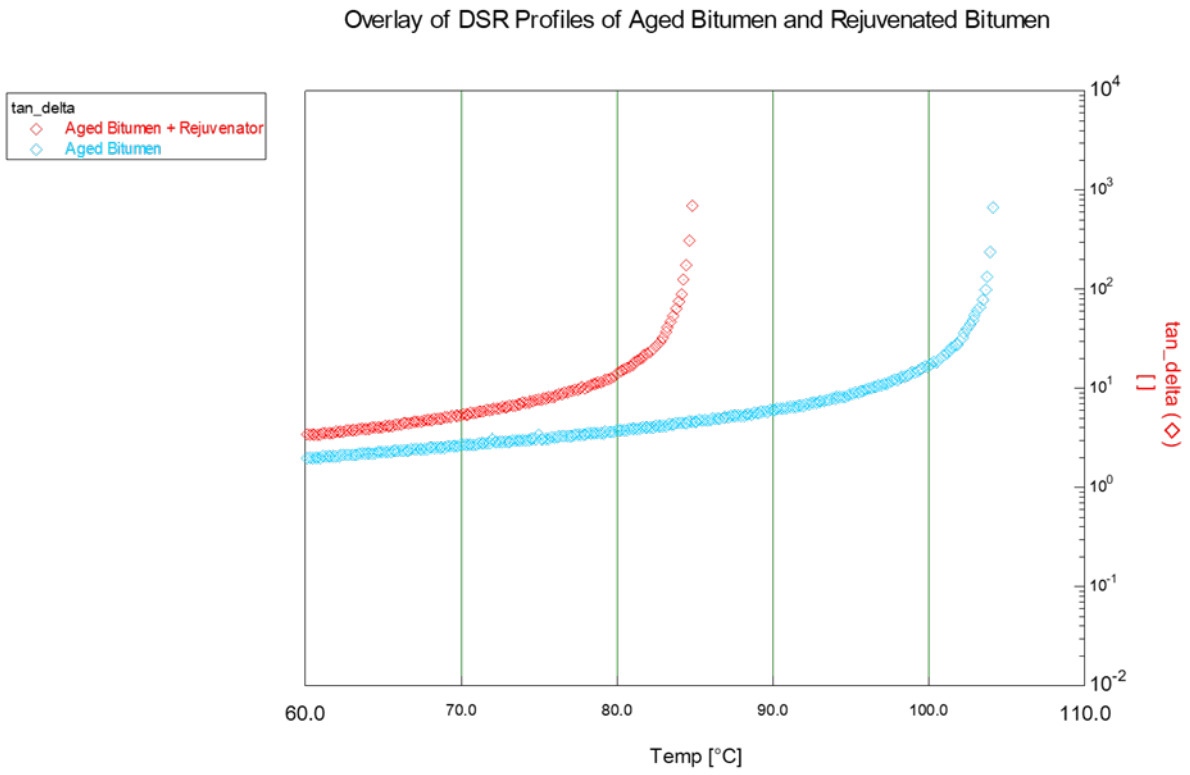

Figure 1: Tan delta versus temperature of the aged and rejuvenated bitumen samples

As seen in Figure 1 and the values shown in Table 2, the transition temperature of the Field Aged Bitumen (FAB) sample is significantly higher (103.9 °C) than that of the sample modified with RRD (84.3 °C) i.e the aged bitumen is more rigid than the rejuvenated one. The reduction in the transition temperature of the RRD-modified sample could be evidence that the rejuvenator recovered some of the aged binder's lost mechanical properties thereby improving its performance so that the Field Aged Bitumen (FAB) obtained from RAP can be reused in new road paving operations. However, rheological analysis is not enough to provide a concise understanding of how the additive rejuvenates aged bitumen and so other more detailed techniques which investigate the changes in bitumen's inner structure are required. For this reason, the following sections will show the physico-chemical investigations to probe this aspect.

Table 2: The transition temperatures obtained from the rheological analysis of the samples

Sample	Transition Temperature ±0.1(°C)
Field Aged Bitumen	103,9
Field Aged Bitumen + 6% RRD	84,3

3.2. Atomic Force Microscopy

Atomic Force Microscopy (AFM) studies provide a great deal of information on bitumen's internal structure. In AFM studies of bitumen, four phases are usually observed consisting of Catana phase (also called bee structures) Peri phase, Para phase and Sal phase. These aforementioned phases are said to correspond to bitumen's SARA fractions although different researchers have differing opinions and interpretation of information obtained from bitumen AFM studies and thus there is no

general consensus on this subject matter at the moment (Tabatabaee and Kurth, 2017; Leusueur, 2009; Pauli et al., 2001; Loeber et al., 1996; Jager et al., 2004). The bee structures (Catana phase) are said to correspond to the asphaltene fraction of bitumen (some researchers refer to it as crystallized paraffin of bitumen as well) while the resins, aromatics and saturates are said to the Peri, Para and Sal phases respectively which generally represent the maltenic fraction (soft, oily part) of bitumen (Li et al., 2020; Fischer et al., 2014; Masson et al., 2006; Tarpoudi Baheri et al., 2020; Yang et al., 2018).

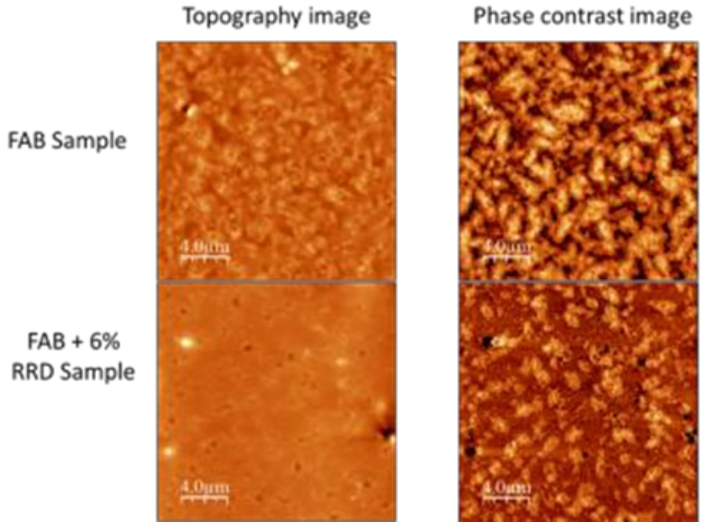

Figure 2: AFM Images of the field aged bitumen and RRD-modified bitumen samples.

From figure 2, it can be observed that the Catana phase (bee structures) of the FAB sample is significantly larger than those of the FAB + 6% RRD sample. The other phases are scarce and relatively constitute the minority of the inner structure of the aged bitumen sample. In the FAB + 6% RRD sample, it can be seen that the size of the bee structures has been reduced and there is a wider distribution of the peri, para and sal phases. This could mean that the rejuvenated sample has been made softer due to the increase of the maltenic fraction and a reduction in the size of the asphaltene and their clusters.

As observed especially from the phase contrast image of the FAB sample, the aged bitumen shows the presence of hard crusts that represents the asphaltenic fraction which has become oxidized via aging and thus increased in size due to the incorporation of oxygen. The asphaltenes in this sample became bigger thus depleting the maltenic fraction in bitumen's colloidal system and increasing the bitumen's rigidity. On the other hand, the RRD-modified sample shows asphaltenic domains (bee structures) which are smaller in size compared to the aged bitumen. The phase contrast image also shows an increase in the size of the maltenic fraction (dark domain) which translates to a softer texture of the modified bitumen.

3.3. Differential Scanning calorimetry

The asphaltenes extracted via deasphaltenization were subjected to calorimetric analysis. The glass transition of the samples was evaluated from the DSC profile of each sample. The inflection point typical of glass transition of asphaltenes represents the temperature at which the asphaltenes transition from a crystalline state to an amorphous state. The DSC profile shows that the typical glass transition inflection point of the aged bitumen is almost 20°C higher than that of the sample modified with the rejuvenator.

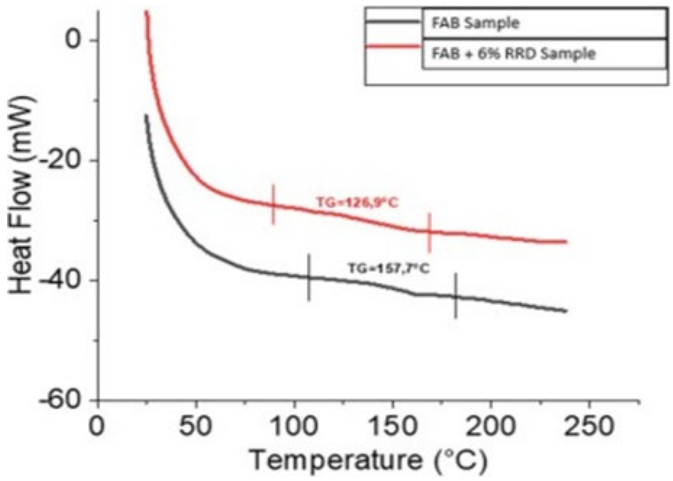

Figure 3: DSC Profiles of Field Aged Bitumen and RRD-modified bitumen.

As indicated in figure 3, the higher inflection point of the aged bitumen sample (157.7 °C) means that the asphaltenes of the FAB + 6% RRD bitumen which have a lower glass transition (126.9 °C) are more similar to those usually observed for virgin bitumen (Loise et al., 2020). This is due to the fact that upon aging, the asphaltenes in bitumen form clusters and become more rigid thereby increasing the glass transition point (Caputo and Oliviero, 2021; Calandra et al., 2019; Hoepfner et al., 2013; Headen et al., 2017; Porto et al., 2019; Goual et al., 2011). The calorimetric analysis indicates the effectiveness of the rejuvenating additive on aged bitumen as shown by the values in Table 3.

Table 3: Glass transition temperatures (Tg) of the asphaltenes of aged and modified bitumen samples

Sample	Glass Transition (°C)
Field Aged Bitumen	157,7
Field Aged Bitumen + 6% RRD	126,9

3.4. Light Microscopy of Asphaltene Melting Point

Light Microscopy analysis was carried out on the asphaltenes subjected to steadily increasing temperature. This technique is based on the same concept of calorimetry which indicates that aging causes the asphaltenes to have inflection points (in this case, melting point) at higher temperatures compared to asphaltenes usually observed in non- aged bitumen (Caputo and Oliviero Rossi, 2021). Figure 4 shows that the asphaltenes derived from the aged bitumen melt at a temperature 25 °C higher than that of the RRD-modified samples.

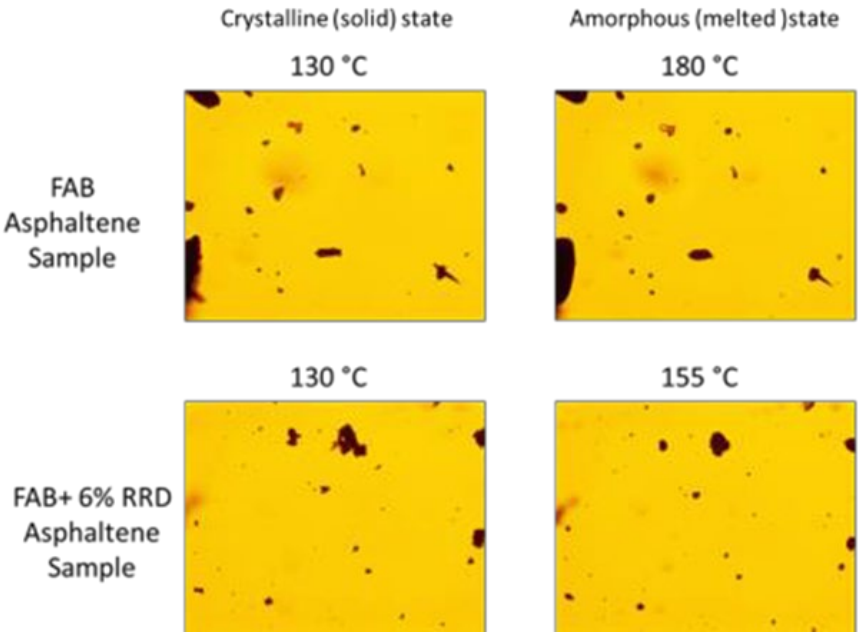

Fig. 4. Light microscopy images of the asphaltene samples with their respective melting points.

When an additive with a rejuvenating effect is added to aged bitumen, it interacts chemically with the asphaltenic part of the bitumen. This enables the restoration of the aromatic components and the reduction of the oxidized parts. This reduces the size of the asphaltene clusters and above all gives the asphaltene sample a chemical composition very similar to what is usually observed in non-aged bitumen (Prosperi and Bocci, 2021). Once again, this evidences the efficiency of the additive in reversing the effects of oxidative aging on bitumen as indicated by the values shown in Table 4.

Table 4: Melting point of the asphaltenes of aged and modified bitumen samples

Sample	Melting Point (°C)
Field Aged Bitumen	180
Field Aged Bitumen + 6% RRD	155

4. Conclusions

In recent years, researchers working on bitumen technology have sought to find ways to rejuvenate aged bitumen extracted from reclaimed asphalt pavement due to the current existing incentives to recycle and conserve resources and the environment in general. Results obtained in this study could help in standardizing the detection of rejuvenating effect in bitumen additives, thus fostering the recovery, recycling and re-use of aged asphalt pavements for the durable production of new asphalt pavements. This study showed that rejuvenating additives are effective in restoring bitumen's properties which have been lost via oxidative aging. Considering the results obtained from all the techniques carried out in this study, it can be said that the RRD additive is an effective rejuvenating agent. The rheological studies showed that the mechanical characteristics of aged bitumen can be recovered, AFM studies showed that a rejuvenator can modify and reverse the effects of aging on bitumen's inner structure, DSC and light microscopy studies also indicate that an efficient rejuvenator would interact chemically with aged bitumen, restoring its aromatic components. The authors believe that the results provided by this study could be insightful and promising for developing an advanced method for investigating the rejuvenation action of rejuvenating agents in the ambit of recycling Reclaimed Asphalt Pavement (RAP).

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Chapter 6

Biomaterial Additives in Warm Mix Asphalt

6.1. Results Part 5

"How Organic waste improves Bitumen's characteristics"

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1. Introduction

Waste management is a problem of growing concern globally and industrialization amongst other avenues of waste production has contributed significantly to the production of organic waste in recent years. This has led to waste management problems as conventional waste disposal methods are not eco-friendly and are mostly inefficient [1]. About a million tons of waste are produced globally every day and incineration which is arguably the most common conventional waste disposal method is known to produce over 200 different types of toxic compounds such as nitrous oxide, sulphuric acids, fluorides, hydrogen chloride [2, 3]. Research in recent years is drifting towards looking for sustainable ways such as reducing landfill usage to treat and manage the environmental impact brought about by waste products that are produced from human and industrial activities in the 21st century. This has facilitated the drift of research towards the development of green eco-friendly technologies to recycle waste thus creating a circular economy [4–10].

In the road pavement sector, bitumen is used as the binder for preparing asphalt conglomerate. More often than not, conventional bitumen does not have all the performance requirements for road pavement construction. These roads, depending on the geographical location, are increasingly subjected to conditions such as heavy traffic, harsh climatic conditions, oxidation and heavy loads. If the bituminous mixture obtained does not meet these performance requirements, the bitumen binder needs to be modified with additives to improve its performance thereby improving the performance of the asphalt conglomerate as a whole [11–13]. Most additives on the market are not eco-friendly and research in this field keeps looking for more eco-friendly and sustainable ways to improve asphalt performance. Bitumen is a viscoelastic complex mixture of organic compounds derived from the heavy petroleum fractionation process in the refinery. It is a substance used to bind inorganic conglomerates in road pavement preparation. This binder is mixed with the aggregates at high temperatures, and the presence of oxygen causes the bitumen to undergo strong oxidation which is a detrimental process reducing its mechanical characteristics.

In order to limit oxidation, specific additives are added to the bitumen before the mixing process. On the market, there are no eco-friendly additives [14, 15] and so recent attention is being paid to ecological additives with high performance in order to reduce the oxidation process [16–18]. Since further oxidation can take place also after paving in a slower process called ageing which also involves loss of more volatile components and structural aggregations [19], the same problem holds

also for longer times. For this, additives, usually based on strong acids or bases, are present on the market [20–22], but eco-friendly additives are recently being studied [23–28].

The idea to use eco-friendly substances can be extended to eco-friendly processes such as the recycling of aged road pavements (the so-called Recycled Asphalt Pavement – RAP) to be partially reused in new road pavements while maintaining the performance and duration of the latter over time [29–31]. Also in this case, specific (regenerating) additives, generally based on amines, surfactants, oils, etc. are used [32–34]. To make the whole cycle entirely eco-friendly, research in recent years has focused on the use of recycled material from wastes to create new environmentally friendly additives for improving road pavement characteristics, with obvious advantages in terms of environment protection and safeguarding of human health [35–37].

Furthermore, the problem of the disposal of organic waste exists all over the world and so the purpose of this work is to identify possible reuse of this type of waste as an additive for road pavements in accordance with a circular economy facilitated by circular chemistry practices which are constantly gaining widespread acceptance in the industrial research sector [38–41]. One major limiting factor of organic waste is that there is never a homogeneous composition. This composition changes according to the nation, the geographical area, the number of inhabitants, ethnic culture, etc. To further improve the quality of the waste, it was chemically pre-treated (FENTON process) in the laboratory. On the final samples, rheological measurements were performed and to evaluate the performance of the additives as an antioxidant, the aging process in the plant was simulated in the laboratory using Rolling Thin Film Oven Test.

2. Experimental part

Waste was obtained in the ambit of the project "RESIFAC" (realization and experimentation of pilot plants for fast composting of civil and industrial organic waste). In the present study our attention is focused on the organic fraction of municipal solid waste, which includes food residues or food preparations and assimilable fractions, and which constitutes more than 30% of the total weight of municipal solid waste. Such residues were collected through a sampling procedure lasting 12 days. On each of these days, waste was taken from a group of four different families, each day a different one. The waste collected on each sampling day (about 5 kg) was mixed and milled to a millimeter size by means of a steel blender. The resulting minced material was stored at -20 °C for 12 days. After this time, all the daily rates were defrosted and mixed; the material obtained was divided into bags of 200 g, re-frozen and then used after heat treatment at 110 °C. This was the starting matrix for the oxidative treatment. The oxidation reaction [42] was carried out using a laboratory-scale glass reactor apparatus. The compounds which are mainly oxidized by Fenton reagent are aromatic and aliphatic hydrocarbons. The details are reported in the work by Salvino et al. [43] which gives details on the whole oxidation process. The sample of organic material, 200 g, was placed into the glass reactor and the Fenton reagents were added: 10 mL of a $FeSO_4$ solution followed by the addition of 10 mL of hydrogen peroxide (H_2O_2) solution. The mixture was kept under stirring conditions, the reactor was placed in a water bath, and the internal temperature was kept at 60 °C for the duration of the reaction. The pH of the mixture, initially at 4.5, changed to 3.0 during the reaction. The samples used were collected during the phases of oxidation procedure and were differentiated according to the different percentages of $H_2O_2/FeSO_4$ used [43]. Six samples were prepared at different concentrations of $FeSO_4$ and H_2O_2 as shown in Table 1. Sample 1 is the reference sample and was not treated with either $FeSO_4$ or H_2O_2. Samples 2, 3 and 4 had the same percentage of $FeSO_4$, 0.05%wt, but different concentrations of H_2O_2, i.e., 0.002%wt, 0.015%wt, and 0.02%wt respectively while for samples 5 and 6, $FeSO_4$ was added in the percentage of 0.04% and 0.03% respectively and the H_2O_2 percentage was constant at 0.002%.

Table 1: Different percentages of H_2O_2 and $FeSO_4$ used for treating the waste samples in FENTON process

Sample	% $FeSO_4$	% H_2O_2
CD1	-	-
CD2	0.05	0.002
CD3	0.05	0.015
CD4	0.05	0.02
CD5	0.04	0.002
CD6	0.03	0.002

Dynamic rheological analysis, including viscosity measurements (steady state), Time cure and Frequency Sweep experiments, were recorded from room temperature up to 120 °C. All rheological measurements were carried out using an SR5000 rheometer (Rheometrics, Piscataway, NJ, USA) controlled by shear stress and equipped with plate geometry (2 mm gap, 25 mm diameter).

3. Results and discussion

Bitumen with a penetration grade of 50/70 was used and this bitumen was aged by means of standardized oxidative processes Rolling thin film ovens (RTFOT) according to the EN 12607-1 standard [44]. This was done in order to create an "aged" reference to be treated with the additives. Both additives were added to the aged bitumen at a dosage of 2% by weight of the binder [45, 46]. This percentage was used because it appears to be the one commonly used for the regenerating additives available on the market. The resulting samples were analysed by dynamic and stationary rheological measurements to understand the effects on the mechanical properties and also on the structural and morphological variations induced by the single additives on the bitumen itself.

3.1. Viscosity tests

The rheological analysis was done more thoroughly by recording the mechanical spectra. To study the effect of the various additives on the rheological behaviour of bitumens, viscosity measurements were carried out at different temperatures for all the samples. Figure 2 shows the viscosity values for the various samples at the temperatures of 60, 80, 100, 120 °C. First of all, it must be noted that the general sharp decreasing of the viscosity with temperature is expected. This is the consequence of the disordering effect of temperature in soft matter since the thermal motion can easily loosen the bonds hold up by weaker interaction, which are quite common in soft matter and complex systems. As it can be seen, the only sample that brings a significant increase in viscosity and consequently shows good capabilities as a viscosifier is the CD2 sample. Its values appear to be higher while all the other samples show small variations with respect to the reference systems. It worthy to note that this speculation is valid at different temperatures (60, 80, 100, 120 °C).

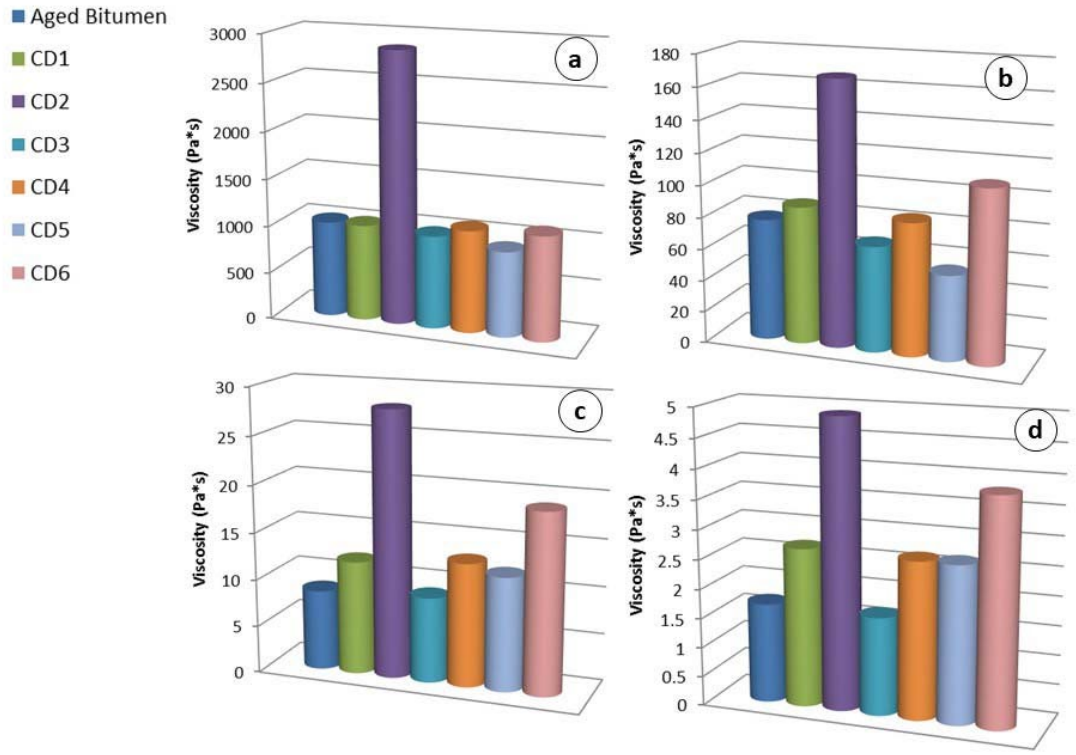

Fig. 1: Viscosity (steady state) of all the samples at different temperatures: a) 60 °C, b) 80 °C, c) 100 °C and d)120 °C.

As a consequence of this finding, CD 2 will be selected as the representative of all the FENTON-treated samples in the other tests. We can try to give an interpretation of why the relative influence of the different additives does changes with temperature. We think that the lower amount of hydrogen peroxide in CD2 sample can guarantee disruption of bigger molecules (fat, proteins) into small components (fatty acids, peptides, alcohols) which are responsible for the observed behaviour (see for example the effect of polysaccharides [25]) preserving their integrity without further molecular fragmentations. Further oxidation would further deteriorate the organic waste to smaller chemical species with no action in the bitumen structure. Of course, due to the heterogeneities of the organic materials involved, the reaction pattern is complex with many chemical species involved, and this justifies why the relative influence of the different additives change with temperature.

3.2. Anti-aging tests

The effect of an anti-aging agent is evaluated by observing the plastic-fluid transition temperature as probed by rheometry [47–50]. Upon increasing temperature, G' monotonously decreases, but at a certain temperature it suddenly drops. This is the temperature at which the binder can be considered almost as a Newtonian fluid, so from the microscopic point of view, it can be intended as the temperature at which the thermal motion is sufficiently high to destroy the whole structure and therefore no storage of energy can be afforded by the sample.

Now, aging generally causes an increase in the transition temperature due to the oxidation of components; an additive must limit this phenomenon, maintaining the transition temperature, after aging, very similar to that of non-aged bitumen. From Table 2, it can be seen that the organic waste did not bring any significant improvement compared to the starting bitumen leaving the transition temperature almost unchanged. The additive obtained from FENTON treated organic waste, CD2, at

the same concentration 2% demonstrated a stricter interaction with bitumen, increasing the transition temperature of the unaged bitumen as well as the aged bitumen. However, the increase in the transition temperature when passing from unaged to aged bitumen (about 6 °C) is about of the same magnitude as in the case of non-additivated bitumen and the CD1- additivated bitumen (4 °C).

Table 2: Transition temperatures (in °C) for unaged and aged bitumens with and without CD1 and CD2

Additive	Unaged	Aged bitumen
---	74.2	78.3
CD1 2%	74.3	78.6
CD2 2%	78.3	84.2

The tests were carried out using RT-FOT for 75 min due to the fact that road pavement administration agencies (such as ANAS in Italy, NCAT and NAPA in U.S.A., AIA in U.K., etc.) recommend that the difference between unaged bitumen and bitumen aged with RT-FOT be monitored closely and so there would have been no need to age the bitumen for 225 min with RT-FOT [51]. The test highlights that no anti-aging effect has been revealed but CD2 can be used to increase the resistance of bitumen to temperature.

3.3. Regeneration Tests

Regenerating agents are additives to be added to recycled asphalt (RAP), allowing its reuse in the production of new road pavements with a partial recovery of the pristine characteristics. To evaluate this effect, a 50/70 bitumen was aged by RTFOT for 225 min, and then 2% of CD1 or CD2 was added to the bitumen under stirring at 150 °C and left to mix for 15 min.

Time cure tests were carried out on these samples and the pseudoplastic-to-fluid transition temperatures were recorded. They are shown in Table 3. Time cure tests show that the addition of CD1 or CD2 at 2% brings no regeneration to the oxidized bitumen since their addition does not bring the transition temperature value of the aged bitumen closer to the value of the pristine bitumen (74.2 °C).

Table 3: Transition temperatures for unaged and aged bitumens

Sample	Transition temperature (±0.5 °C) Bitumen 50/70
Bitumen 50/70	74.2
Bitumen 50/70 RTFOT 225	85.5
Bitumen 50/70 RTFOT 225 +2% CD1	85.0
Bitumen 50/70 RTFOT 225 +2% CD2	90.0

3.4. Frequency sweep tests

To understand whether the added compounds are engaged in effective interactions with the components of the bitumen thus stabilizing or destabilizing the supramolecular network, frequency sweep tests have been made and analyzed in the framework of the colloidal gel model.

According to the theory of Bohlin [52] and Winter [53], widely reported in literature as the "weak-gel model" [54], which can be applied in the context of the study of viscoelastic materials like bitumen [55], the material is characterized by a cooperative arrangement of flow units connected by weak physical interactions that cooperatively ensure the stability of the structure. This model matches also the complex inter-molecular structure typical of bitumen, where molecules are arranged together to form assemblies at various levels of aggregation and complexity [56], which are held up by weak interactions. In this model, the number of flow units interacting with each other to give the observed flow response z, can be derived by the use of the following equation:

$$|G^*(\omega)| = \sqrt{G'(\omega)^2 + G''(\omega)^2} = A\omega^{\frac{1}{z}}$$

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, and G' and G'' are the real and imaginary parts of complex modulus (G*) which are derived by rheological measurements. G' represents the elastic response of the material (storage of energy) under oscillation, and G'' represents the inelastic contribution (dissipation of energy) during the same deformation.

In few words, A represents the force of interaction between the rheological units and z the coordination number, i.e. the number of rheological units interacting with a reference unit. The derived values, calculated from the non-linear fitting of viscoelastic data to equation, are reported in Fig. 2. The figure shows a higher impact of CD2 on both A and z parameters, which confirms its more effective interactions with the structure of the bitumen.

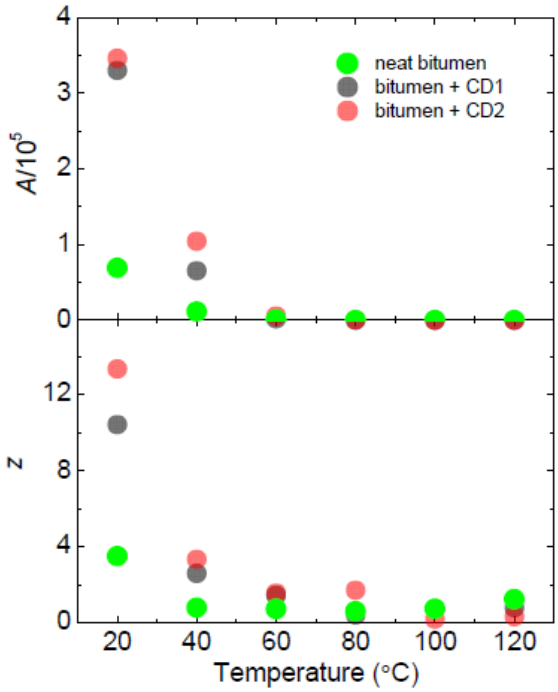

Fig. 2: A and z values as derived through equation for the neat bitumen, and that additivated by CD1 and CD2. The uncertainty associated to the values is of the same order of the symbol size.

4. Conclusions

Organic waste materials can be used in bitumen and asphalt concrete production with great benefits, providing better asphalt pavements and helping to develop proper and efficient waste management technology. The present study was prompted by the need of safeguarding the environment through a circular, eco-friendly and sustainable economy. We showed, by rheology, bare organic waste cannot be used as an anti-aging additive or as a regenerator of "aged" bitumen but could be used, instead, as a possible filler in bituminous conglomerates since it does not modify its characteristics/performance. We also showed that the FENTON-treated waste with low amounts of hydrogen peroxide can be used very suitable as a viscosifying agent, with a high capability of interacting with the complex structure of the bitumen.

FENTON-treated waste with high amounts of hydrogen peroxide can be used, instead, as filler in bituminous conglomerates, like the un-treated waste. These effects can be used for industrial applications for which further studies are needed to quantify the scaling-up convenience.

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6.2. **Results Part 6**

"Waste Food Wax Additive as a Bitumen Modifier for Warm Mix Asphalt production"

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M.P. Shulgin State Road Research Institute State Enterprise - DerzhdorNDI SE

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WASTE FOOD WAX ADDITIVE AS A BITUMEN MODIFIER FOR WARM MIX ASPHALT PRODUCTION

1. Introduction

Bitumen is a viscoelastic multi-component material generally derived from petroleum industry processes. It consists of a complex solid or semisolid colloidal dispersion of asphaltenes in a continuous oily phase of saturated paraffin, aromatics and resins [1-3]. Bitumen mechanical properties show both time and temperature dependence [4-6]. It is used as a binder for road paving by mixing it - in a percentage of about 5 % - with crushed stone materials, sand and filler. Such mixture is commonly denoted as asphalt. [7,8]. It is very important that the selection of asphalt materials takes into account the wide variation in geographical and climatic conditions [9]. To reduce cost and emissions, nowadays different organic or chemical additives [10] - as well as modern technologies like foaming techniques - are used to enhance asphalt workability and aggregate coating by reducing bitumen viscosity or modifying its surface tension for better wettability of the aggregate, therefore reducing operation temperatures and viscosity of the asphalt conglomerate by producing what is known as Warm Mix Asphalt (WMA) [11]. It has also been proven that the reduction has a direct impact on the reduction of greenhouse gases in the atmosphere [12,13]. This reduction of emissions is the most important reason the European asphalt industry has continuously recommended the use of Warm Mix Asphalt. [14,15].

Currently, the most common types of WMA additives generally consist of surfactants [16-19] or waxes materials able to flush the bitumen and consequentially to get better workability of the asphalt concretes at lower temperatures (100 °C - 140 °C) [20-22]. The mechanism of action of the warm mix agent is not yet understood; some wax-based technologies seem to modify the ligand alone, while other alternative technologies – like that using surfactants - seem to act on the bitumen-aggregate interaction. This research should be considered as preliminary paper since it focuses only on the bituminous binder blended with the warm mix agents trying to find a correlation between chemico-physical parameters and the fluxing effects, by comparing the results of rheological, NMR and DSC

measures of different warm mix agents. On the contrary the effect of the aggregates – that seems to be relevant in the bitumen surfactant system – will not be studied here. It will be only shown that the rheological properties of the bitumen will remain unaltered upon the inclusion of the liquid surfactant – in particular its viscosity as compared to that obtained using waxes additives – confirming that somehow aggregates plays a fundamental role in the binder surfactant system. This role will be investigated in a successive paper in which mechanical properties – like round press, Marshall, Indirect Tensile Strength (ITS) – of asphalt conglomerates obtained through bitumen-surfactant-aggregate system will also be taken into account. However, it has to be said that the invariance of rheological properties of the bitumen/surfactant system was observed only in the high temperature range, while a more significative change has been observed in the low one, in particular below -10 °C. This somewhat strange behaviour, necessitate more deeper investigation that is out of the goal of the present paper, but could be studied in future work on the topic. In this study, a waste wax derived from food industry - used mainly for food packaging - was tested and compared with a surfactant-based additive and - more important - with two commercial waxes. Physical chemistry characterization was performed in order to outline a possible physical mechanism induced by the bitumen modifier.

2. Materials and Methods

2.1. Materials

The bitumen used in this study is produced in Saudi Arabia and supplied by Lo Prete costruzioni s.r.l.. It has a 50/70 penetration grade. More details about it can be found elsewhere in Caputo et al. [23]. The other material used are:

- Sasobit (**SB**) waxes provided by Polyglass s.p.a.. (solid sample)
- PE Wax (**PE**) provided by SER s.p.a.. (solid sample)
- Evotherm (**WH30**) surfactant provided by Ingevity corp.. (liquid sample)
- Waste Wax (**WW**) provided by KimiCal s.r.l. (solid sample)

All chemicals were used immediately after purchase.

2.2 Methods

2.2.1 Sample preparation

Modified bitumen samples were prepared by using a high shear mixing homogenizer (IKEA model). Bitumen was heated up to flow point at about 150±5 °C and then various percentages of additive – ranging from 0.4 % to 3% on the total mass of the bitumen- were gradually added (1 g/min) to the melted bitumen samples (100 g) under a high-speed shear mixing of 500 to 700 rpm. The mixtures have been stirred at 150 °C for 15 min to guarantee an essentially homogenous sample.

2.3 Rheological characterization

Dynamic Shear Rheological (DSR) tests on modified and on the reference virgin bitumen samples were carried out using a controlled shear stress rheometer (SR5000, Rheometric Scientific, USA) in a plate-plate geometry mode. Plate tools of ϕ = 25 mm and ϕ = 8 mm has been used for tests in the temperature range 20 °C to 110 °C and 25 °C to -30 °C respectively. Plate – plate gap was set to 2 mm. A Peltier system (±0.1 °C) was used for temperature control.

Rheological responses were determined under the kinematics of both steady and oscillatory simple shears.

In steady-shear experiments, the viscosity of bitumen samples was determined from the ratio of measured shear stress to applied shear rate, as a function of shear rate that was varied from 1 to 100 s^{-1}. Steady states were previously checked by transient experiments (step-rate test). For all samples it was observed that 10 s was a sufficient scanning time to ensure the steady state condition. It has been found that all samples show a Newtonian behavior in the investigated shear rate range.
Dynamic tests have been carried out in conditions of linear regime where measured material features are independent of the amplitude of applied load and are function only of microstructure [24,25]. Aimed at investigating the material viscoelastic phase transition, dynamic temperature ramp tests were performed both at 1 Hz and rate of 1 °C/min in the high and low temperature range by applying the proper stress values – previously determined by stress sweep tests - to guarantee linear viscoelastic conditions at all tested temperatures.
For low temperature measurements, the samples were initially kept at 25 °C for 4 mins, to obtain uniform temperature conditions, and then the test was started by cooling down from 25 °C to -30 °C [26]. More details about the mechanical characterization can be found in literature [27-30].

2.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was used as a convenient and reliable thermal analysis technique to analyze the characteristics of wax used in this work.
The DSC studies were performed using a SETARAM 131 instrument. The amount of each sample analyzed was around 40 – 60 mg. Analyses were performed from 25°C to 150°C at a temperature scan rate of 5°C/min under nitrogen flux. [31]

2.5 **Nuclear Magnetic Resonance (NMR) characterization**

The NMR characterization was conducted at three different temperatures (100 °C, 110 °C and 120 °C) using a Bruker 300 Spectrometer (Bruker, Italy) equipped with a Diff30 NMR probe for diffusion measurements. PFG-STE technique was used to measure molecular diffusivity [32,33]. Sixteen scans, a sequence of three π/2 rf pulses (π/2-τ_1- π/2-τ_m- π/2) and two gradient pulses δ, Δ - applied after the first and third rf pulses - has been used during the measurements. The echo was characterized when $\tau_1 = 2\tau_1 + \tau_m$ and its amplitude attenuation was derived from the Stejskal - Tanner equation:

$$I\,(2\tau_1 + \tau_m) = I_0 e^{-\left[\frac{\tau_m}{T_1}+\frac{3\tau_1}{T_2}+(\gamma g\delta)^2\, \mathrm{D}\left(\Delta-\frac{\delta}{3}\right)\right]} \qquad (1)$$

where D represents the self-diffusion coefficient, δ the gradient length pulse; Δ, the diffusion delay time g the gradient amplitude, γ the gyroscopic ratio of the proton nucleus and T_1 and T_2 respectively the spin-lattice and spin-spin relaxation times.
Values of 2 ms, 30 ms and 100 – 900 G/cm were used for δ Δ and g respectively. The NMR experiments had a very low fitting standard deviation and reproducibility of measurements. The uncertainty of D is approximately 3%.

According to the colloidal model, two principal types of molecules constitute the general composition of bitumen on the molecular level: asphaltenes and maltenes. Asphaltenes are rigid, polar molecules and are characterized by high melting points while the maltenes on the other hand are soft, oily and they disperse the asphaltenes in the compound (bitumen). Taking into consideration the asphaltene's low T_2 relaxation times [34], the self-diffusion coefficients can be attributed to the oily part (maltene) of the bitumen. In fact, the NMR signal of the asphaltenes relaxes during the application of the pulses [35].

3. Results and Discussion

To start, the solid – liquid phase transitions temperatures of waxes were determined by DSC in order to know the temperature values at which the waxes are liquid and consequently can show their fluxing effect. As it can be seen from figure 1, DSC thermogram shows that there is a huge difference in transition temperature between WW and the other (PE and SB) waxes.

In fact, the commercial waxes softens/melt in a broad interval peaked at about 100 °C and melt completely at 120 °C. On the contrary the WW shows a soften/melt interval peaked at about 49 °C, becoming completely melt at 60 °C. Moreover, SB shows 2 broad peaks centred at around 100 and 116 °C indicating the presence of two different hydrocarbon molecules, probably isomers.

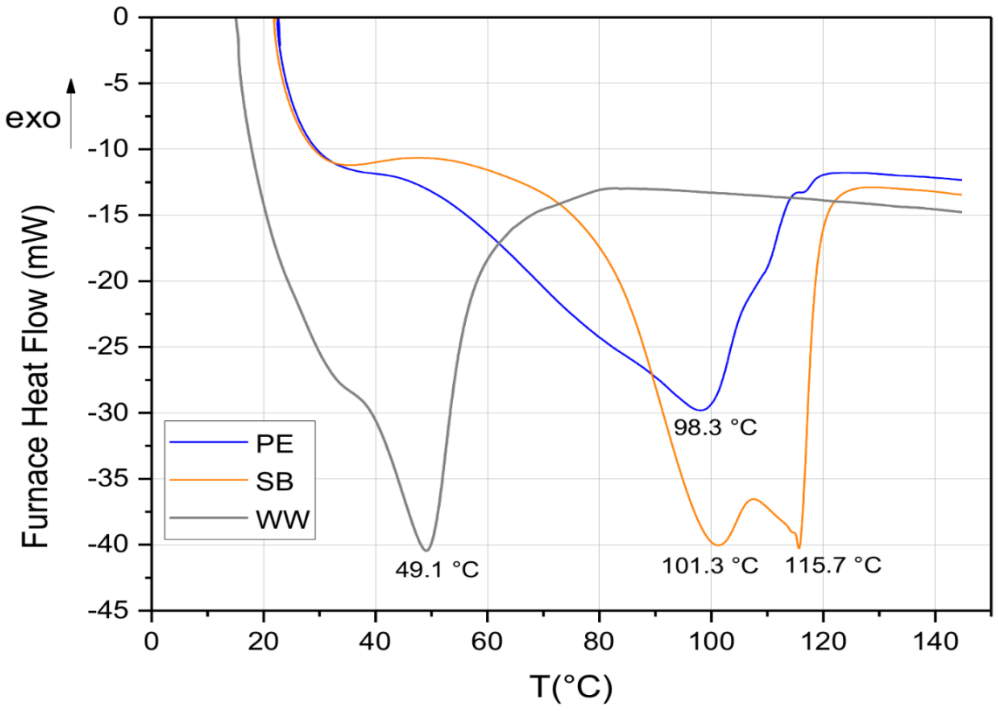

Figure 1: Differential Scanning Calorimetry (DSC). Grey curve represents Waste food Wax (WW), blue curve represents PE wax, whlie orange curve represents Sasobit wax (SB).

From these results it can be argued that the WW could have a better flow improving power under 100°C compared to the other waxes. To very this hypothesis – as we will show hereafter – we perform rheological and NMR investigations.

Table 1 shows the viscosity values - obtained from DSR measurements – of the virgin and modified bitumen in the temperature range from 100 °C to 140 °C.

Table 1. Viscosity of bitumen with and without additives at different temperatures

Sample	Eta 100°C (Pa-s)	Eta 110°C (Pa-s)	Eta 120°C (Pa-s)	Eta 130°C (Pa-s)	Eta 140°C (Pa-s)
Virgin Bitumen	10.3	5.3	2.8	1.4	1.3
Bit. + 0.4% WH30	10.1	4.9	2.7	1.5	0.9
Bit. + 1% SB	15	4.8	2.1	1.1	0.7
Bit+ 1% WW	7.3	3.6	2	1.1	0.7
Bit. + 1% PE	10.4	4.6	2.3	1.3	0.8
Bit. + 3% SB	16.2	5.3	2	1	0.7
Bit+ 3% WW	7.1	3.4	1.9		
Bit. + 3% PE	9.8	4.6	2.5	1.4	0.8

All the viscosity data shown in table 1 are obtained by averaging data recorded in three different experiments made by the same operator. As it can be seen the viscosity of the waste food wax WW modified bitumen is significantly lower than that of the virgin one at temperature below 120 °C. It can also be noted that SB – at both percentages studied – increases the bitumen viscosity at temperature values lower than the solid – liquid transition temperature of the additive itself. This – as could be easily guessed – is due to the presence of incompletely melted additive. As temperature increases above its melting point, viscosity values lower becoming similar to that of WW additive. PE waxes shows a similar trend. On the contrary, as expected, the liquid surfactant additive (WH30) does not significantly affect the viscosity of the virgin bitumen. In conclusion, it can be said that the additive composed of waxes derived from food scraps (WW) shows results comparable to SB and PE waxes at high temperatures but show better effects at temperatures lower than 120 °C. This can be of huge advantage in the preparation and spreading of the conglomerates at temperatures lower than 120 °C. In fact, the viscosities recorded and shown in table 1 are always lower compared to that of virgin bitumen. Furthermore, as we will show below, this additive does not significantly change the rheological properties of the bitumen particularly in the high temperature range (25 °C-120 °C). In fact, as it can be seen from figure 2, the only additive capable of modifying the rheological properties of the virgin bitumen is the SB wax [36] which shows – at both used percentages - a remarkable increase in the viscoelastic transition temperature (higher $\tan\delta$). On the contrary the other additives show very similar profiles to the virgin binder. The latter aspect however, can be seen in a positive way because an additive is often required to act only as a warm mix agent and not as a rheological modifier.

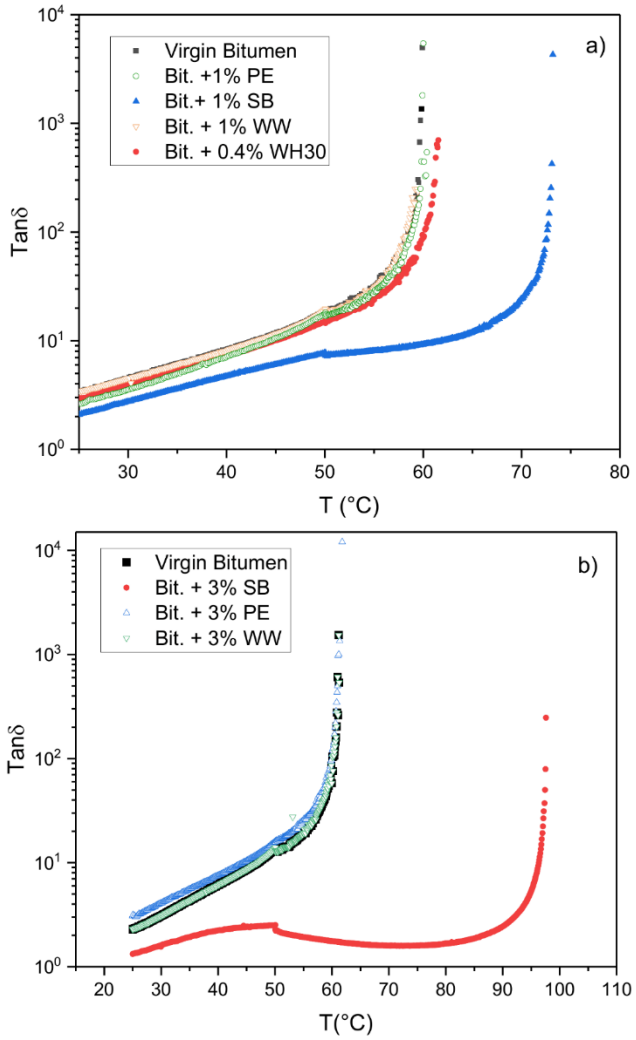

Figure 2 Rheological properties of virgin and modified bitumen in the high temperature range: a) virgin bitumen, virgin bitumen +1% waxes and virgin bitumen + 0.4% surfactant; b) virgin bitumen and virgin bitumen + 3% waxes

Table 2 summarizes the values of the various viscoelastic transition temperatures, the ΔT of viscoelastic transitions (respect to the virgin bitumen) and the percentages of the increased transition temperature.

Table 2: Transition Temperatures, ΔT of viscoelastic transition and percentage of the increment of transition temperature (Ref. to virgin bitumen)

Sample	**Transition Temperature (°C)**	**ΔT (°C)***	**Increased transition temperature (%)**
Virgin Bitumen	59.9	--	--
Bit. + 1% PE	60	+0.1	+ 0.2
Bit. + 1% SB	73.1	+13.2	+ 22.0
Bit. + 1% WW	59.4	-0.5	- 0.8
Bit. + 3% PE	61.8	+1.9	+ 3.2
Bit. + 3% SB	97.4	+37.5	+ 62.6
Bit. + 3% WW	61.2	+1.3	+ 2.2

Bit. +0.4% WH30	61.5	+1.6	+ 2.7

* Difference between the transition temperature of the modified bitumen and virgin bitumen.

From table 2 it is evident that SB waxes lead to a significant change to the rheological properties of virgin bitumen. In particular, a concentration increase leads to an increase in the transition temperatures – higher than 60 % - as compared to virgin bitumen. On the other hand, the other additives, even at concentrations of 3%, leave these properties almost unchanged (no significantly variation from bitumen transition temperature is observed), even though they act on the viscosity of the binder. Rheological studies have also been performed at low temperature from 25 °C to -30 °C. The effect of various modifiers is depicted in figures 3. It is worthy to note the effect of the WW additive in the temperature range from -30 to -10 °C where its warm mix ability is evident particularly at 3 % w/w concentration. Tanδ of WW bitumen is lower than all other additives showing that the bitumen kept a good deformability of the bitumen. It seems that WW is really efficient for cold countries where the climate is more severe.

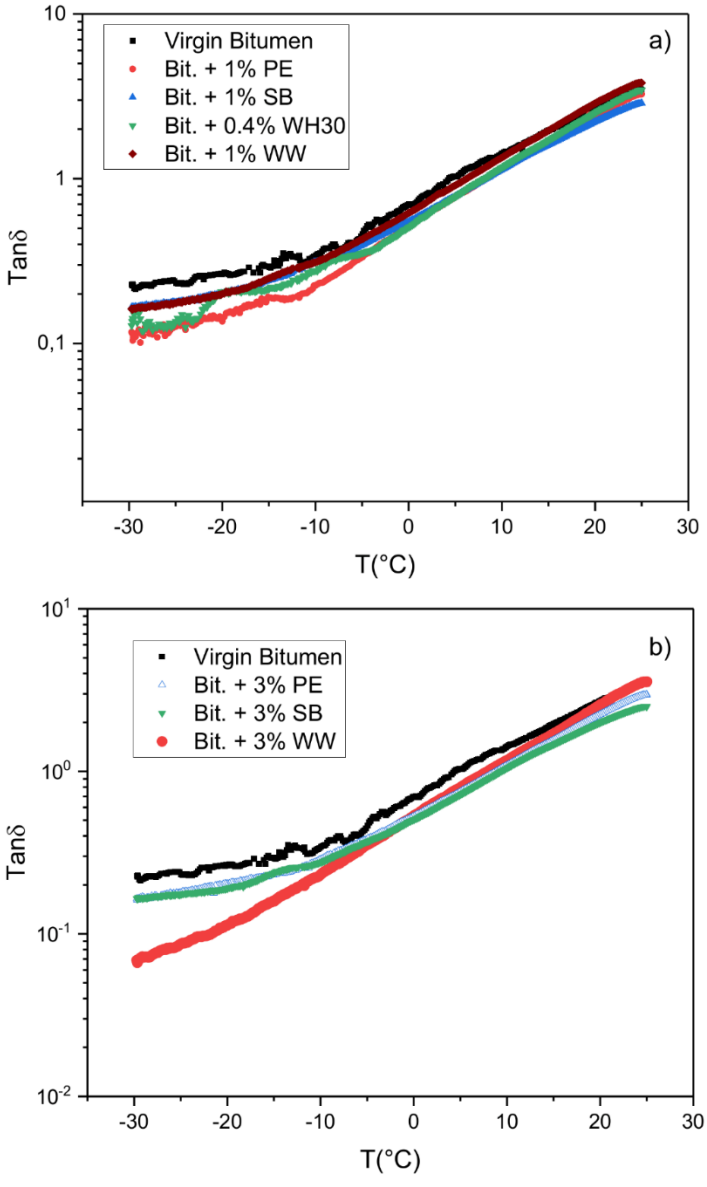

Figure 3. Rheological properties of virgin and modified bitumen at low temperature range: a) virgin bitumen, virgin bitumen +1% waxes and virgin bitumen + 0.4% surfactant; b) virgin bitumen and virgin bitumen + 3% waxes

Finally, a molecular self-diffusion investigation was conducted in order to study the influence of the additives studied on the microstructural modification of bitumen. Indeed, the observation of the phenomenon of self-diffusion is based on the mobility of molecules. The motion of these molecules can be impeded due to the obstruction they face during their mobility in their media. Therefore, the SDC data, can be considered as an adequate representation of the microstructural behavior. As previously mentioned, NMR self-diffusion coefficients (SDC) give better insight into bitumen's microstructure by detecting the long-range mobility of the mixture constituents. Motion determination over long distances, in comparison with ideal micelles, facilitates a sensitive probe for the state of aggregates [33, 37]. It is important to note that the SDC values of asphaltene molecules cannot be detected due to the short transverse relaxation times (T_2) of their protons; thus, the measured SDC values are related to the maltene phase. The SDC data for each sample investigated are summarized in table 3 and represented in Figure 4 a) and Figure 4 b) respectively for 1% (and 0.4% of WH30) and 3% additive added.

Table 3 Self Diffusion Coefficients (SDC) of virgin bitumen and modified bitumen samples at different temperatures.

Sample	SDC (m^2/s) at 100°C	SDC (m^2/s) at 110°C	SDC (m^2/s) at 120°C
Virgin Bitumen	2.43E-12	3.27E-12	4.57E-12
Bit. + 1% SB	2.70E-12	3.63E-12	5.03E-12
Bit. + 1% PE	3.72E-12	4.29E-12	5.95E-12
Bit. + 1% WW	2.76E-12	3.75E-12	5.11E-12
Bit. + 3% SB	3.50E-12	4.63E-12	6.27E-12
Bit. + 3% PE	4.04E-12	5.31E-12	7.04E-12
Bit. + 3% WW	3.55E-12	4.61E-12	6.24E-12
Bit. + 0.4% WH30	2.45E-12	3.38E-12	4.73E-12

As it can be seen from figure 4 (a and b), the effect of the surfactant WH30 does not promote any significant improvement of the bitumen's maltene self-diffusion meaning that no particular structure modification of bitumen arises from the use of the surfactant. This support the hypotheses that the use of surfactants acts only when the biphasic system – bitumen/aggregates –is taken into account. The bitumen structure modification induced by the Sasobit and by Waste Wax is more significant than that of WH30 (at all three temperatures), and almost the same for both additives' concentrations, although at the 1% concentration there is slightly difference between SB and WW.

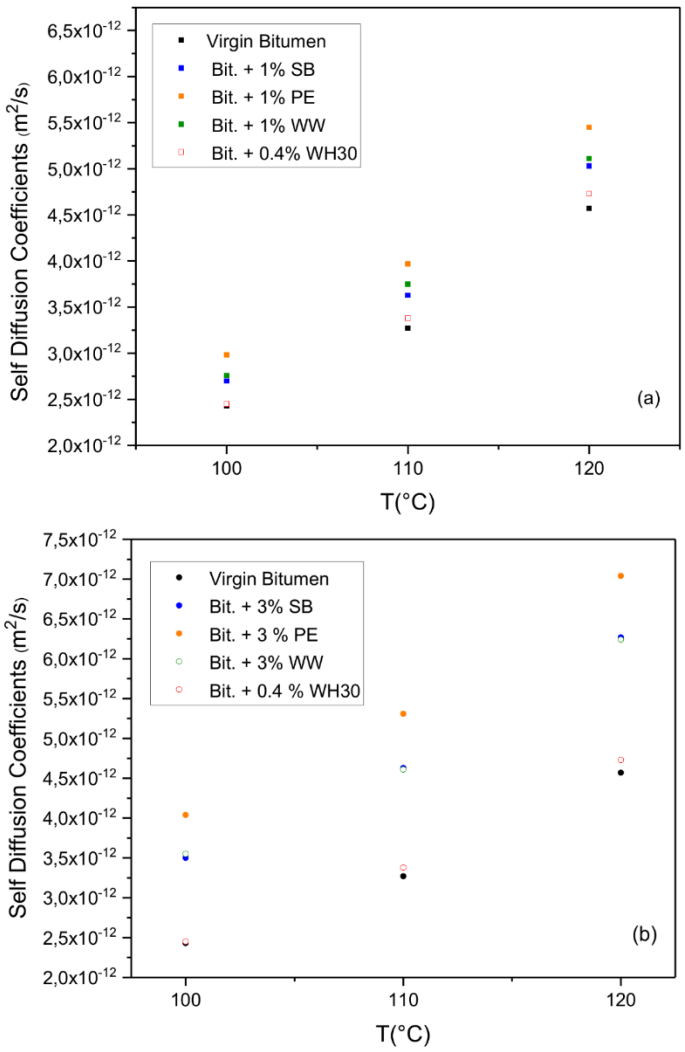

Figure 4: NMR Self-Diffusion Coefficient in the temperature range 100-120°C for: a) 1% w/w and 0.4% w/w concentration and b) 3 % w/w concentration

On the other hand, PE shows a more marked difference in diffusion values compared to virgin bitumen, SB and WW. Moreover, as it can be seen from table 4 and Figure 5 this difference increases in the 3% w/w concentration PE bitumen blend.

Table 4: Increased Self Diffusion Coefficients (SDC) of modified bitumen samples in comparison with virgin bitumen at different temperature.

Sample	**Δ SDC (m^2/s) at 100°C**	**Δ SDC (m^2/s) at 110°C**	**Δ SDC (m^2/s) at 120°C**
Virgin Bitumen	--	--	--
Bit. + 1% SB	2.70E-13	3.60E-13	4.60E-13
Bit. + 1% PE	5,5E-13	7E-13	8.8E-13
Bit. + 1% WW	3.30E-13	4.80E-13	5.40E-13
Bit. + 3% SB	1.07E-12	1.36E-12	1.70E-12
Bit. + 3% PE	1.61E-12	2.04E-12	2.47E-12
Bit. + 3% WW	1.12E-12	1.34E-12	1.67E-12
Bit. + 0.4% WH30	2.00E-14	1.10E-13	1.60E-13

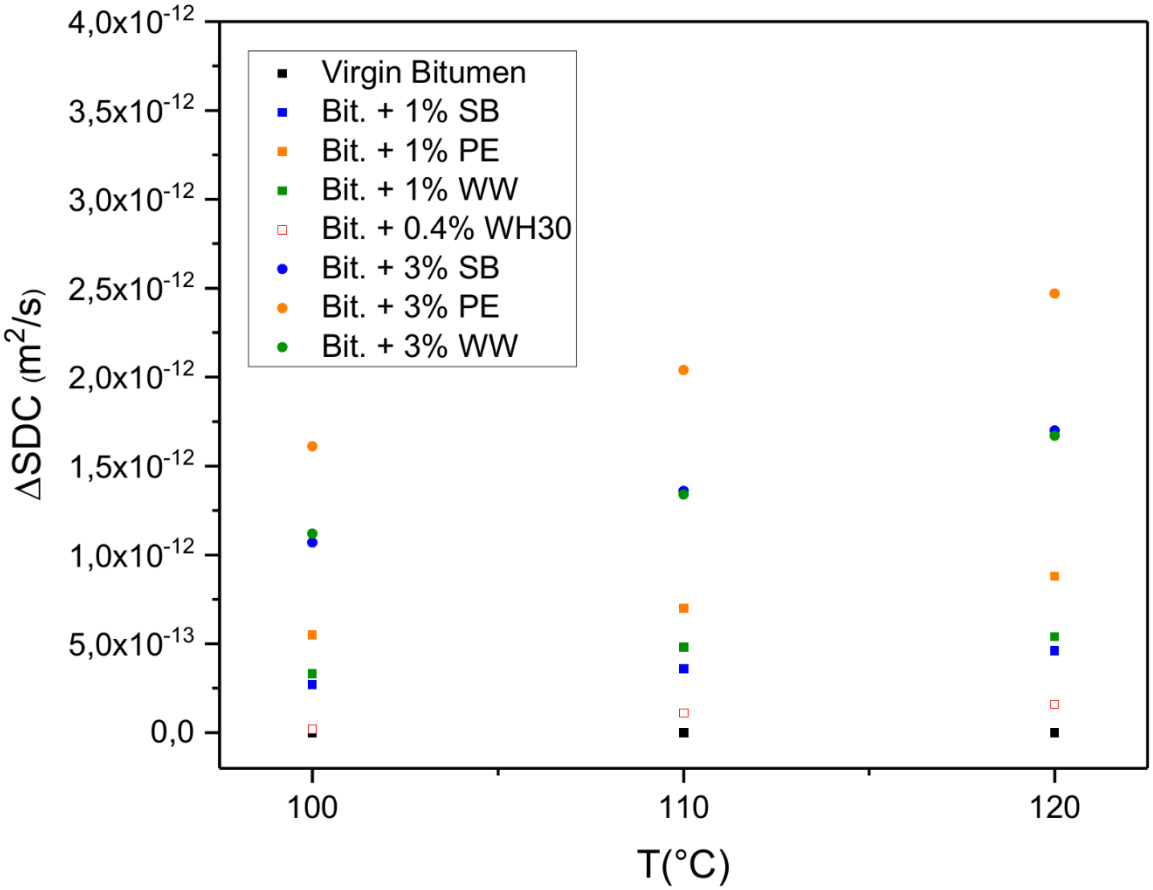

Figure 5. Trend of the ΔSDC respect to the virgin bitumen of 1% and 3 % waxes additives and 0.4% of surfactant additive in the temperature range 100 °C-120 °C

The interesting point to be noted is that, although the WW is completely melted at the three temperatures tested, the molecular diffusion of the maltene phase of the WW modified bitumen is very similar to that of the SB one at all temperatures and for each concentration. In particular at 100 °C where both SB an PE additives are partially melted, we would have expected a higher diffusion of the WW modified bitumen respect to both SB and PE. However, the higher diffusion showed by PE at 100 °C have led us to hypothesize that the molecular structure of the WW should be more cumbersome than that of PE (for example it could consist of more branched hydrocarbons unlike the linear one of PE). This hypothesis should be also valid for SB sample, because at 120 °C – where all the three waxes are melted – the PE sample shows a higher diffusion than its SB counterpart. However, this hypothesis has to be verified by a more detailed study on molecular structures of each wax, but this is not the goal of the present paper.

Overall, it can be said that Waste Wax studied is a suitable additive to be used in warm mix asphalt production. In fact, it does not modify the bitumen rheology but decreases its viscosity at temperatures lower than 120 °C although on a molecular lever it does not enhance the maltene mobility as much as PE additive.

Conclusions

The waste wax derived from the food industry improves the workability of the conglomerate at temperatures lower than the typical operating ones. The rheological results show that these additives act only on the viscosity of the binder without changing the rheological properties of the

bitumen. Their effectiveness is similar to the commercial additives currently used in road pavements. These results demonstrate that this product can be used in the asphalt industry as Warm Mix Asphalt with consequent economic savings and above all with reduction of harmful fume emissions into the environment. In fact, for Food Companies, these waxes are currently a waste, therefore transforming it into a commercial product for the road industry, they will save the cost of disposal and will also obtain earnings from its sale.

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6.3. Results part 7

"Curcumin's effects on the Rheological and Adhesion properties of Asphalt"

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1. Introduction

Bitumen is a black, soft, viscoelastic material, consisting of several components (predominantly hydrocarbons and their derivatives). It is obtained by fractional distillation during petroleum industry refinery processes of crude oil. Bitumen is a colloidal dispersion of asphaltenes in a continuous (maltenic) phase composed of aromatic compounds, saturated paraffins, and resins. However, the specific chemical composition of bitumen is highly related to both the nature of the initial crude oil used as starting material and the cracking process carried out on it. Bitumen is employed globally in asphalt mixes as the main binder for road pavement construction. Due to the viscoelastic properties of bitumen, its mechanical response is both temperature and time dependent. However, due to the hugely significant variation in climatic conditions on a geographical basis, asphalt materials need to be selected carefully in order to increase the longevity and lifespan of the road pavement thus reducing the possible huge cost of road maintenance [1]. The durability and sustainability of bitumen is a concept based on the resistance to variations of its physical properties due to environmental exposure. At room temperature, bitumen is chemically stable and inert and when exposed to the atmosphere as a thin film, bitu-men starts hardening quickly becoming very fragile. Therefore, different modifiers and additives have been incorporated into bitumen in order to enhance its performance [2–7]. However, not all of these additives can be considered as "green" additives that would in addition to their properties safeguard the environment.

The main physical change of bitumen occurs as a rheological variation, with a systematic increase in stiffness. This phenomenon is partly due to the loss of bitumen's lighter fractions during manufacturing or mixing processes with stone aggregates. Common additives such as polyphosphoric acid react chemically with bitumen to improve its rheological properties [8,9]. Polymers such as SBS also improve rheological properties but they do so physically by imparting their own properties into the matrix thus improving its properties [10,11]. Adhesion promoters such as amides and hy-drated lime either chemically interact with bitumen to reduce the surface free energy of the constituents of the asphalt conglomerate or increase water resistance of asphalt by preventing water molecules from getting into the bituminous matrix [12,13]. Reju-venating agents are used to recycle the old road pavements (reclaimed asphalt pave-ment otherwise known as RAP) due to their ability to interact with aged bitumen ag-gregates to regenerate the original unaged bitumen structure [14–17].

Anti-oxidant agents function by taking part in the oxidation process themselves thereby preventing or reducing the possibility of oxidation on the fundamental con-stituents of the asphalt pavement itself. These agents reduce changes in bitumen's chemical structure which are caused by its reaction with atmospheric oxygen [7,18]. The aforementioned additives, even though are proven to be effective, generally are not eco-friendly as they are either too acidic, too basic or in one way or

another, adversely affect the environment in which the road is paved. As a matter of fact, recently some bio-polymers are starting to get tested and utilized as modifiers in road paving [19,20]. What this study aims at is to achieve the improvement of rheological properties, adhesion promotion and anti-oxidant properties of road pavements in an eco-friendly way.

Turmeric, obtained from the rhizomes of *Curcuma longa* L., is one of the main culinary spices in Asian cooking—especially Indian. It is also known as the golden spice, denoted by different names in different languages worldwide and is an important in-gredient in curry. It is known for its bright yellow colour and is also added in European cuisine to enhance the colour of the prepared dish [21,22]. The orange-yellow colour and taste of turmeric rhizome is attributed to the presence of curcuminoids—which are regarded and accepted as one of its major biomolecular components (3–5%) [23]. Chemically, in relation to this type of turmeric constituents, all curcuminoids feature a conjugated system with a characteristic skeleton of two aromatic rings joined by an aliphatic chain—usually a heptane chain and in some cases, a 1,3-diketone group. Generally, the principal constituent of these three polyphenols, is curcumin (1) which is widely used as food colouring, preservative, additive and flavour agent (E100). De-methoxycurcumin (2) and bis-demethoxycurcumin (3) in which one or both -OCH3 functionalities over phenol rings are removed, are the minor curcuminoid components (Figure 1) [23,24]. Turmeric, the "natural and commercial curcumin" is the powder obtained from the dried and crushed rhizomes of *Curcuma longa* L. For this reason, the main part of the product is indeed of a carbohydrate nature (ca. 70%) [25].

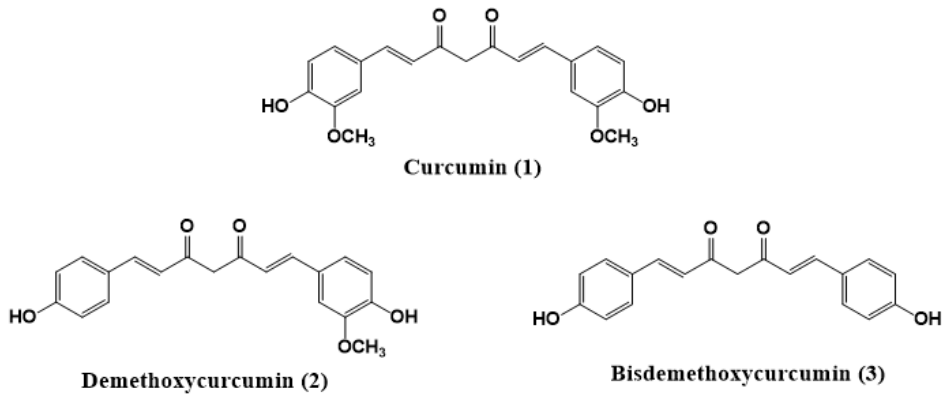

Figure 1: Structures of curcuminoids

Only ca. 20 to 25% of turmeric powder can contain curcuminoid derivatives which typically are a mixture of three curcuminoids, whose composition of is about 70% curcumin (curcumin I) (1), 19% demethoxycurcumin (2), and 9% bisdemethoxy-curcumin (3) [26,27]. Curcumin was first isolated in 1815, but only in 1910 was the ex-act chemical structure depicted [28]. Pabon however, successfully prepared this mole-cule for the first time in excellent yield in 1964 [29]. In recent years, curcuminoids and in particular, curcumin have attracted a lot of attention due to their pharmacological activity and biological effects, tested directly or chelated to metal centres [30–33]. Furthermore, curcumin has been deeply studied for its antioxidant properties in mo-lecular biology research [34,35]. Previous work carried out by our group already demonstrated that carbohydrate rich compounds such as flours, extracts from vegetable products and gums containing polysaccharides demonstrated that polysaccharides increase the rigidity of bitumen and improve the mechanical properties of bitumen with an increase in temperature [36]. For these reasons, it was expected that turmeric could be a good candidate to be tested in bitumen matrix as a multi-functional agent. Indeed,

turmeric has the right chemico-physical characteristics to be a multifunctional bio-additive that will act as a chemical modifier improving the anti-oxidant properties of the bitumen binder, improving the asphalt concrete mechanical properties and fi-nally that might also promote adhesion between the bitumen binder and the aggre-gates. Owing to the multi-component nature of turmeric (food grade curcuma, FGC), two different pure grades of curcumin were also investigated in order to examine the effects of curcuminoids on the bitumen properties. Thus, the functionality and effec-tiveness of each one was determined. The reagent grade curcumin (RGC) which con-tains ca. 20% of various methoxy-derivatives of curcumin was used since its composi-tion is close to the natural composition in curcuminoids present in turmeric. A high purity grade curcumin (HPGC) was also used as reference to probe the effect of the main active compound (Figure 2).

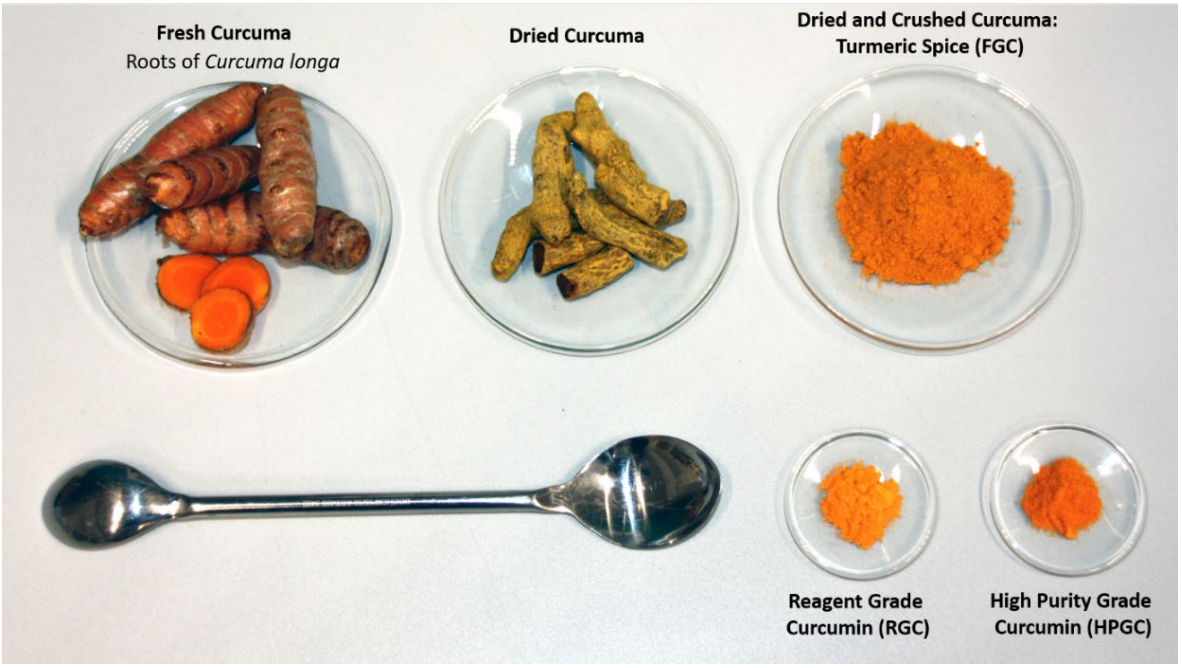

Figure 2: Fresh and dry curcuma rhizomes and resulting turmeric powder (FGC), together with the two differently pure grades of curcumin used in this work (RGC and HPGC).

Furthermore, since bitumen is also a complex matrix, two different kinds of bitumen were probed. The bitumen samples were modified at various percentages to effectively evaluate the extent of the investigated mechanism. To determine the sol-transition temperature of the modified bitumen samples, time-cure rheological tests were carried out [8]. An empirical standard method—the boiling test (Riedel and Wieber test) [13] was also performed in order to test the adhesion capacity of the modified bitumen. To evaluate the changes in the morphology of the bitumen with the addition of the new additives, Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) sample analysis were carried out [37,38].

2. Experimental Section

2.1. Materials

The analyzed bitumens LC50 and C170 were supplied by Loprete Costruzioni Stradali (Italy). Both were used as received. The crude oil was from Saudi Arabia. Their penetration grades are 50/70, for LC50, and 170/210, for C170. The penetration grade was determined by the ASTM D946 standardized protocol [39] which entails a standard needle being loaded with a 100 g weight and the

length covered by the needle in the bitumen sample is measured in tenths of a millimeter for a known time, at fixed temperature. An acidic stone (commercial name: "Porfido del Trentino") was chosen as the tested stone material for boiling tests and was supplied by "Porfido Trentino SRL" company (Albiano, Northern Italy) [7]. $CaCO_3$ was also tested as an inert filler for the purpose of comparison. Curcumin (HPGC) was obtained from Biosynth Carbosynth (Carbosynth Ltd., United Kingdom) (purity HPLC min 95%); curcumin (RGC) was obtained from Merck Sigma Aldrich (city, country) (purity for HPLC ≥ 75.0% (a/a), Bisdemethoxycurcumin ≤ 5.0% (a/a), Demethoxycurcumin ≤ 20.0% (a/a)). Turmeric (FGC) was obtained from the local supermarket.

The commercial bitumens used in this study mainly differ by their penetration value—the first one with a low value of 68 dmm, the second one with a higher value of 185 dmm (Table 1). They were selected to determine if their physico-chemical properties might be differently affected by the tested additives, owing to the difference in their chemical composition.

Table 1. Fundamental physical properties of bitumens.

Measured Properties	**Standard**	**Unit**	**LC50**	**C170**
			50/70	**170/210**
Penetration at 25 °C	**EN 1426**	0.1 mm	68 ± 1	185 ± 1
Softening point (R&B)	EN 1427	°C	48.8 ± 0.2	42.6 ± 0.2
Flash point	EN 2592	°C	≥230	≥220
Solubility	EN 12592	% (m/m)	≥99	≥99

2.2. Sample Preparation

All three additives (HPGC, RGC and FGC) are orange solid powders. They were individually mixed with hot bitumen (about 150 °C) within 1–3 wt% ratio. The bitumen modification was carried out by using a mechanical stirrer. Initially, 100 g of bitumen was heated up to 150 °C until it totally melted and flowed freely (about 30 min). Then 1g of additive was added to the melted sample. Meanwhile, the blend was being mixed by a high-speed shear mixer at between 500–700 rpm. The compound was kept under the mixer (and obviously kept on the heater as well to maintain the compound at 150 °C) for 1 h. After the mixing process, some drops of the resulting modified bitumen were laid on a greaseproof paper for further analysis.

2.3. Rheological Analysis

Dynamic Shear Rheology (DSR) analysis was performed using a Dynamic Stress Rheometer (SR-5000 Rheometric Scientific, USA) equipped with a parallel plate geometry with 25 mm of diameter, using a 2 mm gap. The measurements were carried out in a temperature range of 25–130 °C (increasing at 1 °C/min). The frequency was set at 1 Hz and the Stress at 100 Pa. All experiments were performed in the viscoelastic regime. More details are described in the reference [37].

2.4. Boiling Test

The boiling test procedure used in this study was performed according to ASTMD3625. All details can be found in references [7,13].

2.5. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) studies were performed using a Nanoscope VIII Bruker microscope which was set to operate in tapping mode with oscillations of the cantilever regulated close to its resonance frequency (150 kHz). Due to the fact that the cantilever oscillates up and down, the tip touches the surface of the sample sporadically. As the tip descends near the surface, the

interaction between the tip and the surface influences the vibration of the cantilever. The phase angle shift of the cantilever vibration signifies dissipation of energy in the tip-sample ensemble, so it depends on the specific mechanical properties of the sample under testing. Cantilevers with elastic constants of 5 N/m and 42 N/m were used for the measurements. Antimony doped silicon probes (TAP150A, TESPA-V2, Bruker) with resonance frequencies 150 kHz and 320 kHz respectively and nominal tip radius with a 10nm curvature were used. Phase and topography images were taken contemporarily.

2.6. Thermogravimetric Analysis (TGA):

Thermogravimetric studies were performed on a Perkin-Elmer TGA-6 instrument. Analysis was performed on ca. 3 to 5 mg of sample. Thermal decomposition was studied from 30 °C to 850 °C under constant nitrogen flux, at a heating rate of 10 °C min^{-1}.

2.7. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) images were acquired on a Phenom ProX microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA), equipped with a backscattered electron detector for energy dispersive X-ray spectroscopy (EDX). Samples were placed on carbon-conductive, double-coated tabs.

2.8. Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR spectra were recorded on a Bruker WM-300 ($CDCl_3$ solution, internal standard Me_4Si). For the turmeric powder, an extraction in chloroform was performed prior to analysis, after filtration and evaporation of the solvent the residue was dissolved in deuterated chloroform and the spectrum was registered.

3. Results and Discussion

The three additives (HPGC, RGC and FGC) were briefly analyzed. For HPGC and RGC samples, ^{1}H-NMR spectra were recorded by dissolving 5 mg of each compound in 1 mL of deuterated chloroform. For FGC, ^{1}H-NMR was performed after extraction. Two grams of FGC were extracted with 500 mL of chloroform for three hours. The solid residue was dried and weighed (1.7 g). The filtered chloroform solution was evaporated under reduced pressure and the solid deep orange oily residue was dissolved in 1 mL of deuterated chloroform. On the three NMR tubes, thin layer chromatography was also performed on silica gel in a mixture of chloroform/methanol (9.5/0.5 *v*/*v*) solvents used as eluent. Obtained spectra together with the picture of the resulting TLC plate are reported in Figure 3.

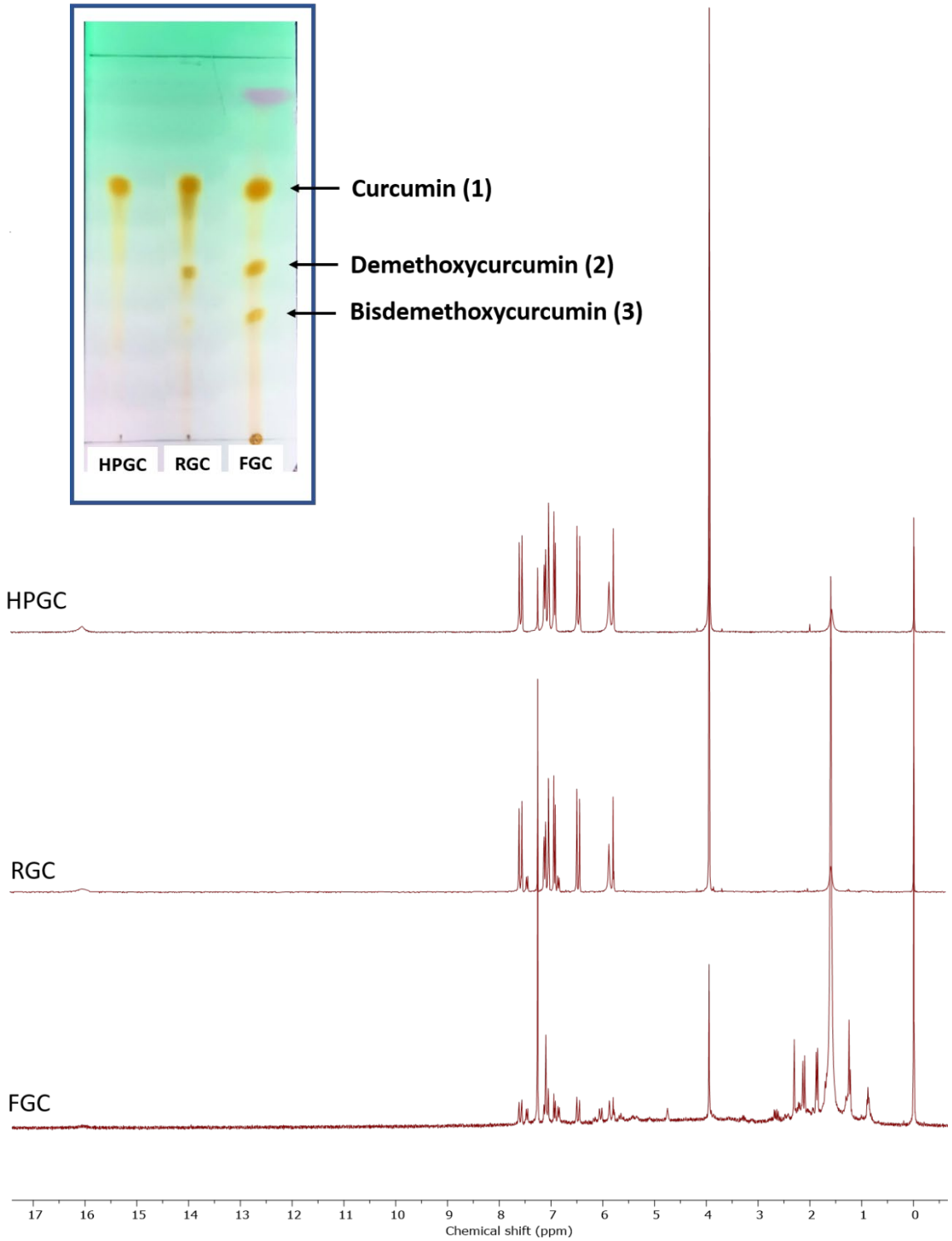

Figure 3. ^{1}H-NMR spectra in $CDCl_3$ of HPGC, RGC and chloroform extracted FGC. In inset photograph of a TLC plate under UV-light (eluent: $CHCl_3$/MeOH 9.5/0.5 *v*/*v*).

These analyses show clearly show the purity grade of the used additives. As expected, the RGC sample is rather close in composition to the curcuminoid extract of FGC, which roughly contains 75.0% of pure curcumin (1) mixed with demethoxycurcumin (**2**) and bisdemethoxycurcumin (**3**). Prior to mixing the three different additives into bitumen, thermogravimetric analyses were

performed in order to check the integrity of the samples during sample preparation, but also during their eventual use in bitumen processing. TGA traces are reported in Figure 4.

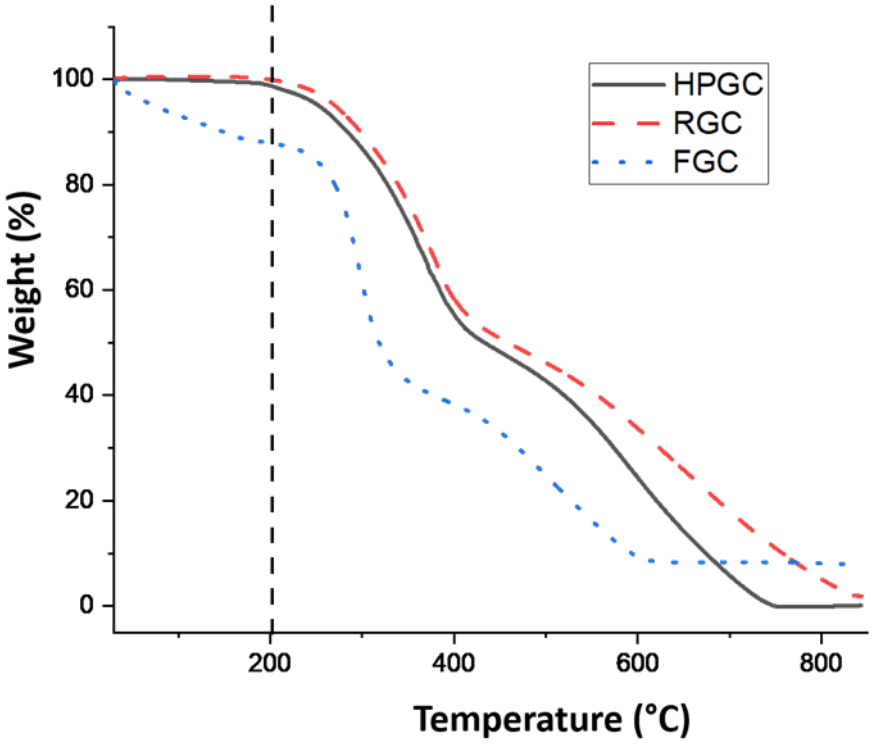

Figure 4. TGA traces of HPGC, RGC and FGC samples.

As expected, the three additives are thermally stable until 200 °C, at which temperature all compounds initiate their decomposition. Note that the weight loss registered for FGC before 200 °C can be attributed to the dehydration of the turmeric powder as already observed in a previous report [25]. While both HPGC and RGC are completely calcinated, for FGC, a solid viscous white residue of ca. 8% of its weight is obtained at 850 °C. The latter is mainly formed by inorganic salts and oxides that are derived from the presence of phosphorous, potassium and magnesium in the turmeric powder (See Figure S1 in ESI for SEM/EDX analysis of the solid residue).

Finally, SEM microscopy images were taken of the three samples revealing their morphological features that are reported in Figure 5. HPGC powder is characterised by nicely defined rounded parallelepipeds, pointing out the high purity and quasi-crystalline nature of the sample, while RGC presents the features of a mixture of various sized aggregates and FGC clearly shows the biological nature of the sample. EDX analysis were performed on each sample. As expected, the atomic concentration in carbon and oxygen atoms of the HQGC sample concords with the theoretical values calculated for curcumin (C: 72.43%, O: 27.57%). The EDX analysis on the FGC sample is also congruent with the biological nature of the sample, showing the characteristic elements expected for vegetal extracts. Indeed, the SEM image of FGC sample shows the expected densely packed sponge-like aggregates of various dimensions inside which the typical cellulosic walls are easily recognizable.

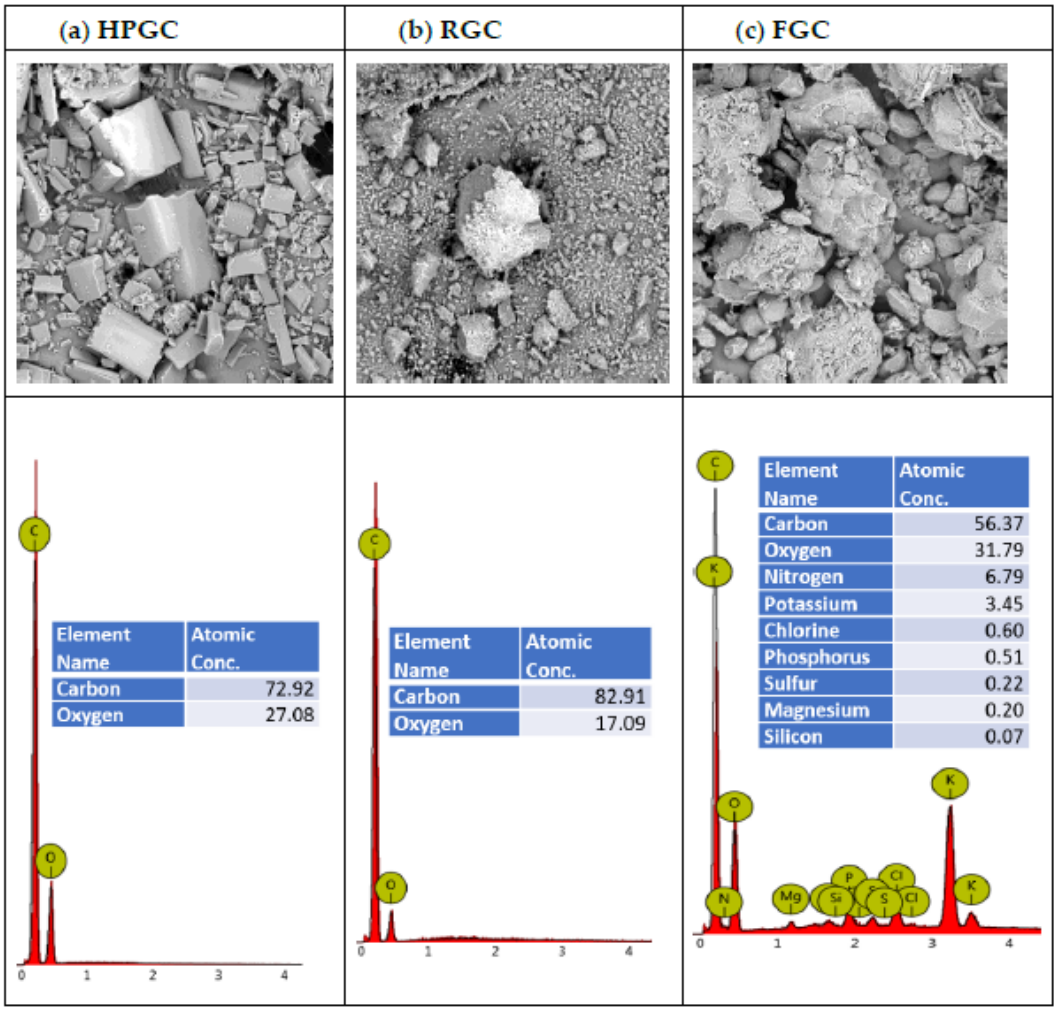

Figure 5: SEM images and relative composition determined by in situ EDX analysis of (**a**) HPGC, (**b**) RGC and (**c**) FGC.

As regards the mechanical behaviour, a fundamental understanding of the bitumen binder's rheological properties is essential in order to predict the end-use performance of these materials [37,38]. The visco-elastic behaviour of bitumen is characterized by its elastic (**G'**) and viscous (**G"**) moduli. These quantities, when are measured with respect to temperature, give the so-called time cure tests (temperature ramp tests). The ratio **G"/G'** is tanδ. During the time cure test, as the temperature increases, bitumen starts to lose most of its G' behaviour and begins to behave as a viscous fluid. At this point, tanδ value will exponentially increase and consequently G" will appear as the main component. Thus, the temperature at which the elastic modulus disappears and obviously tanδ → ∞ allow to unambiguously determine the sol-transition temperature t*. In cooling (inverse temperature experimental conditions), bitumen will recover its elastic feature and consequently tanδ will tend to drift towards its initial value with G' becoming the dominant component. This therefore implies that materials with higher loss moduli have a greater ability to resist deformation while materials with higher storage moduli have a greater ability to recover from deformation [7,8,40–43].

In the following, the time cure tests of both pristine LC50 and bitumen modified with HPGC, RGC and FGC are analyzed to compare the rheological response (feedback) of the tested systems. For comparison, the effect of $CaCO_3$ which is used as an inert filler (1 wt%) was also determined

[44]. As expected, in line with the general trend, an increase in temperature decreases the storage modulus and increases the loss tangent.

To optimize the dosage of the additives, the LC50 bitumen was modified at 1% and 3%. Taking into account the results shown in Table 2 and the possible impact of additives on the production costs of road pavements, 1% was chosen as the ideal dosage. In fact, at higher percentages, either no improvements are obtained, as in the case of the samples of bitumen modified with FGC, or in any case the improvements are not so significant as to justify an increase in the percentage of additive. The effect of an inert filler $CaCO_3$ (1 wt%) was also determined to evaluate the effectiveness of the additive on the bitumen. Obviously, bitumen modified by the filler was mixed for 1 h under the same condition of the modified bitumen samples to evaluate also the possible oxidation phenomenon effect. Both conditions (filler and oxidation effect) did not significantly change the property of the binder and so we can say that the additive interacted with the bitumen to modify it.

Table 2. Difference in transition temperature.

Sample	Transition Temperature (°C) ±0.1	Δ (°C) ±0.2	Δ (%)
LC50	60.5	--	--
LC50 + 1% $CaCO_3$	65.0	4.5	7.4
LC50 + 1% FGC	66.6	6.1	10.1
LC50 + 3% FGC	66.5	6.0	9.9
LC50 + 1% RGC	67.5	7.0	11.6
LC50 + 3% RGC	70.1	9.6	15.9
LC50 + 1% HPGC	65.5	5.0	8.3
LC50 + 3% HPGC	67.5	7.0	11.6

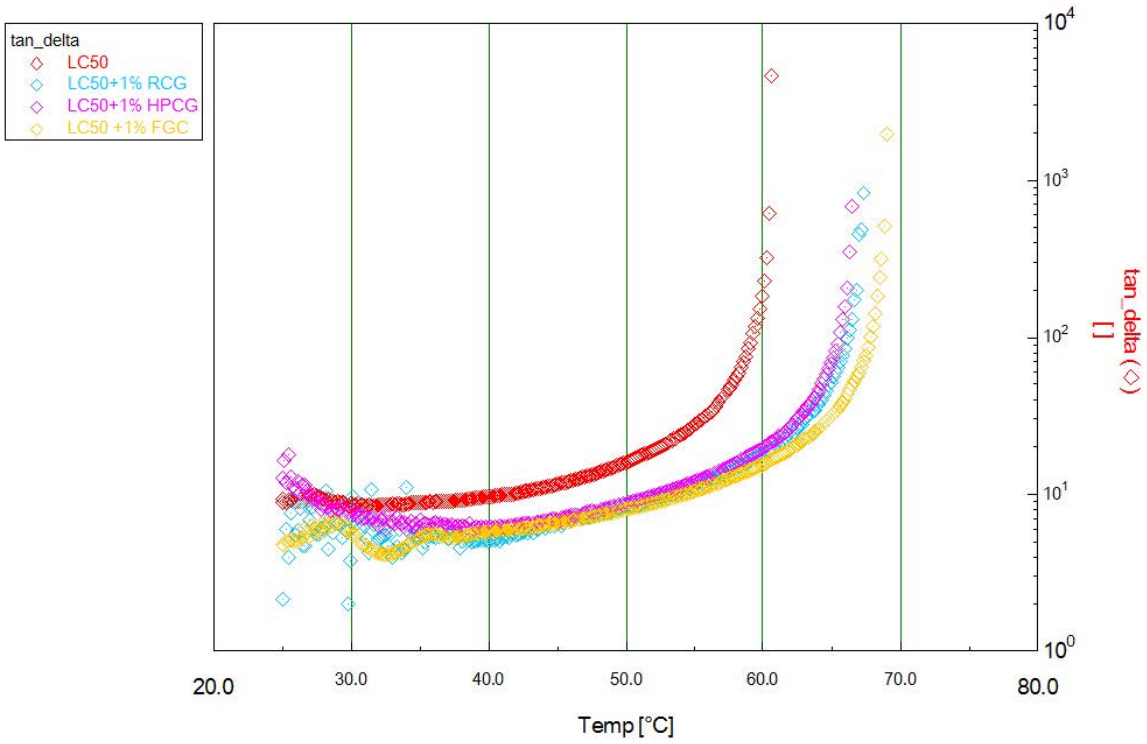

Figure 6: Time Cure Test 1—Semi-log plot of temperature ramp tests for the pristine LC50 and modified bitumen formulated with 1 wt% of bioadditive added as solid powder dispersion.

In Figure 6, we report the results of all modified bitumen samples. A pronounced hardening effect was observed upon addition of the additives already dosed at 1 wt%, this was clearly evidenced by the shift of the sol-transition temperature t* observed at higher temperature values compared to that of the reference sample. The right axis is the loss tangent (tanδ). As previously described, the asymptotic value of tanδ identifies the sol-transition temperature t*. As can be observed, the investigated bio-additives show a real effect to shift the sol transition and RGC seems to have a lighter better effect compared to the other one. A similar behavior, though with slight differences, was also recorded for C170 bitumen-based samples. In this case, while heating, t* was reached at higher values when C170 bitumen has been modified with HPGC.

It is worthy to note that the bio-additive works also on the softer bitumen. The action mechanism of the additive and the explanation of the observed experimental differences could be due to the different chemical composition. Even though the differences are so small that this analysis, generally performed by NMR spectroscopy, is not useful at this point of this research work.
Rheological analysis, concerning C170 bitumen, gave the following results in Figure 7 and Table 3.

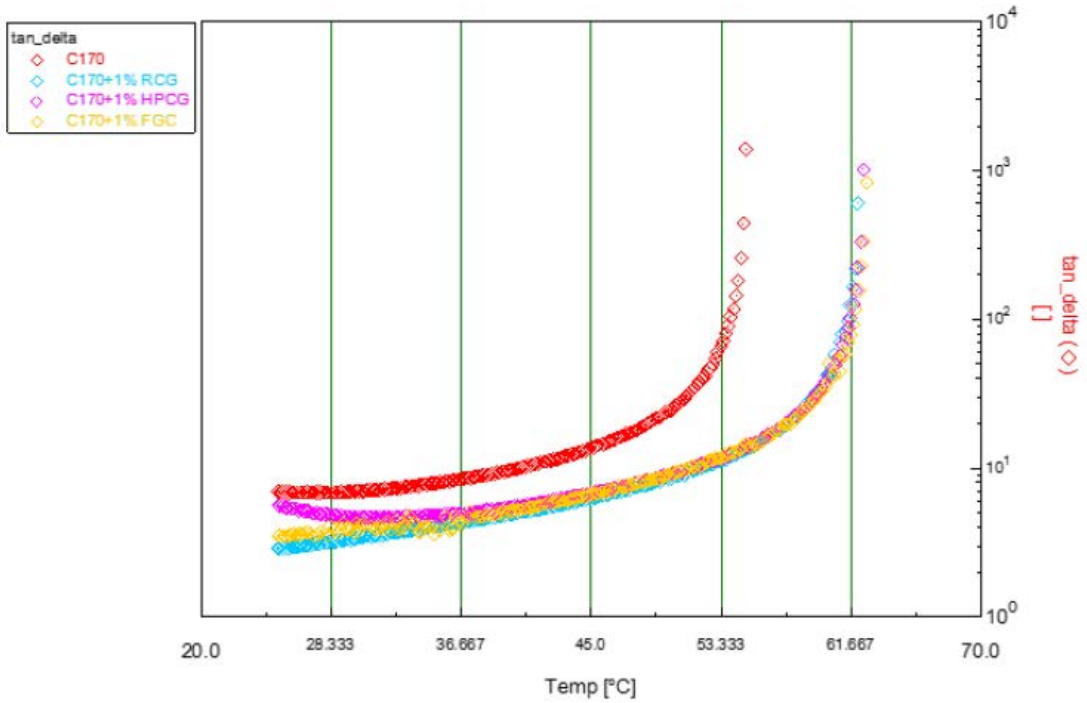

Figure 7: Time Cure Test—Semi-log plot of temperature ramp tests for the pristine C170 and modified bitumen formulated with 1 wt% of bioadditive and $CaCO_3$.

Table 3: Difference in transition temperature between the pure sample and the various modified compounds.

Sample	**Transition Temperature (°C) ±0.1**	**Δ (°C) ±0.2**	**Δ (%)**
C170	51,1	--	--
1% HPGC	62,2	11,1	21,7
1% RGC	60,9	9,8	19,2
1% FGC (1h)	61,5	10,4	20,4
1% FGC (2h)	62,3	11,2	21,9

1% $CaCO_3$	55	3,9	7,6

In Table 3, it is possible to observe closely the difference in transition temperature between the pristine C170 and modified bitumens. Moreover, in this case, the addition of a filler and the oxidation phenomenon which are due to the standard conditions of the modification did not make significant changes to the properties of the bitumen. In this case, there is a more evident change compared to the LC50 bitumen. In fact, from the results it can be seen that the difference between the bitumen + filler sample is much greater than that obtained in the analysis made on the previous bitumen (LC50). For the sample with 1% FGC, the result obtained with a longer modification time (2 h) was also reported as shown in Figure 8.

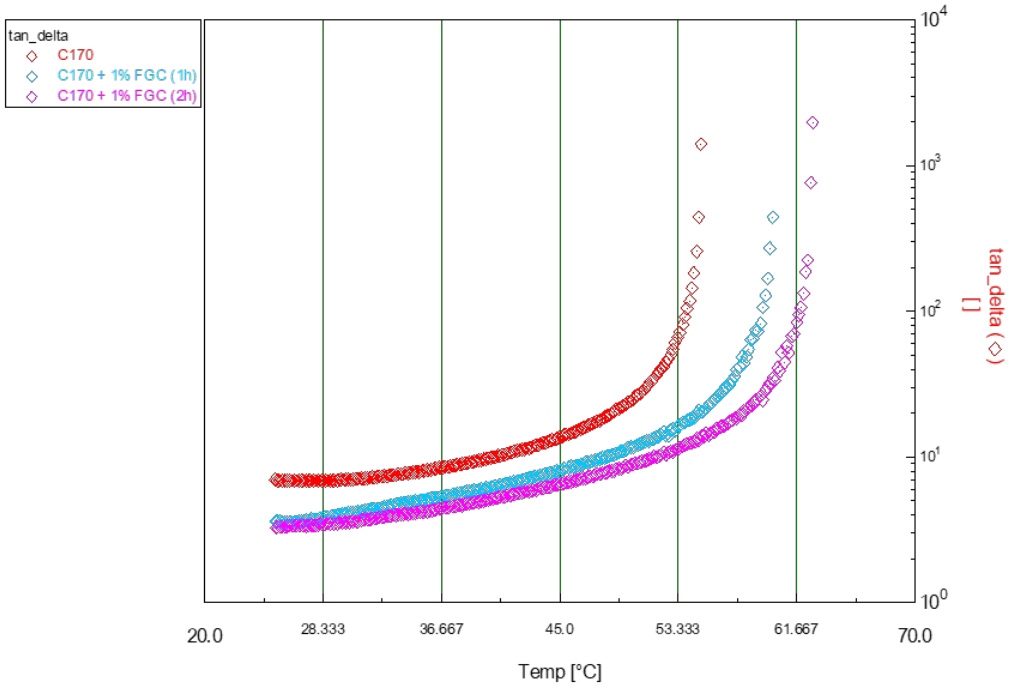

Figure 8: Time Cure Test—Differences in transition temperature between the same sample undergoing an extra hour of mixing at 150 °C.

In Figure 8 and from the values of transition shown in Table 3, it is observed how the performance of the additive is also influenced by the modification time. In fact, by doubling the stirring time of the sample, an increase in performance is observed. However, this increase does not seem to be enough to justify such long times in the production phase of the modified bitumen.

We can conclude by stating that in both cases, a physico-chemical modification of the bitumen is observed. This phenomenon is more evident in the case of C170 bitumen. These differences most certainly are due to the different chemical compositions of the two types of used bitumen. In fact, they come from two crude oils and two different oil refineries. The antioxidant properties of the additives were also tested by aging using Rolling Thin-Film Oven Test (RTFOT) according to ASTM D2872-04 [7,15]. In particular, the performance of the bitumen modified with the various additives was calculated and the transition temperature of the various samples before and after aging was calculated by means of rheological measurements (time cure test 25–120 °C). Unfortunately, none of the additives tested showed efficacy as an antioxidant agent.

3.1. Atomic Force Microscopy (AFM) Observation

Samples were investigated using AFM in tapping mode [45–50]. Images were acquired using probes with 150 kHz resonance frequency in air and at room temperature. Both height (left image) and phase (right image) signals were recorded simultaneously. The phase signal image, related to the mechanical properties of the specimen surface, allows to better distinguish hard domains (bright) from the elastic matrix (dark). Figure 9 refers to the pristine C170 sample. As is clearly visible, the dimensions of the domains do not exceed 4 microns in length, they are homogeneously dispersed and very few of them are interconnected. The vast majority of domains exhibit the typical bee-structure at their centre.

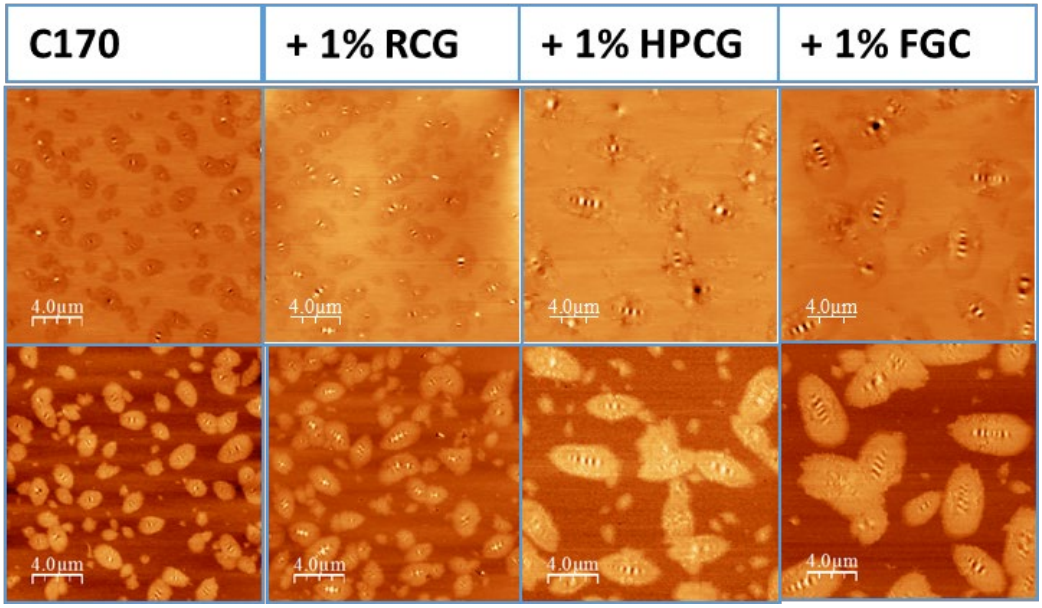

Figure 9: Sample surface: topography (UP), phase image (DOWN) Bitumen C170 Pure and Modified.

Sample C170 + 1% RGC shows similar features compared to the ones observed on pristine samples. The addition of RGC seems not to alter domain dimensions, as well as their arrangement on the sample surface as shown in Figure 9. The addition of HPGC has the effect of increasing the domain dimensions, that are now 5–6 µm in length even if very small hard domains less than 1 µm, are still present. On C170 + 1% HPGC sample surface, we also observe that few domains are indeed interconnected. The same effect was observed when a commercial material is used. The image shows the presence of large domains on the surface of C170 + 1% FGC sample and, as in the previous case, some of them are interconnected. This phenomenon can be attributed to the molecular structure of the additives. The dual polar/non-polar nature allows the curcumin molecule to interact with the asphaltenes with a resin-like function, already present in the bitumen. This role is fundamental in the asphaltene/maltene balance and induces the aggregations observed by the AFM experiments. All domains exhibit a well-developed bee-structure. A peculiar phenomenon is observed when the same blend undergoes 2 h of mixing instead of just 1 h, as in sample C170 + 1% FGC mixed 2 h at height temperature. In this case, domains are very small, less than 2 µm in length and in some cases, they are agglomerated in a giant domain (Figure 10).

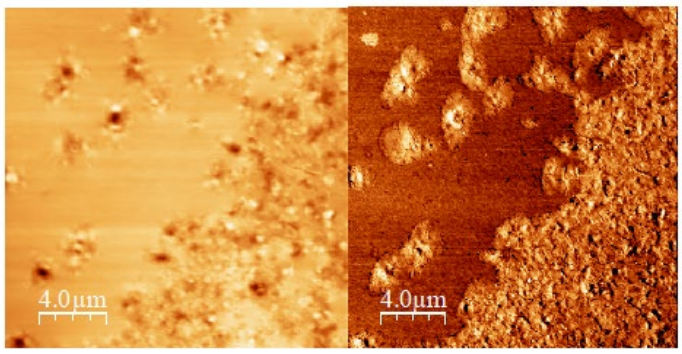

Figure 10: FGC 2 h sample surface: topography (left), phase image (right).

In any case, domains, even if small in length, preserve the bee-structure and are reported in the ESI (Figures S2 and S3). AFM analysis was performed on LC50 bitumen as well, but a very peculiar and unusual phenomenon was observed. In fact, the important phase contrast cannot be observed. This structure observed suggests more in-depth studies to be carried out in other research studies to correctly describe its nature. However, the Figures S4 and S5 of the ESI show some of the samples mentioned above.

3.2. Adhesion Test

Table 4 and Figure S6 in ESI show the results of the boiling tests [13,51,52] of the samples at different percentages of additive with a stone (porphyry) where the bitumen LC50 does not show good adhesion [53,54]. The chemical analysis of this type of stone is reported in the following article [7]. Moreover, in this case, it is observed that percentages higher than 1% of additive do not confer significant improvements. HPGC and RGC additives work very well as adhesion activators, while FGC improves the adhesion between bitumen and stone but much less than the other additives analysed (only 35–40%). Taking into consideration the best result obtained was with 3% (which is a percentage three times higher than that used for the other two additives), it does not achieve results comparable to the latter.

This phenomenon could be due to chemical composition of the FGC additive. FGC is a commercial turmeric. The high percentage of cellulose, present in the mixture, limits the adhesion properties of the additive but according to literature data [36], significantly increases the mechanical behaviour of the binder.

Table 4. Boiling test results for LC50.

Sample	Coverage (%)
PURE LC50	15
LC50 + 1% RGC	80
LC50 + 3% RGC	80
LC50 + 1% HPGC	75
LC50 + 3% HPGC	75
LC50 + 1% FGC	35
LC50 + 3% FGC	40

Table 5 and Figure S7 in ESI show the results of the boiling tests of the tested samples using also in this case, a stone (porphyry) with which the C170 bitumen already shows a good affinity. Given the results obtained from LC50, only the modified bitumen samples with 1% of the various additives were tested. As already mentioned, since bitumen already has an affinity to this type of

stone, we cannot hold in high regard the significant differences between the various samples. We can only say that in this case, only HPGC and FGC improved the adhesion between the bitumen and the stones.

Table 5. Boiling test results for C170.

Sample	Coverage (%)
PURE C170	70
C170 + 1% RGC	75
C170 + 1% HPGC	90
C170 + 1% FGC	90

4. Conclusions

In this study, we investigated the effects that turmeric spice, used as an additive, might induce bitumen's chemico-physical properties. In particular, we investigated its efficiency as a rheological modifier, adhesion promoter and antioxidant agent. Furthermore, we investigated the effect of curcumin, the main bioactive compound of turmeric, compound known for its antioxidant properties. The results showed that turmeric and curcumin are very efficient as adhesion promoters and as rheological modifiers while none of them works as an antioxidant agent. The different performances and efficiencies obtained for each additive with the two types of bitumen used highlight that their effectiveness is strongly influenced by the chemical nature of the neat bitumen. The surfactant nature of the additives plays a role similar to the resins normally present in bitumen. These molecules act on the molecular structure of the asphaltene modifying the supramolecular organization. This effect is reflected in the improved mechanical performances of the modified bitumens. The use of food grade additives will facilitate a reduction in several forms of pollution from affiliated industrial processes in a bid to help protect the environment. The study presented herein shows the possibility of using such economically advantageous food grade additives incorporated in small amounts to improve the rheological and adhesion properties of bitumen. Further work is also in progress to identify the right natural antioxidant.

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Chapter 7

Recycled materials via pyrolysis as bitumen modifiers

7.1. Products of the degradation of biomass and their effect on bitumen's properties

A wide variety of compounds are obtained from the degradation of biomass and some of these compounds can affect the properties of bitumen. Some of the most common products of biomass degradation include organic acids, alcohols, ketones, aldehydes, and phenolic compounds. These compounds can have differing effects on bitumen properties, depending on their chemical nature and concentration. Some of these materials were mentioned in chapter 2, section 2.3.

Some of these compounds can act as natural surfactants, lowering the interfacial tension between bitumen and other materials, making it easier to mix and disperse. They can also lower the viscosity of bitumen, making it easier to handle and pump during paving operations. In addition to their role as natural surfactants, some of the products of the degradation of biomass also have antioxidant properties, which can help to protect bitumen from oxidative aging and degradation. For example, some phenolic compounds that are produced during biomass degradation can act as effective antioxidants for bitumen.

Antioxidants function by inibiting or disrupting the chemical reactions that bring about oxidation in bitumen. This can help to slow down the aging process of bitumen, and prevent the formation of cracks and other forms of damage to asphalt. There has been significant interest in the use of biomass-derived antioxidants for bitumen, as they potentially be a sustainable and cost-effective alternative to synthetic antioxidants. However, the use of these compounds is still in its early phases. Not a lot is known about this and further research is needed to fully understand their effectiveness and how best to incorporate them into bitumen formulations.

In general, the use of biomass-derived additives for bitumen is a promising area of research, with the potential to improve the durability and lifespan of asphalt pavements while also reducing the environmental impact of asphalt production.

7.2. Results part 8

"When Physical Chemistry meets Circular Economy to solve Environmental Issues: Using Waste Pyrolysis Products to improve and rejuvenate Bitumen"

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1. Introduction

Around 2.01 billion tons of municipal solid waste (MSW) are produced worldwide each year, of which 33% are not adequately handled [1]; in many countries, indeed, the urban wastes (household,

school, industrial, hospital wastes, etc. [2]) are still treated by processes lacking in re-utilization or recycling activities. Improper solid waste management practices produce social and economic problems, have significant environmental repercussions, and increase human health risks [1].

Looking at Europe, in 2019, 224.4 million tons of MSW were produced, of which 31% was recycled, 27% was converted into energy, 18% underwent biological treatments, 24% was dumped into a landfill, and 1% was incinerated. In Italy, the percentages of waste treatment are in line with the European trend, but in comparison with German, it was noted that a better waste management process is feasible (Italian vs. German percentages: recycled 33% vs. 48%; energy recovery 21% vs. 32%, biological treatments 23% vs. 18%, landfilling 23% vs. 1%, incineration 1% vs. 1%, respectively) [3]. The disposal to landfills has the following consequences:

- country landscape disfiguring;
- maintenance and transport costs [4], since landfills are often located in remote areas;
- health problems due to the proliferation of bacteria and insects [5];
- pollution of soil, groundwater (due to percolation of liquids from organic matter decomposition), and atmosphere (emission of gaseous decomposition products [6] such as methane, which is twenty times more harmful than CO2 as a greenhouse gas [7]).

Thermochemical conversion processes (pyrolysis, gasification, combustion or incineration) are convenient strategies to produce fuel and energy from MSW [8]. The amount of MSW for thermal treatment reached 921 kton/yr in 2010–2015 [8]. Unfortunately, the combustion and incineration of waste have a non-negligible environmental impact [9–11]. The target of thermal treatment, indeed, should be to provide for an overall reduction in the environmental impact that might arise from improper waste management.

The pyrolysis process for waste transformation [8] is performed in the absence of O2 in specifically designed reactors, under specific temperatures and pressures, allowing for:

(i) the production of three added-value products (bio-oil, gas, and char) [8,12–14];
(ii) a higher energy recovery efficiency, and
(iii) the reduction of polluting gaseous emissions [15]. Although there are undisputed advantages for the use of this specific thermochemical process [8,16], and no significant increase in terms of CO2 emissions occurs, the economic returns associated with the condensable fraction (bio-oil) and solid product (char) are not completely defined because:
    - bio-oil is a complex liquid mixture containing hydrocarbons and oxygenated species with a very wide variety of molecular weights, which are still difficult to exploit and make use of;
    - char is a solid carbon-based material with a high inorganic fraction (depending on the feedstock) that limits its functional exploitation.

Another cycle that is still open in several countries is the asphalt cycle. After ~10–15 years, asphalts become aged, and hence hard and fragile, and are no longer suitable for road paving, so they are replaced with new ones, since expensive chemical treatments are needed for their regeneration. Recently, governments and road authorities demanded that the pavement industry became more

sustainable by reducing the consumption of both costly virgin and increasingly scarce materials and avoiding landfilling. In Italy, like other EU countries, only 20–30% of reclaimed asphalts are reused for new paving processes, and 8–10 wt.% of the available reclaimed asphalts were landfilled in 2018 [17,18]. The re-use of removed asphalt can significantly reduce the overall costs of new road paving materials [18,19]. The use of waste materials in road applications can also help in cost reduction, and an increasing trend for their use for such a scope can be found [20].

In this study, a virtuous pathway for the utilization of pyrolysis-derived residues to improve asphalt performances and increase their life-cycle, thus reducing disposal to landfills, is proposed. The feasibility of this idea is witnessed by the recent financing of a research project (ReScA) aiming at an advantageous use of both solid (char) and liquid (bio-oil) products derived from the pyrolysis of wastes to produce more durable and highly performing bitumens and asphalts, thus guaranteeing greater road safety and lower waste production.

This work is organized as follows: first, the physico-chemical basis underlying the idea of using pyrolysis-derived residues to improve the asphalts characteristics is introduced (Section 2), then the feasibility of the approach, as well as the methodology and the work carried out so far under the ReScA project, are reported in Sections 3 and 4, the expected impacts in technological, social, and economic fields are reported in Section 5, and the conclusions, together with some final comments on future perspectives, are reported in Section 6.

2. The Physico-Chemical Basis for the Integration of Wastes and Asphalt Cycles

Polymers are common additives for the improvement of asphalt properties, but up to now, their use has been uneconomical due to their high cost [20]. Recent research advances demonstrated the possible use of wastes, or products derived from the pyrolysis of wastes, as emerging bitumen and asphalt additives [20–24]. In addition, recently, the physico-chemical bases of the improvement of asphalt mechanical characteristics due to char addition have been assessed [25–30]. Char exhibits antioxidant and anti-aging properties when used as an asphalt additive, and bio-oil can exert regenerative properties on aged asphalts, restoring the maltene phase with low-molecular weight molecules [27,31]. Nano-sized particles, thanks to their high surface-to-volume ratio and tuneable chemical composition, can exert a significant effect on the rheological properties of bitumens and asphalts, even when added to bitumen in very small percentages [32]. In particular, fine particles are able to increase the load capacity of the pavement and decrease the formation of cracks due to fatigue during the pavement's operation life. Carbonaceous particles are expected to give better results, thanks to their chemical compatibility with the bitumen (they are both carbon-rich materials) [25]. The char, being characterized by a porous and fibrous structure, is responsible for strong interactions with the binder [28]. In addition, its high carbon content has been found to affect bitumen hardness and toughness [33]. The use of char as a bitumen modifier has been tested by different authors [34,35] and in all the cases, improved mechanical performances were detected.

The interactions between char and bitumens can also have anti-aging effects. The chemical reasoning supporting this hypothesis is that the interaction of the apolar part of the char with the maltenic phase of bitumen is expected to constrain the latter into more restricted dynamics. Therefore, the presence of solid particles like char, hindering bitumen transformation dynamics, could slow

down the processes responsible for aging, including the dynamics involving asphaltene clusters and their aggregates, at different length scales and interacting with different strengths [36].

Very recently, Rajib et al. in 2021 [37] examined the benefits of using biochar to delay oxidation and UV aging on both binder and asphalt, and Kumar et al. [38] evaluated the thermal storage stability of binders modified with pyrolyzed plastic waste (PPC). Their work demonstrated that the pyrolysis residues can be used as modifiers in bitumens, but it emerges that much work is still needed, in particular to face stability problems [38]. Under aging, cracks or fractures in asphalt can take place [39], since bitumen chemical components become less and less mobile under the applied stress. Aging is the overall result of several processes, each of them characterized by their own timescales:

1. volatilization of lighter components [40], a phenomenon occurring even during new asphalt placement [41,42];
2. oxidation of bitumen constituents by atmospheric oxygen. Oxidized molecules are more polar and can give enhanced self-assembly [43];
3. chemical reactions causing polymerization and formation of larger structures within the bitumen (thixotropy) [44].

After aging, the bitumen's original ductility/viscosity can be somehow restored by the simple addition of softening (usually called fluxing) agents, such as flux oil, soy oil, slurry oil, lube stock, etc. [45,46]. To date, more sophisticated methods to restore the original chemistry of the neat bitumen and its original inter-molecular structure [36,47] (rejuvenation) by delaying the oxidations, agglomerations, and self-assembly processes occurring during the whole aging process have been formulated.

Regarding the use of bio-oil, it has been proven that its composition makes it a possible fluxing agent. The rationale behind this application lies in the presence of amphiphilic molecules that can interact with those already present in the bitumen. The interaction between different types of amphiphilic sites can be various, due to the complex nature of such molecules, and with marked effects, especially if acidic and basic molecules come into contact within the system, due to a favourable energetic push towards strong H-bond formation or, even a definite proton transfer with the formation of charged species [48]. In this framework, a recent example is offered by the work of Ren et al. in 2020 [49], where the addition of bio-oil derived from biomass pyrolysis to bitumen has been tested to improve its performance. The improved bitumen was applied to self-adhesive and doped hot-melt sheets. Bio-oil was tested by FT-IR, by GC-MS and by Karl Fischer titration, whereas the bitumen performances were evaluated by softening point tests, low temperature flexibility tests, peeling strength tests, viscosity, density, hardness and heat resistance determinations, and maintained stickiness tests. Results on physical properties evaluation demonstrate that bio-bitumen is a potential substitute in bitumen coating sheets.

In the next section, details about how these aspects are exploited and further analysed within the ReScA project are reported.

3. Methodology and Preliminary Results: The ReScA Project

The ReScA project focuses on the feasible utilization of both bio-oil and char from pyrolysis processes to produce better and longer-lasting asphalts, as well as to regenerate them on-site once they are aged or exhausted. The ultimate goal of ReScA is the integration of urban wastes and the asphalt cycles. It will be accomplished according to two main pillars (Figure 1): (i) the tuning of the pyrolysis product characteristics through process optimization; (ii) the use of pyrolysis products for asphalt formulation and rejuvenation when they are aged or exhausted.

The proposed approach leads to the following general benefits:

1. replacement of petroleum-derived products (e.g., crude oil) with products from the pyrolysis of urban solid wastes;
2. improvement of the mechanical characteristics and the longevity of asphalts through the use of char;
3. low-cost and on-site rejuvenation of exhausted asphalts through bio-oil.

The above-mentioned benefits are expected to greatly impact aged asphalts disposal in landfills, CO_2 emission, and production costs, as a consequence of the increased as- phalts duration. Moreover, the ReScA concept, adopting the exploitation of pyrolysis from the transformation of urban wastes (focusing on refuse derived fuels, RDFs), at the same time, allows for a significant energy recovery [50] (the heating value is typically around 20 MJ/kg [51]) and the reduction of landfilling, accomplishing the circular economy paradigm which is urged to be adopted in the post-COVID-19 transition.

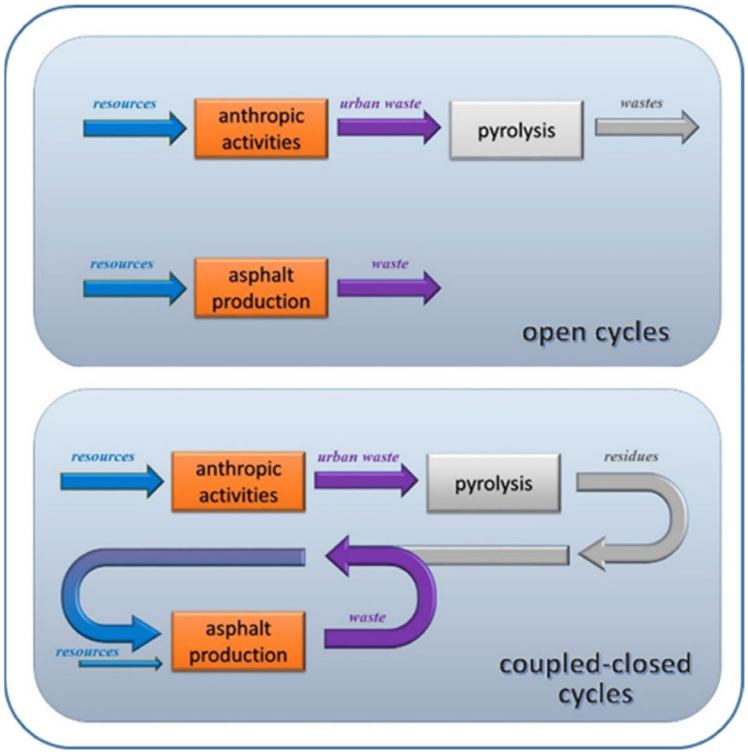

Figure 1: Scheme representing the ReScA concept for the integration of pyrolysis and pavement production cycles.

3.1. *Methodology (Pyrolysis, Rheological Properties of Asphalts)*

ReScA pursues an unconventional exploitation of solid and liquid products (char and bio-oil) for the thermoconversion of urban waste to enhance and improve asphalts, making them more resistant and long-lived (through the use of char) and allowing for their on-site regeneration through the use of bio-oil. ReScA is an interdisciplinary project taking advantage of the collaboration of chemists, physicist, and engineers to ensure both the production and the characterization of additives for asphalts by pyrolysis and the characterization of the improved asphalt performances from a rheological point of view.

3.1.1. Pyrolysis Approach as Waste Thermoconversion

The pyrolysis process allows for the conversion of a feedstock, mostly with a high carbon content (e.g., lignocellulosic biomasses, RDFs, plastics, tires), in three main products:

- a condensable fraction (bio-oil) rich in water, hydrocarbons, and oxygen-containing species [14,52–54];
- a mixture of gases (mainly CO, CO_2, and CH_4) that can be used, thanks to its heating value, to energetically sustain the process [14,52,55–58];
- a solid carbon-rich residue (char) [52,59].

The ranges of operating temperature, heating rate, atmosphere (the typology of inert gases), and residence time of the vapors and solids in the pyrolysis chamber can be adjusted based on the desired outputs, gathering the pyrolysis processes into four broad categories: slow, conventional, fast, and flash pyrolysis [52]. Heating rates vary from 0.1–1 °C/s (slow pyrolysis) to above 1000 °C/s (flash pyrolysis), while conventionally, the temperatures of the process lie between 300–600 °C.

To highlight the influence of the operating parameters on the product yields, in Figure 2, a comparison between the yields of the pyrolysis products derived from a ligno-cellulosic biomass obtained by tests performed at different final temperatures and different heating rates is reported. As a general indication, slow pyrolysis conditions are suitable for char production, especially at low temperatures, while for the same temperatures, fast or flash pyrolysis conditions are suitable for the maximization of gas and liquid productions.

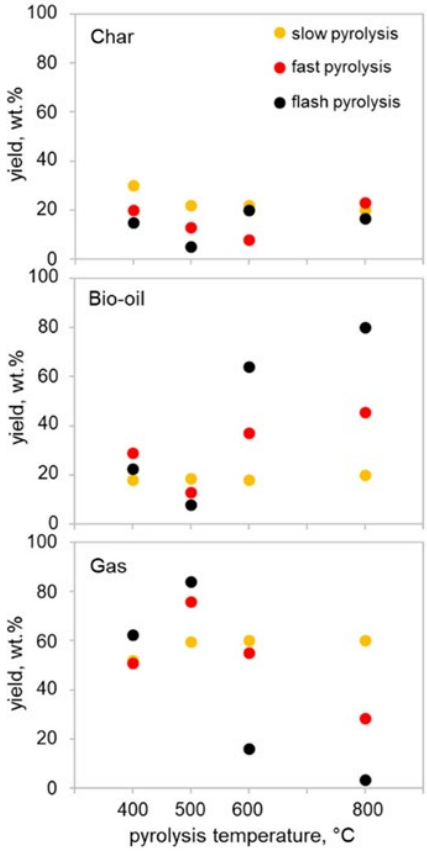

Figure 2: Product yields obtained from pine wood pyrolysis at different temperatures under slow, fast, and flash pyrolysis conditions (adapted from [52]).

Energy consumptions of the various types of processes are another important aspect to be taken into consideration for application purposes. However, to assess the economic performance of a given process, the whole productive chain, including the end-users of the pyrolysis products, should be taken into account. Life cycle assessment (LCA) becomes necessary in such an evaluation.

The pyrolysis process is a flexible thermoconversion strategy, since the composition of each pyrolysis product can be tuned by acting on suitable parameters. This optimization implies the detailed characterization of the composition of the starting feedstock, which is one of the major trending topics of this wide research area [52]. Standardized protocols (ASTM protocols) to define the elemental composition (C, H, N, S contents by ultimate analysis), the contents of moisture, ash, volatiles, and fixed carbon (by proximate analysis), and the heating value of a feedstock are conventionally adopted [61].

Regarding the ReScA project, the selected feedstocks (RDFs) are derived from urban waste management and stabilized according to the current legislation. RDF is the combustible fraction of MSW characterized by a high carbon content and a high calorific value, since its composition includes: hard plastics, packaging waste, textiles, wood, metals, and rubber [62]. RDF is produced in mechanical–biological plants for MSW sorting, as the final residue of the following sequential processes: (i) the recovery of recyclable materials (e.g., plastics, metals, glass, paper); (ii) the biological stabilization of biodegradable waste; (iii) the separation of inert waste [62].

RDF is characterized by a high compositional variability which influences its overall thermal behavior. The average RDF composition reported by different authors is the following: 15–35%

plastics, 15–50% cellulosic paper and cardboard, 2–10% wood, 5–20% organics, and about 5–10% non-combustible matter [62–64]. The overall thermal degradation of RDF is mainly influenced by the thermal degradation of the two more abundant fractions (cellulosic and plastic fractions) [64]. RDF decomposes in a wider temperature range (200–600 ◦C, Figure 4), but at a lower temperature compared to carbon-rich materials [65]. Its low fixed-carbon, the highly volatile matter [64], and the presence of non-volatile matter between 10 and 20% (metals can catalyze decompositions) are responsible for such a pyrolytic behavior. The depolymerization and monomer fragmentation processes of the RDF components regulate the relative quantities of solid (char), liquid (bio-oil), and gaseous fractions, especially those with lower molecular weights.

For a better understanding of the phenomena occurring in the thermal degradation of the RDF, and also to highlight how the heating rate and the final temperature can influence the latter, the mass loss (measured by thermogravimetric analysis, TGA) and the differential thermogravimetric signal (DTG) of a RDF, selected as a case study, are reported in Figure 3 for two different heating rates (5 and 50 ◦C/min). The mass loss as a function of the temperature or residence time is due to the concurrent phenomena of decomposition, oxidation, and loss of volatiles [66]. The differences observed for the two TG curves evidenced that the degradation mechanism is influenced by the heating rate and, as a consequence, that the relative amounts of the three fractions at the output of the pyrolysis process (gas, char, and bio-oil) can be tuned by operating on different parameters (mainly temperature range, heating rate, and gas residence time).

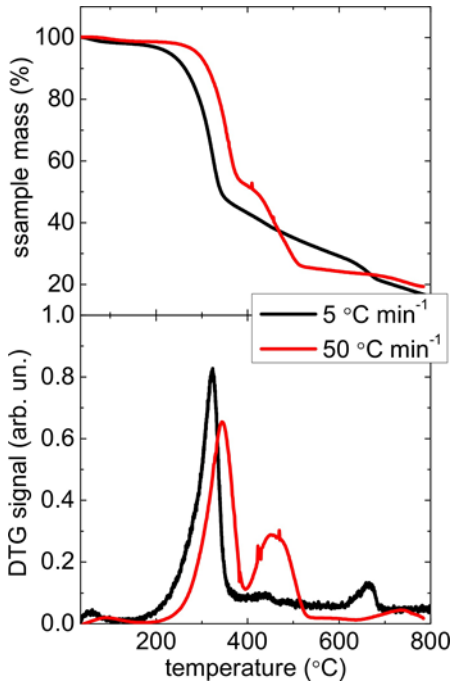

Figure 3: Mass loss (upper panel) and corresponding derivative curve of a RDF. Thermogravimetric analyses have been performed from 30 °C up to 800 °C on a Perkin–Elmer STA6000 under inert atmosphere (N2, flux 40 mL/min), applying two different heating rates: 5 °C/min and 50 °C/min.

As a final remark, the superiority of the pyrolysis treatment of plastic wastes to obtain overall environmental performances better than those of conventional options, such as landfilling or

incineration, has been proven by means of the LCA approach since 2005 [67]. More recently, Jeswani et al. [10] have carried out a deeper LCA analysis showing that, even if the pyrolysis treatment of mixed plastic waste has a 50% lower climate change impact and life cycle energy use than the energy recovery option, other impacts such as acidification, eutrophication, and photochemical and ozone formation, are higher than those for mechanical recycling and energy recovery due to the relatively high energy demand in the pyrolysis and purification processes. Therefore, the results of Jeswani et al. [10] underline the need to improve, in the future, the research effort to increase the carbon conversion efficiency of waste pyrolysis to further reduce its impact.

3.1.2. Asphalts Preparation, Aging, Rejuvenation Testing and Rheological Characterization

A wide array of standard rheological tests is usually employed to characterize the asphalt components (mainly bituminous fraction) and the asphalt prototypes. Within the ReScA project, bitumen samples containing different amounts of char are prepared and the evaluation of their stability is achieved by different techniques: penetration grade experiments (EN 1426: 2015), ring and ball tests (EN 1427: 2015), NMR diffusion experiments, differential scanning calorimetry (DSC) measurements, rheometry measurements for G', G'', and tan delta, rutting and fatigue parameters, black diagrams analysis, microscopy imaging (optical, AFM), and infrared spectroscopy measurements. The char-modified bitumens exhibiting good stability are then used to prepare asphalt pro- totypes. The preparation of asphalt prototypes is carried out in accordance with standard protocols (UNI EN 12697-31) involving a gyratory compactor. In detail, the size distribution of the inorganic particles is chosen according to the Italian Standard Specifications [19], at the same time, meeting the limits imposed by the Superior Performing Asphalt Pavements method under the Strategic Highway Research Program (Superpave SHRP) [20]. Specific aggregate gradation for the asphalt specimen production are chosen to ensure anti-rutting phenomena [21] and following a mix-design method (UNI EN 933-1). Stability evaluation is achieved using the standard Marshall Stability Test (ASTM D6927).

To evaluate the anti-aging effects given by the char addition, aging tests are performed on char modified bitumens. The simulation of aging is carried out by the standard procedure of the rolling thin-film oven test (RTFOT) according to the standard protocol ASTM D2872-04, and the pressure aging vessel (PAV) test, according to the ASTM D6521 protocol. The characterization of the mechanical properties after the aging process is performed by the same analytical techniques used for the stability evaluations.

To test the effectiveness of bio-oil as a rejuvenator or as fluxing agent, aged bitumens samples are characterized by the aforementioned techniques and then treated with increasing amounts of bio-oil. The evaluation of the mechanical properties of the obtained samples and the comparison of such results with those of virgin and aged bitumens allow for the definition of the effect of the bio-oil addition.

The collection of all these characterization results is expected to strengthen the under-standing of the mechanisms of interaction between bitumen constituents and additives in the form of nanoparticles responsible for the increase in performance and durability of the binder and the resulting

asphalt. As proof of the proposed approach, some preliminary results on a RDF, feedstock selected as a case study, are reported in the next section.

4. Preliminary Results: RDF as a Case Study

In this section, preliminary results on the characterization of bio-oil and char pro- duced through RDF pyrolysis, selected as a case study, at different final temperatures, and their feasible use as rheological modifiers, rejuvenating agents, and antioxidant agents are reported. The RDF used as the first feedstock for pyrolysis testing was provided by Calabra Maceri S.p.A. (Rende, CS, Italy).

The RDF was pyrolyzed in a tubular lab-scale quartz reactor under fast pyrolysis conditions (heating rate 30 ◦C/min) at three different final temperatures (550 ◦C, 650 ◦C, 750 ◦C). The final temperatures have been selected on the basis of the TG profiles reported in Figure 3. Figure 4 highlights the chemical composition of bio-oils collected after each pyrolysis test. As it can be seen, the chemical composition of the bio-oil depends on the pyrolysis final temperature. It is interesting to note that the presence of specific compounds (for example, fluorene and 1-nonadecene) is scarcely influenced by the pyrolysis temperature, while other compounds (benzoic acid, for instance) are characterized by amounts that can vary as a consequence of a temperature change. This aspect is related to the occurrence of secondary reactions at high temperatures, leading to the decomposition of more reactive compounds [52].

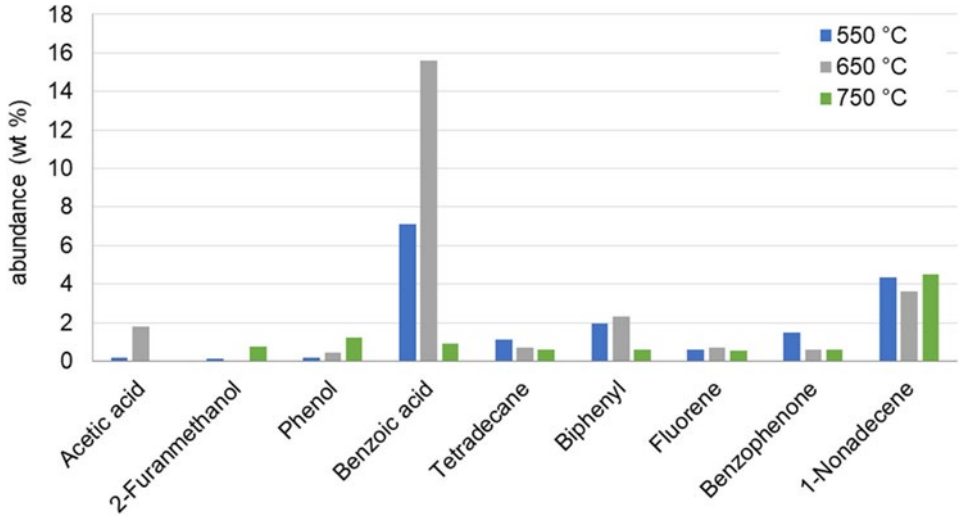

Figure 4: Relative abundance of selected species in bio-oils from RDF fast pyrolysis tests at 550 °C, 650 °C, and 750 °C. The abundances have been estimated by gas chromatographic analysis of acetone- diluted bio-oil solutions performed on an Agilent GC-MS instrument (7890 A/5972 C) equipped with an Agilent DB-624 capillary column.

When using the char as a bitumen filler in asphalt preparation, the relevant char features to take into account are: the composition, the surface chemistry, and the textural and morphological properties. These chemico-physical and morphological characteristics greatly affect the chemical interactions between the char particles (acting as a filler) and the macromolecules forming the bitumen. These influence the stability and/or the mechanical properties of the asphalt [27,68]. By

acting on pyrolysis conditions, the possibility of influencing the chemical composition of the char can be achieved. For this reason, it becomes advisable to optimize the whole process by varying the pyrolysis conditions in such a way that the relative quantities of the desired pyrolysis products and their compositions match as much as possible those of the additives for asphalts.

Figure 5 evidences the influence of the final temperature on the chemical composition of char obtained from RDF fast pyrolysis. The results for the final temperatures of 550 °C, 650 °C, and 750 °C are reported.

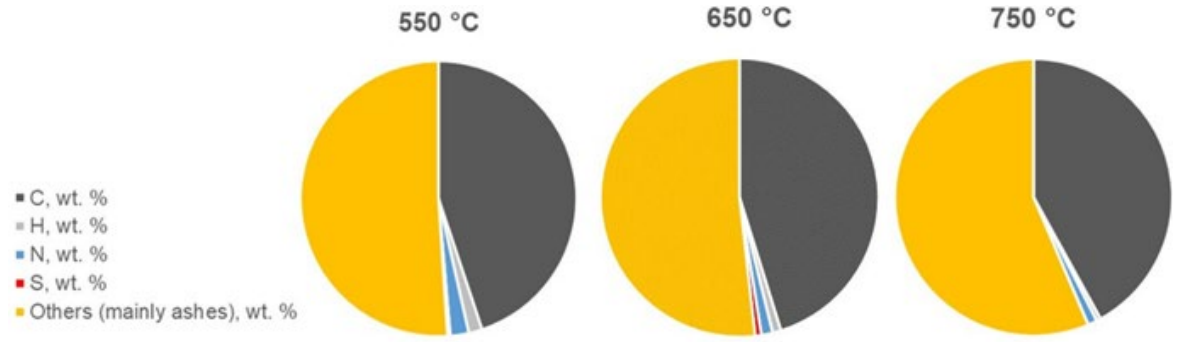

Figure 5: Compositional analysis of char samples derived from RDF fast pyrolysis tests at 550 °C, 650 °C, and 750 °C. C, H, and N contents were determined in accordance with the ASTM D3176 protocol by using a Leco 628 elemental analyser. S content was measured in accordance with the ASTM D4239 protocol by using a Leco 144 analyzer.

To demonstrate the feasibility of the usage of the liquid and solid products from pyrolysis tests as bitumen additives, bio-oil and char produced by the pyrolysis of a wood- based RDF supplied by Calabra Maceri S.p.A. (Rende, CS, Italy), have been tested at two different temperatures (550 ◦C and 750 ◦C):

- neat bio-oil (P-Oil) obtained from a pyrolysis test at 750 ◦C (temperature test allowing for the highest yield of liquid fraction);
- neat char, (P-C1) obtained from a pyrolysis test at 550 ◦C (temperature test allowing for the highest yield of solid fraction);
- a 50:50 w/w mixture of P-Oil and P-C1 (P-C2).

The modified bitumen samples were prepared by adding 2 wt.% of the three additives to different aliquots of a neat bitumen. The bitumen used was a 50/70 penetration grade bitumen kindly supplied by Polyglass SpA (Ponte di Piave, TV, Veneto, Italy) and derived from a crude oil originating from Saudi Arabia, asphaltene content 32.4 wt.%.

Time cure tests to evaluate how the additive addition can change the mechanical properties of a given bitumen were performed. In particular, the effectiveness of their use as a rheological modifier, as a rejuvenating agent, and as antioxidant agents was evaluated. Rheology time cure tests were performed with a temperature ramp at a constant heating rate of 1 °C/min (tan $\delta = G''/G'$) [69] under the regime of a small amplitude oscillatory shear at a frequency of 1Hz using a dynamic stress-controlled rheometer (SR5, Rheometric Scientific, Piscataway, NJ, USA) equipped with a parallel plate geometry (gap 2 mm, diameter 25 mm), and the temperature was controlled by a Peltier element (uncertainty 0.1 °C). These conditions are those generally adopted for accurate studies on bitumen mechanical properties [70,71].

The time cure tests results are reported in Figure 6.

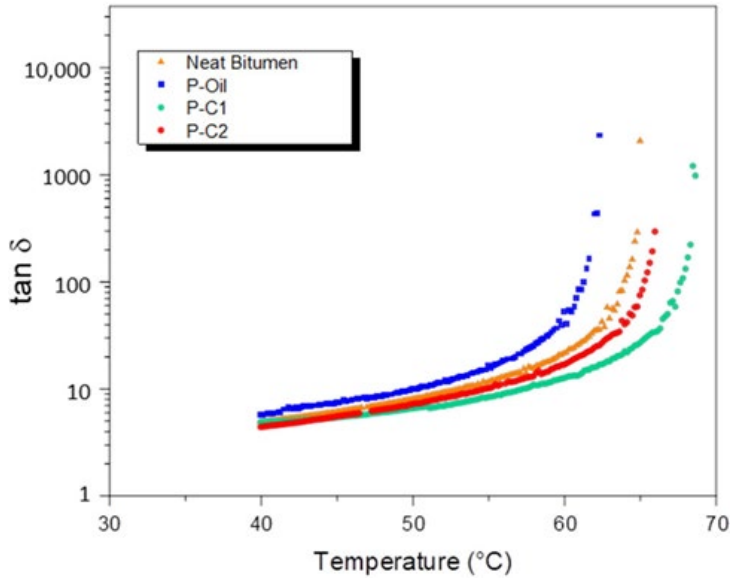

Figure 6. Results obtained from time cure tests on the three modified bitumens.

P-Oil is able to lower the transition temperature of the neat bitumen. This is an expected result because as far as it is known, only an oily compound has a softening ability, so bio-oil can be considered a bituminous fluxing agent. Conversely, *P-C1* and *P-C2*, showing a moderate modifying action, might be used as bituminous conglomerates fillers. All the additive formulations were also tested as anti-aging agents. In Table 1, the transition temperatures of bitumens modified by *P-Oil*, *P-C1,* and *P-C2,* before and after the aging procedure, are reported.

Table 1. Transition temperature of bitumen samples modified by *P-Oil*, *P-C1,* and *P-C2* before and after aging.

Sample	**Transition T (°C) ± 0.1 before aging**	**Transition T (°C) ± 0.1 after aging**	**Δ (°C)**
Neat Bitumen	65.0	73.6	8.6
Bitumen + P-Oil	62.3	71.5	9.2
Bitumen + P-C1	68.5	75.5	7.0
Bitumen + P-C2	66.0	73.4	7.4

The rheological analysis showed that P-Oil is the only additive that can be used as a bituminous antioxidant. In fact, its tan δ tends to resist the hardening induced by oxidation. The effect of pyrolysis-derived additives on the oxidized bitumen (aging simulated by the standard procedure of RTFOT, according to the standard protocol ASTM D2872) are shown by the mechanical spectra (results of time cure tests) reported in Figure 7.

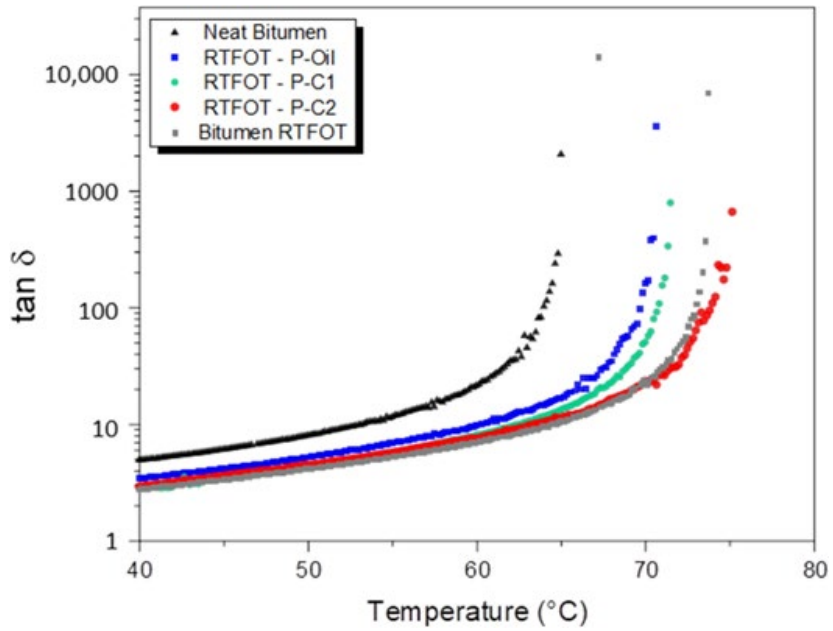

Figure 7: Time cure tests of neat bitumen, aged bitumen (bitumen RTFOT), and the three samples obtained by adding P-Oil, P-C1, and P-C2 to aged bitumen.

As widely demonstrated in literature, in order to understand the real regenerative capacity of an additive, it is necessary to make a preliminary rheological analysis. Since tan δ trend is similar to that for virgin bitumen, it is possible to claim that this additive might act as a rejuvenating agent [68]. According to the results in Figure 6, P-Oil and P-C1 seemed to have the ability to rejuvenate the aged bitumen, since both showed an intermediate rheological behavior between the virgin and aged samples. On the other hand, P-C2 had a profile almost similar to that of the aged bitumen, so the possibility of using it as a bituminous regenerator is excluded.

These preliminary tests demonstrated that the pyrolysis products act in different ways when integrated in the formulation of a bitumen, and they can also effectively act as rejuvenating agents.

5. Expected Impacts in Technological, Social, and Economic Fields

The approach proposed by the ReScA project is expected to impact the quality of people's lives, fostering technological, economic, and social development. The focus on the pyrolysis process foresees related advantages: the production of energy vectors, smaller dimensions of treatment plants and their cleaning sections, with consequent lower investment costs, and in general, greater global efficiencies, as well as operating flexibility and reduced greenhouse gas emissions. In the vision of the ReScA project, RDF is not used to produce energy ("quaternary recovery", according to the European waste hierarchy introduced by the waste directive (Dir. 2008/98/EC) and recently amended in the Circular Economy Package of 4/7/2018), but as a starting point for added-value materials recovery ("tertiary recovery") to be used for the production of asphalts.

From the technological point of view, the use of char to enhance bitumen is a promising strategy to exploit the use of carbonaceous nanoparticles as modifiers since, at the present, their application, in spite of the advantageous results achieved on fullerenes, nanotubes, and graphene related materials [25,26], is limited due to the high production costs. The availability of carbonaceous particles at a

low cost and with high performance as bitumen enhancers will explode studies in this sector. It has been predicted that the bitumen modified with char will have a greater resistance to cracking and rutting phenomena occurring at both high and low temperatures. This greater resistance to thermal fluctuations would undoubtedly offer greater safety for motorists and a drastic reduction in road maintenance activities. Moreover, it can be stated that the use of char as a modifier for asphalt, in addition to giving better mechanical performance and an increase in shelf- life, can also lead to significant advantages in the regeneration phase. Indeed, the use of bio-oil for the regenerative purposes for an aged asphalt could reasonably be effective in establishing synergistic effects with the char already present in the improved asphalt. The hydrocarbon molecules present as a fraction of the bio-oil are chemically similar to the carbonaceous particles of char, offering an enhanced rejuvenating effect, thanks to adsorption and chemical interaction phenomena. This would represent a breakthrough in the use of multi-functional and multi-effect additives, providing safer, longer-lasting, easy- to-regenerate roads with reduced maintenance and production costs. A study conducted in 2008 [72] estimated that the energy consumption reduction would be about 23% if an asphalt was reused for the construction of new road pavements. This result is in accordance with those obtained by a project financed by the European Community [73] and highlights the environmental advantages of the reuse of exhaust asphalts (a lower release of heavy metals and polycyclic aromatic hydrocarbons (PAHs)).

The recent work of Moins et al. [19] indeed, demonstrated through LCA studies that with respect to the total economic and environmental impact of asphalt industry:

- the bitumen production is the main hotspot and accounts for 12% to 41% of the environmental impact and 10% to 39% of the economic impact;
- the virgin aggregates supply has an economic impact from 5% to 16%;
- the transport of raw materials contributes between 10% and 24% to the environmental impact and between 6% to 14% to the economic impact;
- plant operation activities have an economic impact from 12% to 24%;
- the energy use in asphalt mixture production has an environmental impact ranging between 11% and 24%.

The approach suggested by ReScA pointed towards a reduction in the consumption of bitumen for the production of any new asphalts and would boost the strategies for the regeneration of aged asphalts, thus limiting exhaust asphalt landfilling and new asphalt production. All this, therefore, would lead to a reduced and rationalized use of petroleum materials and derivatives, as well as aggregates and sands, constituent elements of asphalts extracted from natural resources, achieving economic returns, resource preservation, and landscape and environmental protection.

6. Conclusions and Future Perspectives

The simultaneous coupling and closing of waste pyrolysis and asphalt cycles has been proposed. In this approach, the solid (char) and liquid (bio-oil) residues of waste pyrolysis can be used as added-value ingredients to (i) produce improved asphalts, with increased performances for motorists' safety and with an increased life-cycle, and (ii) regenerate exhaust asphalt. In this way a virtuous mechanism where urban wastes are no longer disposed to landfills has been individuated. In addition, the asphalt

prolonged life-cycle and the possibility to regenerate asphalt by pyrolysis-derived oil will reduce wastes, slowing down landfilling. Of course, the pyrolysis conditions (temperature, temperature ramp, duration of thermal treatment) are all factors that can be tuned to optimize the pyrolysis process to obtain residues with ad-hoc characteristics for asphalt technology. The benefit of this approach is also to be seen in a circular economy perspective. Sustainable development is pursued through research and innovation and through the improvement of infrastructure. To increase the knowledge on process development, scientists, policymakers, and entrepreneurs must work together to develop new and innovative approaches to waste re-use that address both safety and sustainability.

The overall perspective of the ReScA project is to contribute to the recovery of added value materials through the valorisation of wastes and their exploitation as additives for improved bitumens and asphalt production. The main goal of the ReScA project is to pursue both process sustainability and environment protection by taking these into account for all levels of the production cycle, namely from the limitation of waste disposal in the environment to the development of new protocols for bitumens and asphalt production and management. The choice of pyrolysis, an extremely promising and flexible thermochemical conversion technology (but not yet consolidated on a global scale) will allow the verification of its potential and applicability in terms of sustainability and in the framework of the circular economy paradigm.

The proposed idea integrates the urban waste transformation process with that of asphalt production, leading to:

- the promotion of cleaner technologies for the use of urban wastes;
- the production of road materials with improved properties from the reuse of urban wastes;
- an alternative applications of pyrolysis products (liquids and solids) outside of the fuel and chemicals industries;
- the reduction of the costs for the construction of safer and longer-lasting road pave- ments and those related to maintenance activities;
- the integration of systems and processes;
- the optimization of low-cost processes by operating on the parameters involved;
- energy saving and environmental protection (LCA analysis indicates that the chemical recycling of plastic wastes through pyrolysis has a climate change impact 42% lower than the energy recovery option) [10].

These aspects are in accordance with the community policies dealing with the circular economy approach, the Sustainable Development Goals pillars, and the Kyoto Protocol, since they pursue the security of energy supply, a sustainable use of urban solid wastes, the reduction of gaseous emissions, landscape and environmental protection, and the limited consumption of resources. The recovery and reuse of waste is strongly encouraged, since waste is considered as a source of new functional materials.

The use of char to enhance bitumen properties, exploiting the char composition and characteristics that are very close to those of the carbonaceous nanoparticles currently used for this purpose (fullerenes, nanotubes, and graphenes) [26], is a very promising strategy, first of all, because

a fine modulation of char morphological and functional characteristics(granulometry and porosity, to name a few) can be obtained by operating on the pyrolysis process parameters. These interesting potentials would make char an excellent candidate to replace fullerenes, nanotubes, and graphenes, which, despite being recently considered as very valid additives for bitumen due to their high performance-enhancing abilities [26], currently have a very limited application due to their high production costs [25].

To conclude, one aspect of complex systems physics has to be considered: it is known that often, different additives yield an overall effect that is not the sum of the two single effects, but the result of synergistic effects [74]. Therefore, the simultaneous use of char and bio-oil can enlarge the scenario of beneficial effects in bitumens. For these reasons, the ReScA project will foster future developments in the use of multi-functional and multi-effect additives, a quite novel field in bitumen and asphalt technology. The benefits achievable through safer, longer-lasting roads, with reduced maintenance and production costs, and with an overall reduction of wastes to be disposed into landfills, would be indisputable.

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Chapter 8

Biomaterial additives in Bituminous Emulsions

Results part 9

"Stability of Bituminous Emulsion induced by Waste-based Bio-surfactant"

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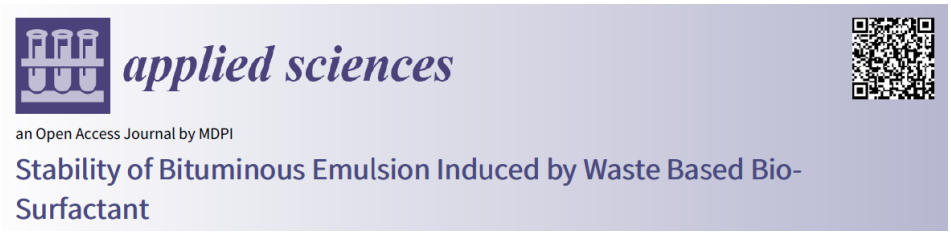

1. Introduction

Bitumen is a viscoelastic material derived from the petroleum industry and for this reason its chemical composition is hugely dependent on the initial crude oil and the cracking process carried out on it. It is not miscible with water and this feature is fundamental for the production of emulsions. From a chemico-physical point of view, the emulsification process involves the dispersion of a fluid in another provided that the two are not miscible with each other. When this phenomenon occurs, one of the two fluids breaks into drops, while the other exists as a continuous medium. Generally, emulsions are of two types: water in oil or oil in water, depending on whether the dispersing part (continuous medium) is water or oil [1,2]. Emulsions of this type are thermodynamically unstable systems; in fact, their free energy decreases over time [3]. However, it is possible to stabilize an emulsion with the use of emulsifiers [4,5].

The latter are surfactants, i.e. molecules with a polar (hydrophilic) head and a non-polar (lipophilic) tail. Thanks to their amphiphilic nature, surfactants are adsorbed at the interface of the two phases, arranging themselves with the polar head in the aqueous phase, and with the non-polar tail in the organic phase. This mechanism facilitates the reduction of the interfacial tension between the droplets and the dispersing phase [6]. Bituminous emulsion is a worldwide technology and its first application was patented in the early 1900s [7] being mainly used for pavement maintenance and road repair. Bituminous emulsions are oil-in-water emulsions in which droplets of bitumen are dispersed in the continuous aqueous phase. In order to reduce the interfacial tension and prevent coalescence phenomena, ionic surfactants are used. The salt form of the fine surfactant is solubilized in water before its addition to the bitumen. The two fluids are poured simultaneously into a colloidal mill, whose rotation speed is between 1000 and 6000 rpm. This speed causes the breaking of the bitumen into small droplets, typically between 1 and 10 μm in diameter, readily covered by the emulsifier. [8,9,10]. The main uses of bitumen emulsions are in road building, roofing and waterproofing [11.12,13,14]. Bituminous emulsions are commonly studied in terms of stability, asphalt performance, breaking times [15,16,17]. Emulsions can be identified according to their chemical nature, basicity or acidity.

The innovative endpoint of the research work behind this article is to make bitumens emulsifiable or rather to understand why some bitumens are not emulsifiable. In this work, only basic

emulsions are investigated, without losing generality to the proposed methodological approach. Not all types of bitumen used in the road paving sector are emulsifiable in a basic environment. This work therefore aims to identify the chemico-physical causes of the non-emulsifiability of the aforementioned bitumens and to find suitable additives capable of making the latter emulsifiable. [14].

2. Materials and Methods

2.1. Chemicals and materials

Three pristine bitumens from different sources are tested in this work: one with a penetration grade of 70/100 from Venezuela (labelled as Cimar), used as reference sample, the second one with a penetration grade of 70/100 from an Italian refinery - Alma Petroli S.p.A. (labelled as Alma) and the third one also from an Italian refinery - Adriatica Bitumi S.p.A. (labelled as Adriatica). All three bitumens were supplied by Cimar Produzione S.r.l. (Italy). A commercial wax (SASOBIT) and a waste from animal fat processing processes supplied by S2A Soluzioni Ambientali in the form of liquid pitches which was labelled as LP were used as additives. Another additive, an aliphatic/aromatic acid surfactant labelled as AS which is used in the field of cosmetics and soap production, supplied by Kimical S.r.l. (Italy) was also used. All of these aforementioned substances were used as additives in this study.

TABLE 1. Physical properties of bitumens used in this study

Measured properties	**Standard**	**Unit**	**Cimar** 70/100	**Adriatica** 170/210	**Alma** 70/100
Penetration at 25°C	EN 1426	0.1 mm	66±1	185±1	68±1
Softening point (R&B)	EN 1427	°C	47.8±0.2	42.6±0.2	47.2±0.2
Flash point	EN 2592	°C	≥ 230	≥ 220	≥ 230
Solubility	EN 12592	% (m/m)	≥ 99	≥ 99	≥ 99

2.2 Sample preparations

In general, the emulsions prepared are composed of 50-60% by weight of bitumen and 40-50% of water. The percentage of emulsifier (1-6%) is weighed based on the total weight of the emulsion. During the emulsion process, the pH was kept stable at 14 thus all the prepared emulsions are basic. This emulsifier was supplied by Cimar Produzione S.r.l. (Italy).

2.2.1 Asphaltene determination

In a vial, a specific mass of bitumen was dissolved in an equal volume in millilitres of Chloroform ($CHCl_3$), for example, 3g of bitumen in 3ml of $CHCl_3$. Thereafter, n-pentane which was forty times the $CHCl_3$ volume was added to the solution (in the case of 3ml of $CHCl_3$, 120 ml of n-pentane would be added). The solution was left in a dark chamber for two hours with occasional homogenization of the solution. The asphaltenes which were precipitated were then filtered using a filter paper (Whatman 42 ashless) in a funnel under vacuum conditions. The residue gathered on the filter paper was then washed several times with n-pentane until the solvent became clear and colourless thus evidencing the absence of any other component other than the asphaltenes. Finally, the filter paper was dried in an oven at 80°C for three hours and then the residue of the solvent was removed in in vacuum for two hours. Just for further facultative analysis, the filtrate containing the maltene fraction was then evaporated to dryness with a rotary evaporator under reduced pressure and the remaining and the residual solvent was removed under vacuum pump [18]. This maltene sample was stored for further analysis.

2.3 Rheological characterization

Dynamic Shear Rheological (DSR) measurements on bitumen samples were carried out using a controlled shear stress rheometer (SR5, Rheometric Scientific, USA) equipped with a parallel plate geometry (gap 2 mm, φ = 25 mm within the temperature range 25-150 °C) and a Peltier system (±0.1 °C) for temperature control [19].

2.4 NMR measurement

The ^{1}H-NMR spectra were recorded at room temperature on a high-resolution Bruker Avance 500 MHz spectrometer (11.74 T) (Bruker, Rheinstetten, Germany) equipped with a 5 mm TBO probe (Triple Resonance Broadband Observe) and a standard variable-temperature unit BVT-3000. The ^{1}H-NMR experiments were performed on bitumen diluted in Carbon Tetrachloride (CCl_4), in order to avoid overlapping with a possible proton signal of the solvent. All three analyzed bitumens showed four different peaks referable to protons as reported by Oliviero Rossi et al. [18].

2.5 Bitumen acidic number determination method

This is a thermometric catalytic titration method carried out according to ASTM D8045 standards. It was used to determine the end point of a chemical reaction (in this case between bitumen in solution and KOH) through the use of a temperature measuring probe and the addition of a chemical to enhance the detection of the endpoint.

3. RESULTS AND DISCUSSION

Before examining the chemical composition of the bitumen, we calculated the acid number of each sample correlating the values obtained to the emulsionability of each bitumen. A relatively simple method known as Catalytic Thermometric Titration (as described in section 2.5) was used to

determine the acid number of the bitumen samples used for this study. The main advantage of this method is that it is relatively easy to carry out and this method can be adopted by industries who need to determine if a certain bitumen to be used for the production of emulsions is up to emulsionable standards. As mentioned earlier, this procedure can be carried out in any laboratory and by any technician who understands the basic principle of titration. In table 2, we show the results obtained.

TABLE 2. Acid Number for each sample.

Bitumen	Acid number (mg/g KOH)
Cimar	22.7
Alma	13.5
Adriatica	14.7

As expected, making the emulsion as indicated in section 2.2, we observed that the Cimar bitumen is the only one among the three analyzed bitumen samples to be emulsionable. We proceeded with the characterization of all samples with the aim of identifying the ideal additives which will make the non-emulsionable bitumen samples emulsionable.

Time cure curves (Fig. 1) acquired for the three neat bitumens show that, as expected, the two bitumen samples with the same 70/100 penetration grade have very similar rheological behaviours, while Adriatica bitumen has a lower sol-gel transition temperature of about 10 °C. In table 3, the transition temperature and percentage asphaltene of all the bitumen samples are reported. The asphaltene content could play a role in the stability of emulsions, in fact, asphaltenes show an important interfacial activity [20]

TABLE 3. Transition temperature and percentage asphaltene of all bitumen samples.

Bitumen	Transition temperature ±0.1 (°C)	Asphaltene ±1 (%)
Cimar	64.1	17
Alma	64.4	31
Adriatica	52.4	19

Adriatica bitumen shows a different rheological behaviour but similar asphaltene concentration to the reference bitumen. Therefore, in order to obtain a mechanical behaviour similar to that of the reference bitumen, only the Adriatica bitumen was treated with several modifier additives. On the market, there are several types of modifying additives with some of them chemically interacting with the bitumen [21,22,23,24,25], others simply impart their own chemico-physical properties to it [26,27,28,29,30,31,32,33]. The criteria on which the additive was chosen was its ability to increase the transition temperature without increasing the viscosity of the binder at high temperatures [34,35,36].

This commercial additive is a wax-based additive called SASOBIT. In fact, at temperatures above 100 ° C it acts as a fluxing agent, lowering the viscosity of the binder thus favoring the emulsion process. This additive was added to the Adriatica bitumen in different dosages. In Figure 1.b, we reported only the time cure of the best sample obtained with 1.5% additive. This modified bitumen was treated according to the reference experimental conditions for emulsion production. Nevertheless, even in this case, no stable emulsion was obtained proving that the mechanical behaviour does not play a decisive role in the formation of bituminous emulsions.

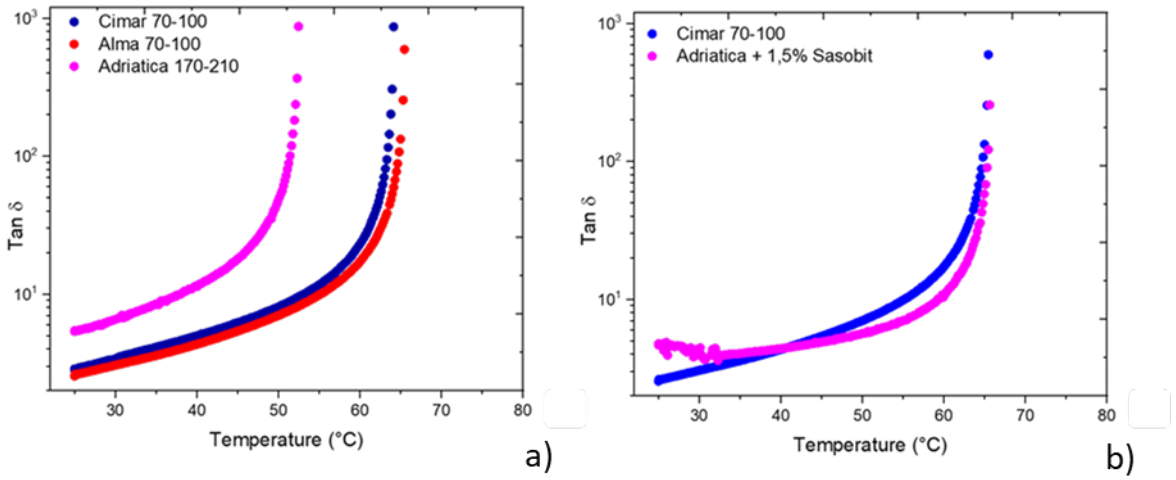

FIGURE 1. (a) Time cure test for Cimar 70-100 (blue); Alma 70-100 (red) and Adriatica 170-210. (b) Comparison between time cure test for Cimar and modified Adriatica with 1.5% of SASOBIT.

Therefore, having established that the mechanical properties do not significantly affect the emulsifiability of the bitumen, a new approach based on the chemical composition of the bitumen was undertaken. Still using Cimar bitumen as reference, NMR analyses were carried out to obtain more information on the chemical composition of all 3 bitumens analysed [18,37,38,39].

The acquisition of the proton NMR spectra (Fig. 2) allowed to characterize the bitumen under examination from a chemical point of view. Table 4 shows the fractional proton distribution obtained from the normalization and integration of the peaks.

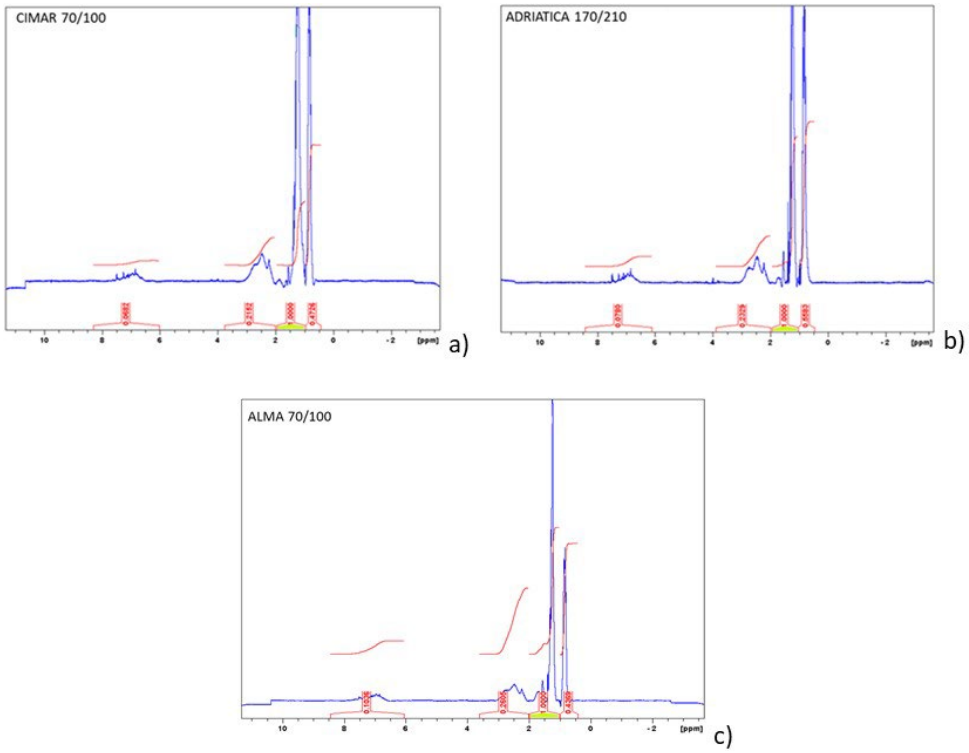

FIGURE 2. ^{1}H-NMR spectra of Cimar bitumen (a), Adriatica bitumen (b) and Alma bitumen (c).

TABLE 4. Fractional proton distribution of Cimar, Adriatica and Alma bitumens.

	Hydrogen Distribution ± 0.05			
Sample	H_{ar}	H_{α}	H_{β}	H_{γ}
Cimar Bitumen	3.88	12.26	56.95	26.91
Adriatica Bitumen	4.17	12.46	53.50	29.87
Alma Bitumen	5.75	14.46	55.52	24.26

By comparing the distribution of the protons of the bitumens analysed, it emerges that the Cimar bitumen has a similar aromatic character (3.88%) to the Adriatica one (4.17%) while the Alma bitumen has greater aromatic character (5.75) in comparison with the other bitumens. Furthermore, Cimar bitumen is characterized: (i) by having the highest percentage of hydrogens in β compared to the aromatic ring (56.95% against 55.52% and 53.50%); (ii) having a percentage of hydrogens in α (12.26%) in the aromatic ring comparable to that of Adriatica bitumen (12.46%) but lower than that of Alma bitumen (14.46%); (iii) finally, the percentage of methyl hydrogens is intermediate between the percentages of the other two bitumens (26.91% against 24.26% and 29.87%). The major differences correspond to methylene hydrogens in β to the aromatic ring and methyl protons in γ position. From the information obtained by NMR spectroscopy, it was possible to identify any surfactants that could compensate for the chemical differences between the bitumens.

Adriatica bitumen has a different rheological profile from the reference bitumen, however it has a similar value of percentage asphaltenes and shows values of aromatic components very close to it. This data pointed towards the choice of an additive capable of making the bitumen more acidic

without altering the aromatic components, that is an acid aliphatic/aromatic surfactant. In light of this, the commercial additive called "AS" was chosen. This additive is a Brønsted acid surfactant [40,41], consisting of an acid group (polar head), as a substituent of an aromatic ring, and a long hydrophobic chain (lipophilic tail) [42,43]. Thanks to these characteristics, the AS additive has been able to balance both the aromatic and aliphatic components to compensate for the differences with Cimar bitumen. In fact, once the Adriatica bitumen was modified with AS at different dosages (2.5 to 7.5%), it was possible to proceed with the preparation of the emulsion in accordance with what was done for the emulsion obtained with the Cimar bitumen. This modified bitumen was able to produce stable emulsions and the best emulsion was obtained after modification with 2.5% AS (see Fig. 3).

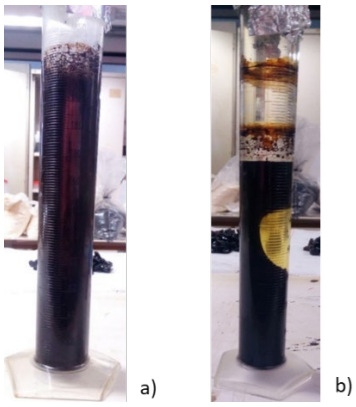

FIGURE 3. Pictorial representation of Adriatica bitumen emulsions obtained with AS additive a), and without AS additive b).

FIGURE 4. Pictorial representation of Alma bitumen emulsions obtained with LP additive a), and without LP additive b)

Alma bitumen has a rheological profile very similar to Cimar bitumen (Fig. 1.a), but has a different percentage of asphaltenes (almost double, see Table 2) [44]. Above all, based on the data obtained by NMR measurements, it is observed that it has a higher aromatic component. Consequently, the function of the additive to be used to make this bitumen more similar to the reference bitumen must be to integrate the maltene part, thus decreasing the asphaltene percentage, lowering the percentage of the aromatic components and also increasing the total acidity of the bitumen with additives. The latter is in fact a central component in the realization of anionic emulsions.

The methodological approach used shows how the fundamentally important the chemical nature of bitumen is for the realization of bituminous emulsions. The NMR data gotten give us

guidance on the choice of the coadjutant potential of the emulsifier. This step also showed us the importance of determining the acidity of bitumen. For all these reasons, an aliphatic acidifier called "LP" was identified as a suitable additive. This additive is ecofriendly and facilitates the development and promotion of a circular economy. Its nature is mainly aliphatic and gives an acidic character to the bitumen system and is mainly made up of a mixture of fatty acids (surfactants) [45,46]. The Alma bitumen was modified with LP additive at different dosages (4 to 10%) before proceeding with the preparation of the emulsion in accordance with what was done. This modified bitumen was able to produce stable emulsions and the best emulsion was obtained after modification with 4% LP (see Fig. 4).

Conclusion

There are emulsifiable and non-emulsifiable bitumens on the market and the aim of this study is to identify the type of additive suitable for making non-emulsifiable bitumens emulsifiable. Two types of approaches were used; one involving the study of the mechanical characteristics and the other a study of the chemical composition of the binders. The first approach was achieved through rheological analysis and led to the conclusion that the mechanical properties of bitumen do not depict its emulsifiability. In fact, Alma bitumen has a rheological profile similar to that of the reference bitumen but is not emulsifiable. On the other hand, the Adriatica bitumen initially had a different rheological profile from the reference bitumen and was subsequently made similar to the reference through the use of suitable additives. Nevertheless, the Adriatica bitumen remains non-emulsifiable.

The second approach, thanks to the data obtained with NMR measurements, allowed to identify the problems of the two non-emulsifiable bitumens. As mentioned earlier, the acid number determination is a useful tool for researchers and most especially for industry personnel to know the acid number of bitumen which they intend to use for production processes. At the moment, we are trying to identify the acid number value limit under which a bitumen sample is non-emulsionable.

In conclusion, we can affirm that thanks to an approach based on the study of the chemical composition of the various bitumens, it is possible to identify any deficiencies present in the sample and identify additives capable of bridging these gaps which make a non-emulsifiable bitumen suitable for the realization of anionic emulsions. In the case of the bitumen analyzed in this study, the use of the appropriate additives; LP for Alma bitumen and AS for Adriatica bitumen, made it possible to make both bitumens emulsifiable. Both these additives are eco-friendly and in the future, have the potential to substitute harmful substances that are used in industrial processes.

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Chapter 9

Plant-derived compound as additive for bitumen

Results Part 10

"Polyalkylated Gallic Esters and Acids: High Performant Warm Mix Asphalt and Adhesion Promoters for Bitumen"

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1. Introduction

Bitumen is a viscoelastic liquid at ambient temperatures and is composed of a wide variety of chemical species with different polarities and molecular weights. Its exact chemical composition depends on the starting crude oil and the distillation process, but mainly it is composed of complex hydrocarbons, amphiphiles, and polar as well as apolar aromatic compounds. Thanks to its intricate structure, bitumen displays the right properties to be a versatile product in the engineering field although its main use remains in the construction of roads as asphalt concrete. [1-3] This worldwide covering of roads however is not without defects or disadvantages. First of all, during road pavement processes, asphalt concrete is heated to rather high temperatures so that toxic fumes are released: they are harmful to workers as well as to the environment. This required heating also contributes to the overall cost of the process. Secondly, a more evident and generally relatable issue is the bad resistance over time of any road pavement that daily has to endure weather conditions and intense traffic activity. For these specific reasons, scientists over the years have been prompted to search for new additives that improve the chemico-physical properties and fatigue performance of bitumen. Different types of additives have been studied such polymers [4,5], nanoparticles [6-8] surfactants, [9] waxes [10-12], fibers [13,14], polysaccharides [15] etc. An additive, in fact, is able to influence the complex molecular self-assembly taking place at different length scales, so that the overall structure, and consequently the overall properties, can be tuned [16].

In the specific, following the analogy with micellar systems, the stable coexistence of polar and apolar domain is guaranteed by the presence of amphiphilic molecules: thanks to the simultaneous presence, within their molecular architecture, of both polar and apolar moieties, amphiphiles can bind on a side the more polar molecules of the bitumens and on the other side, the more apolar ones [17,18] an effect that can be exerted also if inorganic materials are suspended [19]. In the latter case, i.e. when inorganic particles need to be stabilized, research needs to evolve to achieve effective improvement of the adhesion between (macro-sized) stones and bitumen. Simultaneously, the same research is required to propose effective methods to reduce bitumen's fume emission into the atmosphere during the processing of asphalt concrete mainly by Warm Mix Asphalt

(WMA) additives [20-25], a goal which is currently generally pursued by reducing the working temperature.

In this study, polyalkylated gallic esters and acids (Scheme 1) were investigated as new additives for bitumen in particular as adhesion promoters and (WMA) additives. All compounds were added to bitumen in a 1% w/w ratio. By modulation of the length of the alkyl chains grafted onto the gallic core (C8, C14 or C18), the adhesion efficiency of these novel additives was investigated through Boiling test. The modifications of the rheological properties of bitumen were also studied through Time Cure Test and Flow Curve experiments. [26-29] Adhesion is a complex phenomenon; chemists define it as the energy required to disassemble the interface between two materials; physicists and engineers describe it as the maximum force exerted to separate two adhered materials. Due to this complexity, there are many theories to describe the mechanism of adhesion but to understand and formulate an efficient application of coating materials, it is necessary to know the basic principles that predict liquid flow and interfacial interactions: rheology. It is the science of flow and deformation of matter in liquid or solid form, i.e. the response of materials to mechanical stress in terms of viscosity and elasticity.

Nevertheless, adhesion is due to physical and chemical intermolecular interactions between the interface of the species. The physical ones are permanent dipoles, induced dipoles and London dispersion forces, while the chemical ones include covalent bonds and ionic bonds. To have an optimum level of adhesion, the right materials for that substrate must be chosen or a way to enhance adhesion should be carried out using an adhesion promoter or coupling agent: substances that can improve the adhesive strength of the materials that are to be joined. [30]

Adhesion promoters are utilized to improve adhesion between bitumen and a specific aggregate. It is important to enhance this capacity of the binder to cover aggregates because this reduces stripping under water or traffic duress. In fact, roadways undergo continuous mechanical stress or water damage, there are several symptoms which include rutting, stripping, loss of chippings, surface ravelling, susceptibility to freeze-thaw damage, cracking etc. and the cause of this damage on a microscopic level is just the loss of adhesion. Obviously, the quality of the adhesive bond depends by many factors such as chemical composition, surface texture, absorption surface age, surface coatings, particle shape and binder viscosity. [31,32] Aggregates are composed of acidic and basic parts and so they can be schematized as a series of positive and negative charges. For this reason, the performance of additives is strongly influenced by the chemical nature of the aggregate and also by the chemical composition of the binder.[33,34]

It is possible to recognize two aspects of adhesion: when the binder comes in contact with the aggregate (wetting) and when the binder stays in contact with the aggregate during the lifetime of the road (resistance to stripping). Reducing viscosity or changing the chemical nature of the bitumen or the aggregate, it is possible to have a better wetting. Poor wetting leads to uncoated surfaces in mixes, loss of chippings which can be avoided if the surface is more receptive. Usually, the way to achieve a better rapport between asphalt mix constituents is to increase the affinity between bitumen and the aggregates by adding adhesion promoters. The capability of the binder to replace water from aggregate surfaces is known as “active” adhesion.

On the other hand, as regards stripping, there is a cause: water gets between a bitumen film and an aggregate surface and replaces the coating. A close examination of the materials will show uncoated aggregate surfaces. This leads to a loss of structural strength, detachment of seals from the surface etc. Resistance to stripping is called “passive” adhesion that can be also improved by the

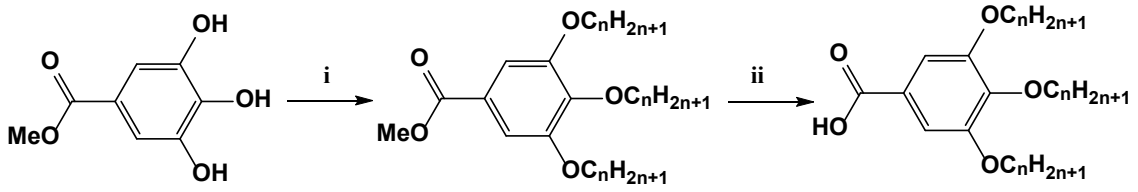
addition of an adhesion promoter. Normally, the percentage of the promoter is 0.1 – 1 % to ensure active adhesion and 0.2 – 0.5% to impart water resistance.

The water susceptibility of bituminous mixtures is evaluated by using empirical methods, the most typical ones are Boiling water test (according to ASTM D3625) and Rolling Bottle Test (EN 12697- 11 A), but there is also a modern surface analysis technique: the contact angle analysis. [35] The reason why adhesion is so investigated is because it is an important property that a good road paving needs to perform optimally and this high performance increases the life of the pavement road. Since the 1970s, researchers have been looking for a method to reduce the mixing/compaction temperature of Hot Mix Asphalt (HMA). To this end, they tried to use moisture in the aggregate, to foam the binder or to use emulsified asphalts.

Nowadays, the response to this issue is WMA technology which is consistently garnering interest because it can lower the viscosity of the asphalt binder and/or improve the workability of mixture applying minimal heat. It involves the use of organic additives, chemical additives and water-based or water-containing foaming processes. Even if warm mixes use different processes to allow the mixing, transporting, and paving processes at significantly lower temperatures, they are inclined to follow similar patterns. These similarities have given rise to various classifications, the most used one divides the warm mixes into three categories: foaming processes; addition of organic additives and addition of chemical additives. [36]

There are numerous benefits of WMA over HMA, some of the most important ones include a drop in production and placement temperatures, lower costs because it requires less fuel/energy consumption, improving longevity of pavement service life (because it is exposed to a lower temperature during plant mixing and placement), a reduced thermal segregation in the road pavement and a decreased gas emission that can improve working conditions for the workers.

These benefits will improve public perception of asphalt paving but in any case, the main benefit is from the economic point of view because WMA leads to great energy savings. [37,38]
Our study shows that the prepared gallic esters are both WMA additives and adhesion activators and we have shown that their efficiency is strictly correlated to the length of the alkyl chains, though both properties are diversely improved with respect to the length of the alkyl chain.



***Scheme 1**: Synthesised and studied polyalkylated gallic esters (**Es-Cn**) and acids (**Ac-Cn**). Reagents and Conditions: i) K_2CO_3, cyclohexanone, $C_nH_{2n+1}Br$, reflux for 48 h ii) KOH in EtOH, reflux for 24 h then HCl (1 M).*

2. Materials and methods

2.1 Reagents and synthesis of additives

Methyl gallate, potassium carbonate, potassium iodide, 1-bromooctane, 1-bromotetradecane and 1-bromooctadecane were purchased form Sigma-Aldrich and were used as received. A conventional paving grade bitumen with a penetration grade of 70/100 bitumen was supplied by Loprete Costruzioni Stradali (Italy). For the preparation of additive-containing bitumen samples, the gallic derivates were added to a fully flowing hot bitumen (140-150°C) at a desired content (1% w/w) and stirred at 500–700 rpm by a mechanical stirrer (IKA RW20, Königswinter, Germany) for 15 min at the same temperature to allow homogenization. After that, the samples were left to cool at room temperature. Melting points (Mp), Fourier Transform Infrared spectroscopy (FTIR), and Proton Nuclear Magnetic Resonance spectroscopy (^{1}H-NMR) were performed as previously reported.[39]

Polyalkylated methyl gallates derivatives

Following the reported procedure, [40] the alkylation of methyl gallate (3 g, $1.62.10^{-2}$ mol) was performed in cyclohexanone (50 mL), in the presence of finely crushed K_2CO_3 (13.5 g, $9.78.10^{-2}$ mol) together with a catalytic amount of potassium iodide (100 mg) and the corresponding bromoalkene (3.5 eq. with respect to methyl gallate). The resulting mixture was refluxed for 48 h. Upon cooling, the reaction mixture was filtered and the solvent was evaporated under reduced pressure. For **Es-C8**, the resulting light brown oil was chromatographed on silica gel, while for **Es-C14** and **Es-C18**, the crude products were recrystallized from a mixture of chloroform/methanol and from ethanol, respectively.

Es-C8 (methyl 3,4,5-tri(octyloxy)benzoate): yield: 90%; light brown oil; FTIR (NaCl crystals): ν (cm^{-1}): 2956vs (CH alif.), 2928s (CH alif.), 1720s (C=O), 1589m, 1501w, 1460m, 1434s, 1337s, 1120s, 116s, 1017m, 957w, 864w, 811m, 767w, 723w; ^{1}H-NMR (300 MHz, $CDCl_3$, TMS): δ (ppm): 7.26 (s, 2H, Ar), 4.02-3.98 (m, 6H), 3.87 (s, 3H, Ar-COO*CH$_3$*), 1.91-1.69 (m, 6H, -OCH$_2$*CH$_2$*(CH$_2$)$_5$CH$_3$), 1.46-1.44 (m, 6H, -OCH$_2$CH$_2$*CH$_2$*(CH$_2$)$_4$CH$_3$), 1.30-1.27(m, 24H, -OCH$_2$CH$_2$CH$_2$*(CH$_2$)$_4$*CH$_3$), 0.9-0.85 (m, 9H, -O(CH$_2$)$_7$*CH$_3$*).

Es-C14 (methyl 3,4,5-tri(tetradecyloxy)benzoate): yield: 79%; white solid; Mp: 55-56 °C; FTIR (KBr disk): ν (cm^{-1}): 2915vs (CH alif.), 2848s (CH alif.), 1716s (C=O), 1588m, 1468s, 1434s, 1336s, 1228s, 1013m, 985w, 962m, 816w, 763m, 720m; ^{1}H-NMR (300 MHz, $CDCl_3$, TMS): δ (ppm): 7.25 (s, 2H, Ar), 4.0-3.9 (m, 6H, -O*CH$_2$*(CH$_2$)$_{12}$CH$_3$), 3.89 (s, 3H, Ar-COO*CH$_3$*), 1.85-1.69(m, 6H, -OCH$_2$*CH$_2$*(CH$_2$)$_{11}$CH$_3$), 1.47-1.42 (m, 6H, -OCH$_2$CH$_2$*CH$_2$*(CH$_2$)$_{10}$CH$_3$), 1.26 (m, 60H, -OCH$_2$CH$_2$CH$_2$*(CH$_2$)$_{10}$*CH$_3$), 0.9-0.86 (m, 9H,-O(CH$_2$)$_{13}$*CH$_3$*).

Es-C18 (methyl 3,4,5-tri(octadecyloxy)benzoate): yield: 62%; white solid; Mp:67-68°C; FTIR (KBr disk): ν (cm^{-1}): 2918vs (CH alif.), 2848vs (CH alif.), 1718s (C=O), 1588m, 1470s, 1433s, 1334s, 1229s, 1132s, 1012w, 961w, 860w, 763m, 720m; ^{1}H-NMR (300 MHz, $CDCl_3$, TMS): δ (ppm): 7.24 (s, 2H, Ar), 4.02-3.90 (m, 6H, -O*CH$_2$*(CH$_2$)$_{16}$CH$_3$), 3.98 (s, 3H, Ar-COO*CH$_3$*), 1.88-1.71 (m, 6H,-OCH$_2$*CH$_2$*(CH$_2$)$_{15}$CH$_3$), 1.47-1.42 (m, 6H, -OCH$_2$CH$_2$*CH$_2$*(CH$_2$)$_{14}$CH$_3$), 1.24-1.19 (m, 84H, -OCH$_2$CH$_2$CH$_2$*(CH$_2$)$_{14}$*CH$_3$), 0.9-0.86(m, 9H, -O(CH$_2$)$_{17}$*CH$_3$*).

Polyalkylated gallic acid derivatives

The saponification of the ester derivatives (6 g) was performed in an ethanolic solution of KOH (3.5 eq., 140 mL) under reflux for 24 h. After cooling down to room temperature the reaction

mixture was slowly acidified with HCl (1M) until pH = 2. The resulting white precipitate was filtered, washed abundantly with water (3x100 mL) and ethanol (2x50 mL).

Ac-C8 (3,4,5-tri(octyloxy)benzoic acid): yield: 87%; white solid; Mp: 56-57 °C; FTIR (KBr disk): ν (cm^{-1}): 3500-3000br (OH), 2922s (CH alif.), 2849s (CH alif.), 1687s (C=O), 1587m, 1505w, 1467m, 1432s, 1330s, 1229s, 1114s, 863m, 765m, 723m, 682w, 618w, 542w, 485w; ^{1}H-NMR (300 MHz, $CDCl_3$, TMS): δ (ppm): 7.26 (s, 2H, Ar), 4.00-3.92 (m, 6H,-O*CH*$_2$(CH_2)$_6$$CH_3$), 1.88-1.76 (m, 6H, -$OCH_2$*CH*$_2$($CH_2$)$_5$$CH_3$), 1.45-1.42 (m, 6H, -$OCH_2CH_2$*CH*$_2$($CH_2$)$_4$$CH_3$), 1.35-1.26 (m, 24H, -$OCH_2CH_2CH_2$*(CH*$_2$*)*$_4$$CH_3$), 0.87-0.85 (m, 9H, -O($CH_2$)$_7$*CH*$_3$).

Ac-C14 (3,4,5-tri(tetradecyloxy)benzoic acid): yield: 92%; white solid; Mp: 70-71 °C; FTIR (KBr disk): ν (cm^{-1}): 3500-3000br (OH), 2953w (CH alif.), 2920vs (CH alif.), 2850s (CH alif.), 1683s (C=O), 1588m, 1505w, 1469m, 1431s, 1335m, 1228w, 1123s, 989w, 969w, 863w, 766w, 719w; ^{1}H-NMR (300 Mhz, $CDCl_3$, TMS): δ (ppm): 7.08 (s, 2H, Ar), 3.90-3.80 (m, 6H, -O*CH*$_2$(CH_2)$_{12}$$CH_3$), 1.72-1.62 (m, 6H,-$OCH_2$*CH*$_2$($CH_2$)$_{11}$ CH_3), 1.45-1.41 (m, 6H, -OCH_2CH_2*CH*$_2$(CH_2)$_{10}$$CH_3$), 1.22-1.18 (m, 60H, -$OCH_2CH_2CH_2$*(CH*$_2$*)*$_{10}$$CH_3$), 0.90-0.86 (m, 9H, -O($CH_2$)$_{13}$*CH*$_3$).

Ac-C18 (3,4,5-tri(octadecyloxy)benzoic acid): yield: 95%; white solid; Mp: 95°C; FTIR (KBr disk): ν (cm^{-1}): 3500-3000br (OH), 2917vs (CH alif.), 2849vs (CH alif.), 1686m (C=O), 1588m, 1505m, 1469s, 1429s, 1385m, 1332m, 1226s, 1123s, 992w, 965w, 863w, 768w, 719m; ^{1}H-NMR (300 Mhz, $CDCl_3$, TMS): δ (ppm): 7.31 (s, 2H, Ar), 4.06-3.97 (m, 6H, -O*CH*$_2$(CH_2)$_{16}$$CH_3$), 1.842-1.72 (m, 6H, -$OCH_2$*CH*$_2$($CH_2$)$_{15}$$CH_3$), 1.53-1.40 (m, 6H, -$OCH_2CH_2$*CH*$_2$($CH_2$)$_{14}$$CH_3$), 1.38-1.24 (m, 84H,-$OCH_2CH_2CH_2$*(CH*$_2$*)*$_{14}$$CH_3$), 0.90-0.86 (m, 9H,-O($CH_2$)$_{17}$*CH*$_3$).

2.2 Differential Scanning Calorimetry (DSC)

DSC analysis was performed on a DSC Q2000 TA instrument on *ca*. 10-15 mg of compound placed in anodized aluminium pans and covered with hermetic lids. The DSC traces were acquired between 30°C and 170°C at a scan rate of 5°C/min.

2.3 Thermogravimetric measurements (TGA)

TGA studies were performed on a Perkin-Elmer TGA-6 instrument. The analysis allows an accurate measurement of the weight loss of the sample during the linear temperature increase. Analysis was carried out on ca. 3 mg of the compound and was performed from 25°C to 650°C at a temperature ramp rate of 5°C/min.

2.4 Dynamic Shear Rheology

Rheometric measurements on the bituminous samples were carried out using a controlled shear stress rheometer SR5 (Rheometrics USA), equipped with a parallel plate geometry (diameter 25 mm, gap 2 mm). The temperature was controlled by a Peltier system with an uncertainty of ± 0.1°C. All samples were subjected to a stress sweep test at a frequency of 1 Hz, to determine the

region of linear viscoelasticity (region in which the moduli G' and G" vs strain are constant) but for bituminous system this region is already known. [40-42]
Two dynamic tests were carried out:

- Temperature ramp test or time cure, in which G' and G" are recorded as functions of temperature at a frequency of 1 Hz within the linear viscoelastic region. The temperature range investigated was from 25 to 120°C, with a scan rate of 1°C/min.
- Flow Curve test, these tests were made at different temperatures (70°C, 80°C, 90°C, 100°C, 110°C and 120°C) to evaluate the viscosity of the samples at each temperature and they were carried out in a stress range from 1 to 100 Pa.

2.5 Boiling test

Boiling tests were performed by using mineral aggregates with sizes ranging from 8 mm to 12 mm. The Boiling test procedure applied in this study was carried out according to ASTM D3625 [38,45].

Fig. 1. *Trentino porphyry used for the Boiling Test.*

Trentino porphyry stone was used as model for adhesion forces probing. This stone has a chemical nature close to that of glass and so they represent the worst conditions since their adhesion to bitumen is indeed very low.

3. Results and Discussion

Polyalkylated gallic methyl esters (**Es-C8**, **Es-C14** and **Es-C18**) and acids (**Ac-C8**, **Ac-C14** and **Ac-C18**) whose chemical structures are reported in Scheme 1, were tested as rheological modifiers, adhesion activators and WMA additives. Prior to their addition to bitumen, all compounds were analyzed through DSC and TGA in order to accurately measure their melting point and probe their thermal stability. Melting points measured by the maximum of the endothermic peak observed by DSC are collected in Table 1, while DSC traces are reported in Figure 2.

Table 1. *Melting points of polyalkylated esters (**Es-Cn**) and acids (**Ac-Cn**) derivatives.*

Sample	Melting point (°C)
Es-C8	Liquid
Es-C14	55.3
Es-C18	67.0
Ac-C8	56.5
Ac-C14	70.6
Ac-C18	85.0

Only **Es-C8** is in liquid state at room temperature. As expected, ester derivatives display lower melting points than their corresponding acid derivatives and for both series, the melting point increases with an increase in the length of the alkyl chains. It is worthy to note that above 85°C all compounds are in liquid state and above this temperature, an easy homogenous dispersion in bitumen is facilitated.

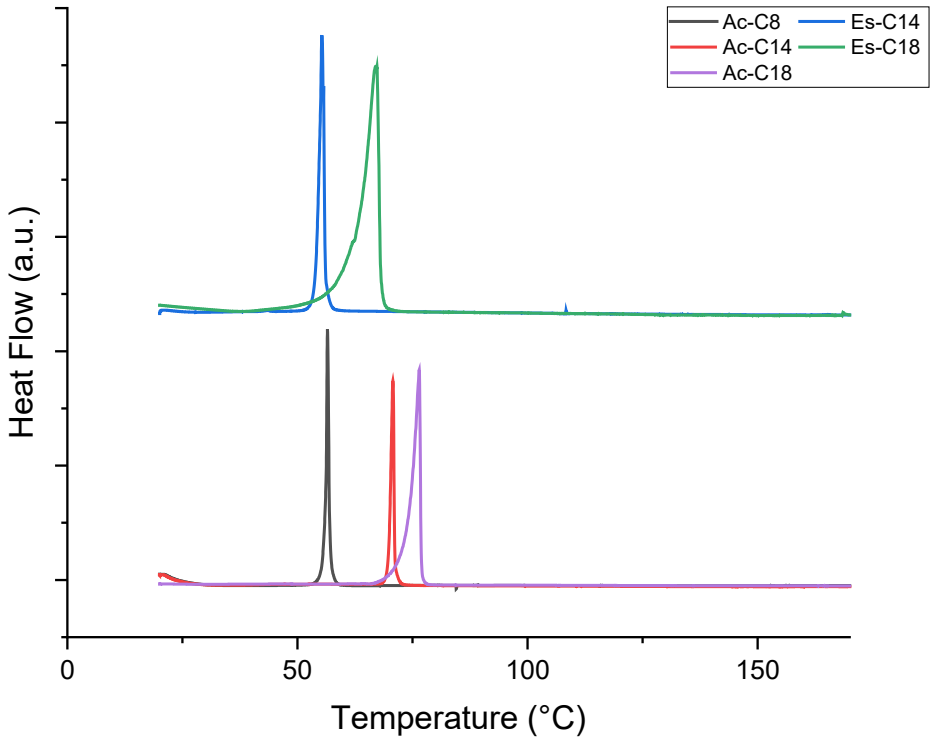


Fig. 2. *DSC traces of studied additives, ester (**Es-Cn**, top traces) and acid (**Ac-Cn**, bottom) derivatives. Note that **Es-C8** is in liquid state at room temperature.*

In order to check the thermal stability of all additives and ensure their integrity during the mixing with the bitumen matrix, thermogravimetric analysis was performed on the samples modified with the additives.

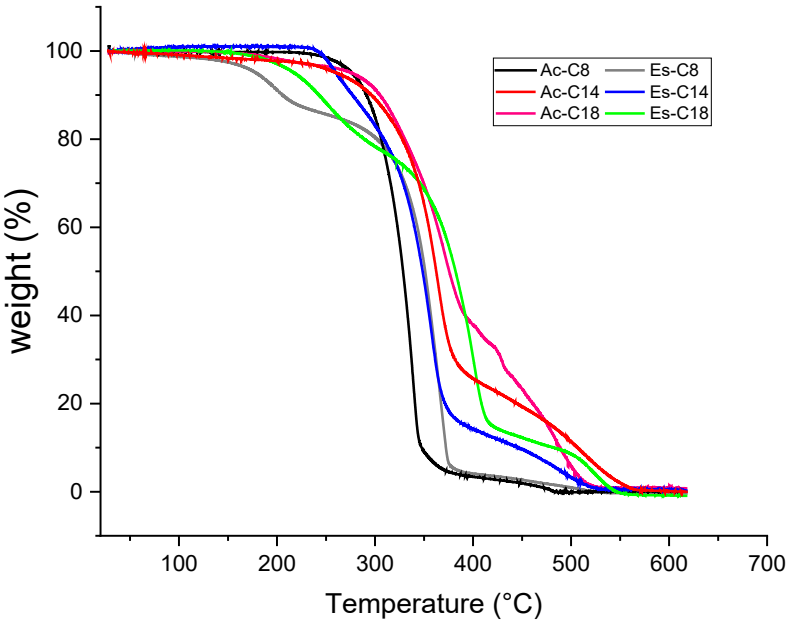


Fig. 3. *TGA curves of all studied additives* ***Es-Cn*** *and* ***Ac-Cn****.*

The TGA curves, reported in Figure 3, show that all samples started to degrade above 170°C which is higher than the temperature required for the preparation of all modified bitumen samples. While acid derivatives are thermally stable until 280°C, ester derivatives are less stable. **Es-C8**, the only compound in liquid state at room temperature, shows the lowest decomposition temperature which started at ca. 170°C. Increasing the length of the alkyl chain results in an increase in stability, thus the thermal decomposition of **Es-C14** starts at 210°C while for **Es-C18** it only occurs at 260°C. Although **Es-C8** presents a decomposition temperature rather low which would exclude its use in road pavement processes, we decided to keep this compound within the present study for completeness of data and to better rationalize the obtained results.

3.1 Rheological properties induced by the addition of additives

All the samples were investigated to determine the influence of the additives on the bituminous system. To evaluate the ability of these additives in terms of rheological modifiers and WMA agents, rheometric measurements with a Rheometer were performed; in particular, a time cure test. To understand the capacity of being a warm mix asphalt additive, the analysis was carried out still with a Rheometer but in this case, a flow curve test was performed. A dynamic rheological analysis was carried out a 70/100 paving bitumen. This analysis was also done on the 70/100 paving modified bitumen to test if they can be considered as rheological modifiers.

Figure 4 shows a typical trend of the mechanical moduli and their ratio (tanδ) as a function of the temperature of the bitumen. [46-48] These experiments are called "time cure" and are carried out in linearity and at a frequency of 1 Hz.
The Time Cure shows the development of G', G" and tanδ against temperature. Tanδ is the ratio of the viscous modulus to the elastic modulus. High values of tanδ indicate a liquid-like system.

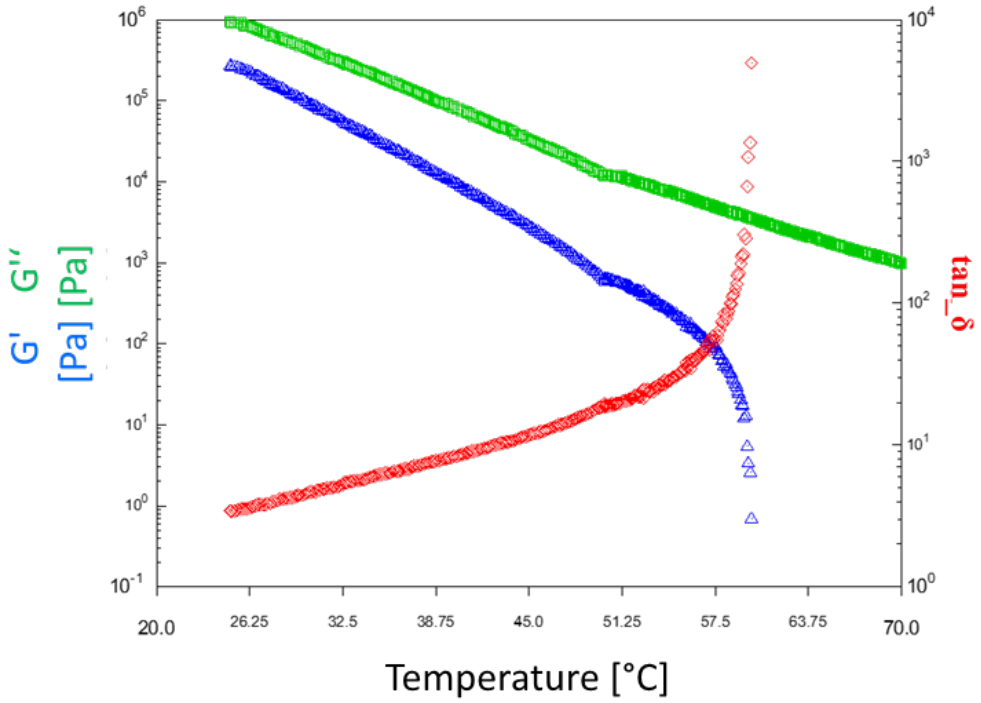


Fig. 4. *Time Cure Test of the neat bitumen.*

The paving reference bitumen shows an increasing trend of tanδ with temperature and at about 60°C there is a clear transition, from viscoelastic to liquid which is evidenced by the divergence of tanδ. All the synthesized compounds were tested as rheological modifiers of bitumen. A good rheological modifier increases the transition temperature of bitumen, thus delaying the transition to the liquid-viscous phase. The results of the test are illustrated in Figure 4.

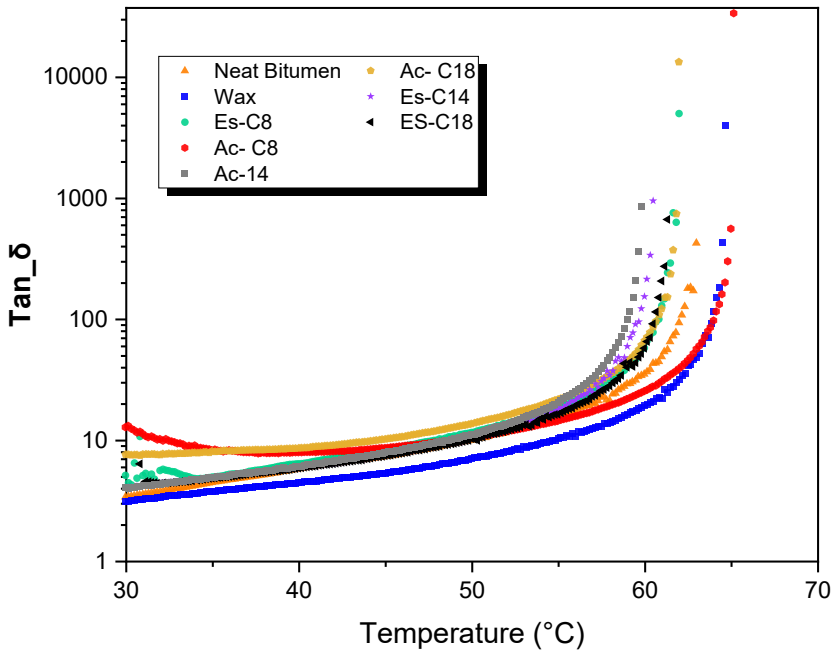


Fig. 5 *Time Cure Test of neat BLASI bitumen and the additive-modified bituminous system.*

From the results obtained from the Time Cure Tests, it can be seen that the transition temperatures of the non-additive bituminous matrix and the transition temperatures of the additive bituminous matrices are within a very narrow range (60-65°C), therefore they are very similar to each other. The fact that the additives used did not significantly increase the transition temperature means that no additive improved the chemico-physical properties of the bitumen. According to these results, we can state that none of the tested additives can be classified as rheological modifiers of bitumen. The transition temperatures are reported in Table 2.

Table 2 Transition temperature of the bituminous samples

Sample	Transition temperature (°C) ± 0.1
Neat Bitumen	63.2
Es-C8	63.0
Ac-C8	65.0
Es-C14	60.0
Ac-C14	60.6
Es-C18	61.3
Ac-C18	62.0
Wax	64.5

3.2 WMA agent

Figure 6 shows the temperature as a function of viscosity.

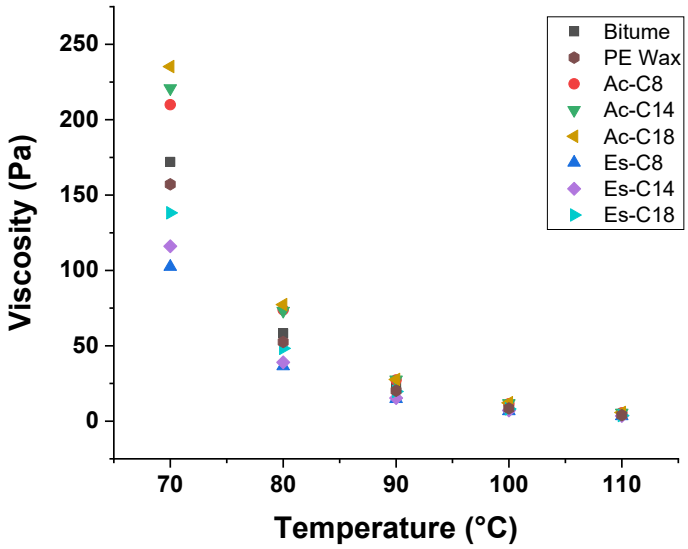


Fig 6. *Flow cure results of neat BLASI bitumen and the bituminous samples with the gallic ester/acid derivatives.*

The viscosity was obtained using a stress controlled rheometer. By applying a force mode to the material, it is possible to measure the subsequent deformation and thus deduce the mechanical properties of the samples but also probe the structural and morphological variations induced by each additive on the bituminous system. In particular, DSR was used to understand the influence of the additives on the bitumen's viscosity, in particular to assert their eventual ability to act as a WMA additive. [49,50] Nowadays, waxes are currently used in the road sector as WMA additives. They allow bitumen to maintain its chemical and physical characteristics at temperatures below the melting point of the waxes (70-100°C) but flux it at temperatures above their melting point. Consequently, they lower the bitumen's viscosity and facilitate the coating of stones during the preparation of mixes. In order to test this property, measurements were carried out under stationary flow experiments which resulted in the production of flow curves. The flow curves were carried out at different temperatures (70°C, 80°C, 90°C, 100°C, 110°C and 120°C) to evaluate the effect that gallic acid derivates additives could have on bitumen viscosity [51,52]. The tests were carried out in a stress range from 1 to 100 Pa. All samples have shown a Newtonian behavior in agreement with the fact that the viscosity is independent of the shear rate. The alkylated gallic acid derivatives increase the viscosity of the bitumen, the corresponding methyl esters on the other hand, decrease it. This observation is more evident at low temperature (70°C). In particular, another trend can be extracted from the collected data: independent of the nature of the additive (ester vs. acid), when the length of the alkyl chains is increased, the viscosity of the modified bitumen increases accordingly.

This effect can be rationalized considering for the peculiar structure of bituminous materials. The micellar model usually adopted for such materials involves a supra-molecular assembly typical of micellar systems: clusters of asphaltene molecules piled in stacks (polar domains) are stabilized by resins (amphiphilic part) and dispersed in saturates and aromatics (apolar matrix). In this picture, the role of resin is essential in the delicate equilibrium of intermolecular interactions (polar-polar, polar-apolar and Van deer Waals interactions) which holds up the overall structure, since amphiphilic molecules are well-known to bind from a side the polar molecules clusters and from the other side the apolar phase will tend to reduce the associative interactions between the asphaltene particles by interposing itself between the asphaltenes and the maltenes [53]. This phenomenon might be alike to the one found in the deactivation of hydrophobic cross-links in hydrophobically modified polymers by surfactants [54].

However, when the gallic esters or acids are added to the bitumen, another mechanism concurrently present involves the competitive interactions between the amphiphilic additive and the amphiphilic resins pre-existent in the bitumen. In fact, it has been recently highlighted that, in addition to polar and apolar interactions, further specific interactions between surfactants themselves with consequent peculiar self-assembly processes [55] dictating the final overall aggregation pattern [56] and the (usually slowed down) dynamics [57,58]. Evidently, gallic acids, due to the marked acidity of the polar headgroup, can more effectively make molecular adducts with the amphiphilic basic resins already present in the bitumen increasing the viscosity and the long-range structure. This possibility is an effective mechanism of supra-molecular self-assembly in amphiphilic systems recently discovered [59-61] and has been already hypothesized also in aged bitumen [62].

This also explains why **Es-C8** induces the lowest viscosity. The amphiphilic nature helps in stabilizing the asphaltenes clusters avoiding the asphaltene-asphaltene interactions and supra-molecular assembly which usually takes place at different length-scales and levels of complexity.

However, their lack of strongly acidic character in its polar headgroup does not allow resins-additive supramolecular structuring.

Through the use of **Es-Cn** derivatives, it is therefore possible to lower the mixing and paving temperatures of the asphalt mixes with a consequent reduction in the emission of potentially harmful fumes into the environment and a reduction in the costs of heating the bitumen at high temperatures. In addition, this effect could not only reduce environmental pollution but also help to safeguard the health of those working in the industry. To compare the efficiency of **Es-Cn** to act as efficient WMA additive, a sample of bitumen was also modified, under identical conditions, by a commercial wax (Polyethylene (PE) based) already used as warm mix asphalt in the road paving industry. [63-64] The ability of these new additives to decrease the viscosity at working temperature is greater than that of the commercial wax. In detail, at 70°C the **Es-Cn** are 19,7% (n=18), 32,5% (n=14) and 40,4% (n=8) more performant WMA than the commercial wax which in the same conditions decrease the viscosity bitumen of only the 8,7%. These data confirm that alkylatedmethyl-gallates are ideal candidates for that purpose. The same consideration made above for the viscosity changes here hold: esters of gallic acids, thanks to their slightly amphiphilc nature and lack of acidic headgroups, help in lowering the bitumen working temperature more than waxes, which, due to its pretty apolar nature, is expected to be confined basically in the apolar maltenic phase. Furthermore, looking at the melting point values (Table 1), we observe that the viscosity trend is strongly linked to the melting point. In fact, the liquid additive (Es C8) is the one that works best as WMA agent, fluxing the bitumen at lower temperatures while the difference between the two gallic acid esters (Es C14 and Es C18) is probably due to the difference in their melting points. In this regard, Es C14 having a lower melting point (55.3 °C), fluxes bitumen better than Es C18 which melts at 67°C.

3.3 Adhesion promoter evaluation (Boiling test)

Initially a Boiling test was carried out on the bitumen without additives to define its adhesion capacity to the selected stones (Trentino porphyry), which were chosen because these stones aggregates display chemico-physical features very similar to glass i.e., they do not have good affinity with bitumen. [65] In fact, this stone consists of over 70% silica, approximately 14% alumina, 8% alkali and small percentages of calcium, iron and magnesium (mineralogical composition: quartz crystals, sandstone, plagioclase, and to a lesser extent biotite and pyroxenes immersed in a glassy paste).

In a second step, Boiling tests were performed on the bitumen modified with the six additives derived from gallic acid in a weight percentage compared to bitumen of 1%. This is a typical dosage of the adhesion promoter additive. The results are all reported as follows:

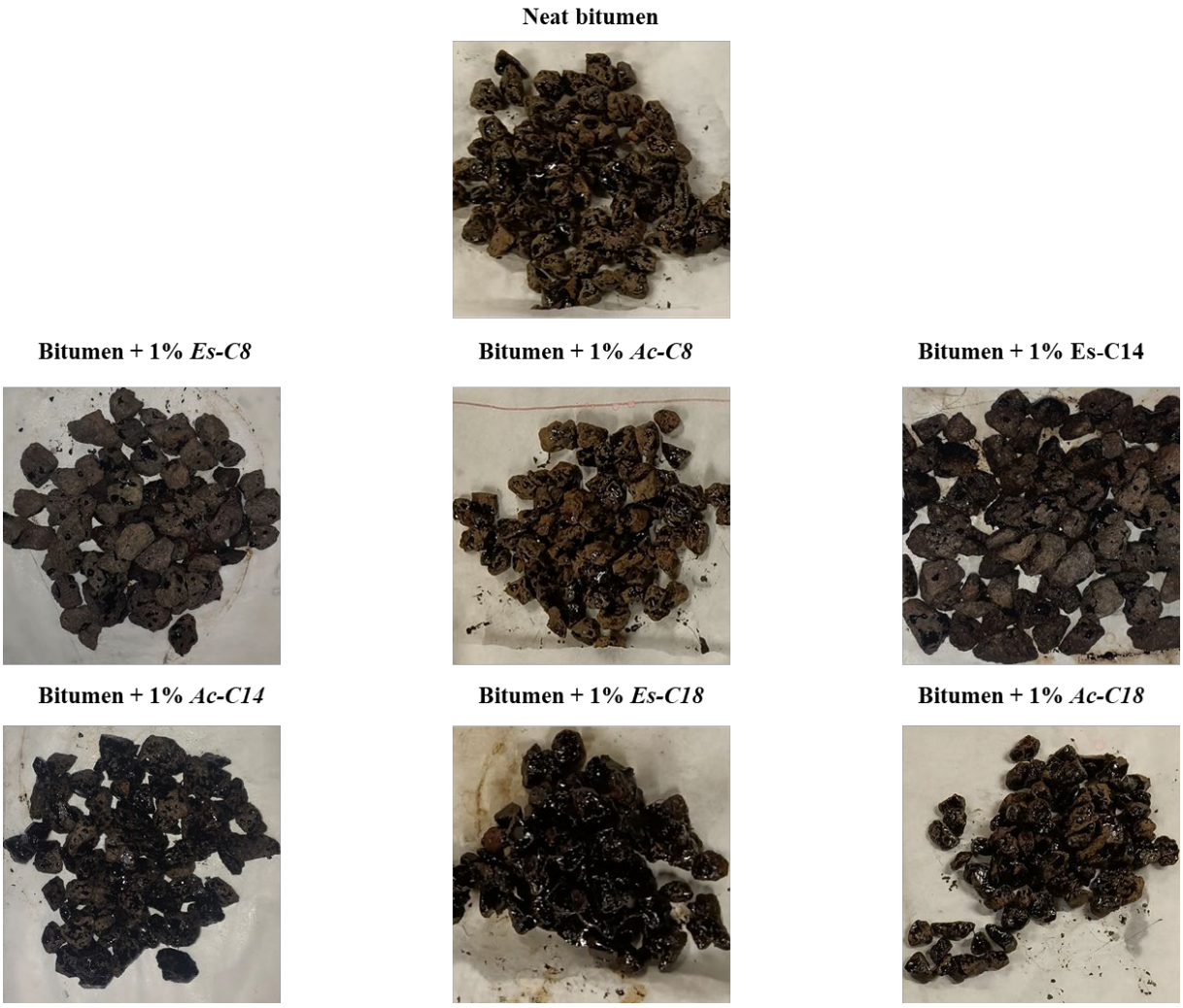


Fig 7. Boiling test results of the samples.

The values of coating are reported in **Table 3.**

Table 3 *Boiling test results*

Sample	Covering value % (±5)
Pure bitumen	10
Bitumen + 1% *Es-C8*	5
Bitumen + 1% *Ac-C8*	10
Bitumen + 1% *Es-C14*	15
Bitumen + 1% *Ac-C14*	15
Bitumen + 1% *Es-C18*	95
Bitumen + 1% *Ac-C18*	65

The sample was placed in boiling water for 10 minutes and then cooled to room temperature; the water decanted and the sample spread to dry on a paper towel. The degree of bitumen coverage in % was evaluated by visual observation. A lit magnifying glass was used to examine the samples. The average of the ratings was approximated to the nearest 5%. As expected, the obtained results confirm that bitumen does not have a good adhesion with this type of aggregates, in fact only 10%

coverage was obtained after the test. Concerning the tested additives, the best result was obtained with **Es-C18** showing an almost complete stone coverage. However, bitumen with **Ac-C18** also achieves a good result as it increases the coating percentage of pure bitumen by approximately 55%. [66,67] In contrast, all other additives have negligible effect on the adhesion of the binder, their corresponding percentage values are reported in Table 3. In this case we observed that the longer the alkyl chain is, the greater the adhesion, regardless of the polar part (ester or acid group).
In fact, the adhesion promoter connects the bitumen with the stone acting as chemical bridge between them. The long alkyl chain (lipophilic part) ensures a major interaction with the bitumen matrix, increasing the affinity with the aggregate. While in this specific case regarding the adhesion, the polar part of the acid or ester, shows a similar behavior between them, even if a major adhesion for the ester derivatives have been observed compared their acid counterparts.

4. Conclusion

In conclusion, we can state that the polyalkylated methyl gallates **Es-Cn** are all efficient warm mix agents because they lower the viscosity of the binder, better than the waxes already used in the road sector, and the shorter the length of the alky chain, the better the performance. However, as rheological modifiers they did not bring any improvement, while as adhesion promoters only **Es-C18** significantly enhances the affinity between bitumen and aggregates. The acid-based additives do not have WMA agent or rheological modifier characteristics. It is true that they increase the viscosity of the binder but do not raise its transition temperature. This study therefore shows that opportunely functionalization of the methyl gallates can be a good strategy to devise new efficient WMA agents as adhesion promoters, keeping their amount in bitumen as low as 1% w/w ratios. At the present time, although its performance is only slightly better as WMA agent than the reference PE wax, **Es-C18** allows to reach high level of adhesion with standard rocks used for road pavements. We can therefore forecast that new double-role additives derived from methyl gallates could be designed. Branched alkyl chains or polyglycol chains could for example be employed for such a purpose and such a possibility is currently under study.

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Chapter 10

Development of recycled material-based alternative binders as partial or total replacement of bitumen binder in asphalt

Results Part 11

"Preliminary Study on New Alternative Binders through Re-refined Oil Bottoms (REOBs) and Industrial by-product Additives"

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1. Introduction

An ever-increasing pressure for resources conservation and environmental protection—e.g., CO_2 reduction [1]—has led to a systemic change in the use and recovery of resources towards a clear transition to a regenerative circular economy [2,3]. This has been done by creating a closed-loop system, minimizing the use of resource inputs and the creation of wastes, pollution, and carbon emissions [3]. New potential pathways in innovation and investment, reducing wastes and promoting the continual use of resources, have therefore been proposed [4,5]. Considering this aspect, waste ceases to be waste and acquires the status of End of Waste product (EoW). The End of Waste (EoW) criteria include recovery and treatment processes under which waste could be converted in a new potential product. In particular, according to the European standards [6], the main requirements to satisfy the EoW criteria for a given waste (possibly treated by industrial processes) are:

(a) the substance or object is intended to be used for specific purposes; (b) there is a market or demand for this substance or object; (c) the substance or object meets the technical requirements for the specific purposes and complies with the existing legislation and standards applicable to the products; (d) the use of the substance or object will not lead to overall negative impacts on the environment or human health (in accordance with the Substance of Very High Concern (SVHC) list [7]).

From this perspective, the reuse of re-refined exhausted oils from vehicles and industrial hydraulic applications [4,5] that have become unfit for the use for which they were originally intended completely fulfils circular economy goals. In the view of a circular economy and considering the opportunity to reduce as much as possible the extraction of crude oil, a study has been started between universities and industries [8–11] that aims to produce new potential alternative binders (or eco-binders) by using recycled materials and/or by-products. In detail, the present research used Re-refined Engine Oil Bottoms (REOBs) to obtain suitable petroleum-based binders, enhancing the properties of these by- products, which are mainly used as bitumen-like product or bituminous membrane additive. The physical properties of the REOBs were enhanced by using a set of synthetic and/or natural additives such as powdered rubber from End-of-Life Tyres (ELTs) or other waste polymers [12], cellulose from waste paper or from olive pomace wastes, other suit- able wastes or industrial by-products, and cheap chemical products. The incorporation of additives into REOBs aims to create alternative binders that could be used for producing asphalt concretes whose mechanical

properties satisfy the technical requirements. More- over, Reclaimed Asphalt Pavement (RAP) aggregates were used to obtain the asphalt concrete samples that underwent testing in order to study their behaviour with the goal of substituting the virgin aggregates, which are commonly employed in asphalt pavement. This would allow for meeting the standards of many European countries where RAP is already re-introduced in Hot Mix Asphalt (HMA) and Warm Mix Asphalt (WMA) mixes in the range of 70–90% by the total weight of available RAP material [13]. In Italy, an average RAP content of 20–30%wt. is usually introduced in WMA and HMA mixes, alternatively [13,14]. The aged and more brittle bituminous binder that coats the recycled aggregates limits the use of RAP material, as it stiffens the final asphalt mixtures, making the pavements more brittle and sometimes more prone to cracking, especially at low temperatures. To overcome this problem, a rejuvenating agent could be used [15,16].

Every year, the European Union (EU) produces around 15 million tons of bitumen [17]. Most of this amount is mixed with aggregates to create asphalt concrete for roads paving. Approximately 90% of all paved roads are surfaced with bituminous materials. Annually, the EU produces more than 200 million tons of bituminous materials for maintenance operations on the existing asphalt pavements and for paving new transportation infrastructure [18]. However, the bitumen used and the virgin aggregates are non- renewable resources. This has led researchers to look for alternative binders (or eco-binders) to reduce the consumption of petroleum bitumen and for recycled aggregates to substitute the virgin ones in the asphalt mixture skeleton. On one hand, the employment of recycled aggregates is becoming a consolidated practice in the production of asphalt concretes, especially in terms of RAP material as previously mentioned, and the use of recycled asphalt mixture with high or very high content of RAP is becoming feasible [19,20]. On the other hand, the partial substitution of neat bitumen with recycled materials and/or by-products is still a challenge. The possible substitutes for neat bitumen can either come from recycled materials from non-renewable resources such as REOBs or come from renewable resources such as wood or vegetable waste oils. The bituminous binders that partially consist of the latter products are referred as bio-binders [21,22], which are an eco- friendly alternative to bitumen obtained from non-petroleum-based renewable resources. The chemical composition of the majority of these alternative binders is similar to that of a traditional bitumen, which includes resins, saturates, aromatics, and asphaltenes [23]. Regardless of the origin of the bitumen substitutes, i.e., renewable or non-renewable re- sources, the waste and/or recycled products can partially replace neat bitumen. In general, substitutes can be introduced in neat bitumen in four different ways based on the type and quantity of waste materials and/or by-products used, and they are referred to as [24]:

(a) Bitumen modifier (<10%wt.); (b) Bitumen fluxes (7–15%wt.); (c) Bitumen extender (25–75%wt.); (d) Alternative binders (>75%wt.). Currently, the bitumen modifiers, fluxes, and extenders are the most-used solutions to add waste materials and/or by-products to bituminous binders for the production of asphalt mixtures. Nonetheless, the use of alternative binders to partially and/or completely replace the bitumen in new asphalt formulations is the final goal of the current research inspired by the circular economy concept.

Up to date, several different alternative binders have been studied, including engine oil residue, soy- bean oil, palm oil, fossil fuel, swine waste, and materials from pyrolysis [25]. Different vegetable oils have been investigated in recent times to determine their physical and chemical properties and to evaluate their applicability as bio-binders in the pavement industry [26–28]. Bio-oils are produced from plant matter and residues, such as municipal wastes, agricultural crops, and by-products from agriculture and forestry. Other biomass sources include molasses, rice, sugar, potato starches, corn, gum resins and natural tree resins, vegetable oils, natural latex rubber, cellulose, lignin,

palm oil waste, peanut oil waste, coconut waste, potato starch, canola oil waste, dried sewerage effluent, and others [29]. Rauf and Williams [23] have conducted a study about bio-oils. They have produced different bio-oils from different sources, i.e., oakwood, switch grass, and corn stover, which exhibited similar behaviour to neat bitumen. Fini et al. [30] produced bio-oil from swine manure and used it as a partial replacement of bitumen. This recycled product was a promising candidate for partial replacement for standard bitumen. In particular, this bio-binder would improve the low-temperature properties of a petroleum-based binder while reducing asphalt pavement construction costs. A Dutch study tested asphalt roads and cycle paths paved with a bitumen-like product made from the natural binder lignin [31]. Lignin is a structural polymer in plants and trees that is released as a waste product from a number of industrial processes. The used lignin came from various sources including different types of paper pulp production and a bio-refinery that produces cellulosic ethanol from straw. On the demonstration roads, the material appeared to be performing in a similar way to a standard bitumen, and a slight noise reduction was observed. In 2018, Yang et al. developed a process to break down the organic parts of household waste, e.g., food waste, plastic, paper, and textiles, to produce a sticky, gloopy black liquid that is very similar to bitumen [32]. The bio-bitumen was produced by pyrolysis. By changing the processing parameters, such as temperature, processing time, and product collection strategy, the research team was able to alter the characteristics and quantities of the final bitumen-like substance. In conclusion, this preliminary study on alternative binders tried to fulfil circular economy goals by identifying suitable additives, coming from recycled materials and industrial by-products, in order to modify REOBs and to achieve the minimum rheo-mechanical performance required for bituminous binders and mixtures. Thus, the new alternative binders underwent rheological and mechanical analysis to measure some of the parameters required for road construction materials. Nevertheless, beyond this preliminary research, additional investigation is needed in order to fully characterize the rheo-mechanical performances and durability of the binders and the corresponding asphalt mix.

2. Materials

Various recycled materials and/or by-products were used to define alternative binders intended to fully replace neat bitumen for the production of more sustainable asphalt mixtures. The main constituents of alternative binders are REOBs that have been modified by specific additives to obtain a material similar to the standard bitumen.

2.1. REOBs

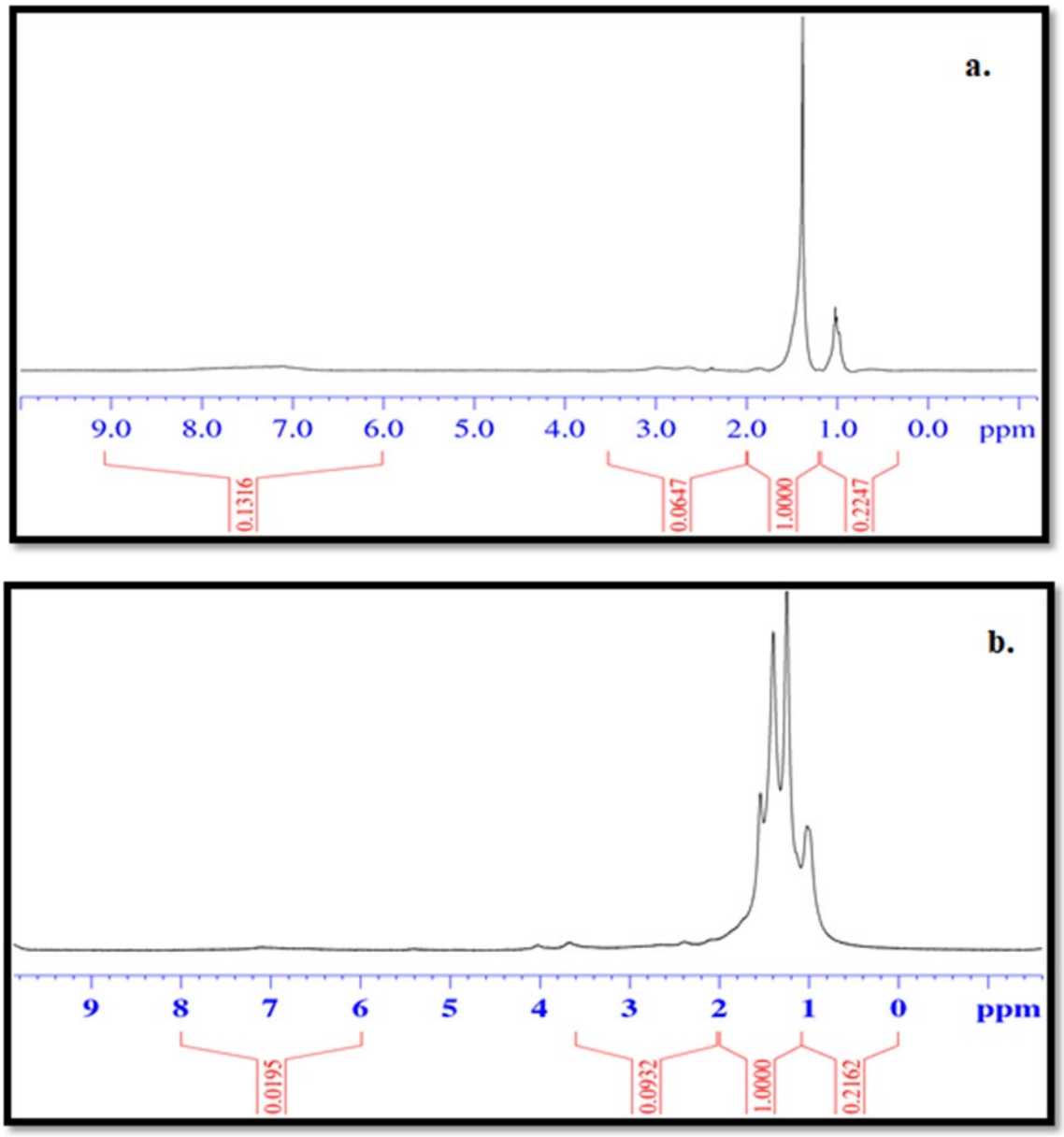
Two different REOBs were supplied by Itelyum Regeneration s.r.l, Lodi (LO), Italy. The by-products were produced in two distinct refinery plants of the same company and are marketed as Viscoflex 1000® (V1) and Viscoflex 2000® (V2TQ). The by-product V2 is usually fluxed with low molecular weight oils—in a quantity equal to 20 or 30%wt.—to facilitate materials handling. In particular, the fluxed REOB with 20%wt. and 30%wt. of the low molecular oil are referred to hereafter as V2F (F stands for fluid) and V2D (D stands for dense), respectively. The two petroleum-based by-products are viscous liquids at room temperature and are obtained by different processes. The V1 is the heavier fraction, obtained in a distillation column working at 365 °C and 15 mmHg; while the V2 is obtained through a propane de-asphalting process. Table 1 reports the main physico-chemical characteristics of both products.

Table 1. Main physical and chemical characteristics of V1 and V2F.

Property	Standard	Results	
		V1	V2F
Needle Penetration Test	EN 1462	/	>500 (0.1 mm)
Softening Point	UNI EN 1427	/	<4 °C
Density at 15 °C	ASTM D70	1003 kg/m³	0.975 kg/m³
Kinematic Viscosity at 100 °C	ISO 3104	Not determinable	580 mm²/s
Kinematic Viscosity at 135 °C	ISO 3104	110.0 mm²/s	/
Dynamic Viscosity at 60 °C	EN 13702	25.13 Pa s	0.380 Pa s
Pour Point	ASTM D97	> 50 °C	/
Insoluble Matter	ASTM D 2042	14% w/w	/
Soluble Matter	ASTM D 2042	86.10 % w/w	/
Water Content	ASTM D6304 (Procedure C)	290 mg/kg	/
Sulphur	ISO 8754	1.13 % *w/w*	/
Nitrogen Content	ASTM D3228	0.32 % *w/w*	/
Gasoline Fuel	ASTM D3525	< 0.01 % *w/w*	/
Gasoline Diluent	ASTM D322	< 0.1% *V/V*	/
Diesel Fuel	ASTM D3524	< 0.1 % *w/w*	/
Ash	ASTM D482	8.089 % *w/w*	/
Conradson Carbon Residue	ASTM D189	19.2 % *w/w*	/
TSE Remark	ISO 10307-1	Filtration Time exceeds 25 min	/
Saturates	IP 469	32.9 % *w/w*	37.0 % *w/w*
Aromatics		0 % *w/w*	1.6 % *w/w*
Polars (I)		19.6 % *w/w*	18.1 % *w/w*
Polars (II)		47.5 % *w/w*	43.3 % *w/w*
Asphaltene	IP 143	16.6 % *w/w*	3.7 % *w/w*
Pensky–Martens Flash Point (Closed Cup) Procedure B	ASTM D93/IP34/EN ISO 2719	270 °C	/
Cleveland Flash Point (Open Cup)	ASTM D92/EN ISO 2592	284 °C	180 °C
PCB Content	EN 12766-3	< 4 mg /kg	/
PCT	EN 12766-3	< 10 mg /kg	/

With the aim of replacing neat bitumen mainly with REOBs, the two available REOBs were preliminarily characterized by the use of spectroscopic analysis in order to identify the possible similarities of these materials with a standard 50/70 penetration grade bitumen (Pen 50/70). The Pen 50/70 was considered as the reference bituminous binder throughout the present study. The REOBs were firstly characterized through high-resolution 1H-NMR spectroscopy. In Figure 1, the 1H-NMR spectra of (a) Pen 50/70, (b) V2TQ, (c) V1, (d) V2D, and (e) V2F are reported. As can be seen from Figure 1, all samples are characterized by a rich aliphatic part (0.8 to 2.5 ppm). The areas under the curves for the aliphatic part are of the same order of magnitude for the 50/70 reference bitumen as well as for all REOBs samples. From this point of view, it can be said that REOBs and classic bitumen

are very similar., On the other hand, it can be seen from the integral of the aromatic region that the various REOBs have a total aromatic content (asphaltene plus aromatic molecules) about one order of magnitude lower than Pen 50/70. This is in accordance with the results of the analysis shown in Table 1.



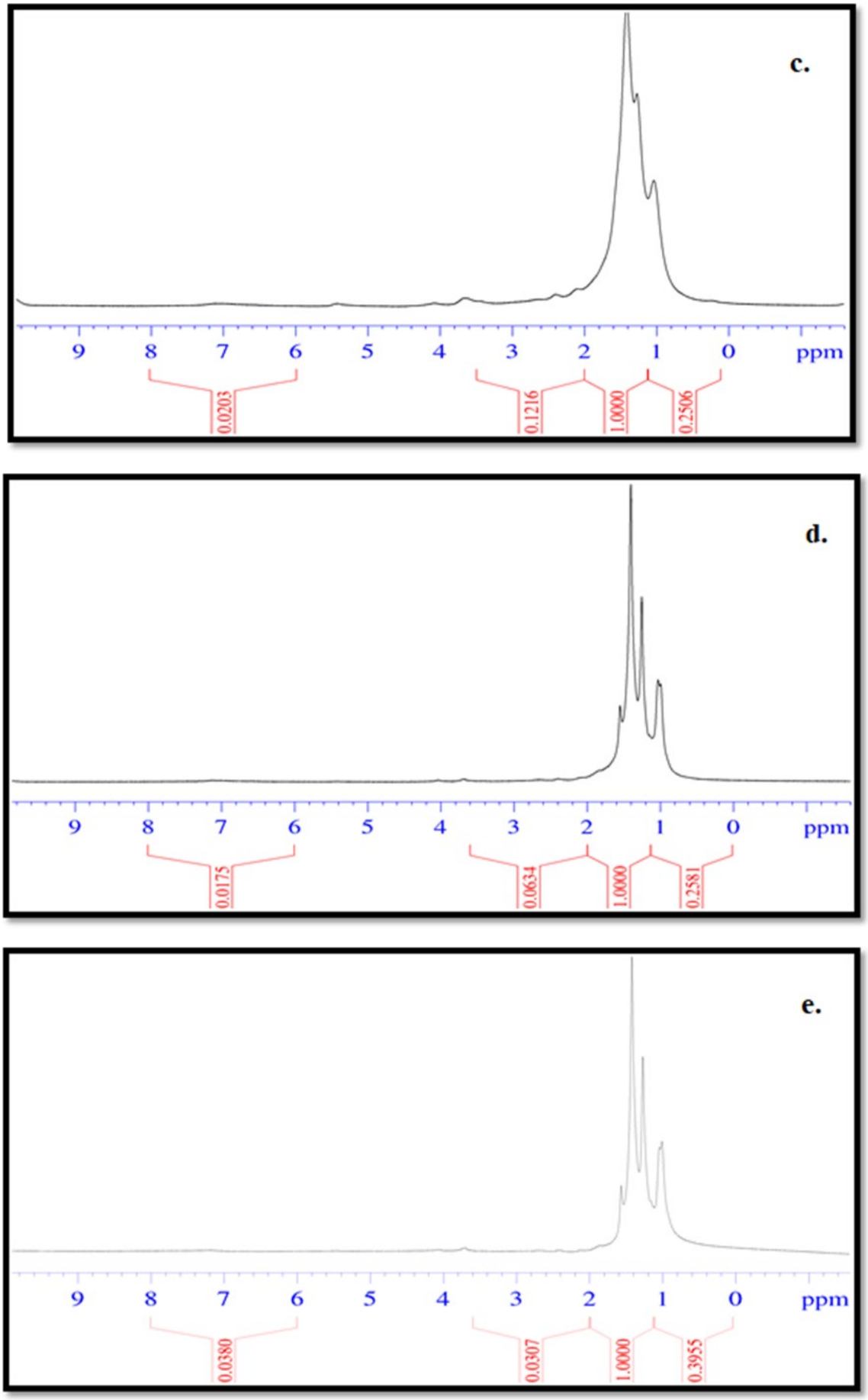


Figure 1. 1H-NMR spectra of (a) Pen 50/70 (b) V2TQ, (c) V1, (d) V2D, (e) V2F.

2.2. Additives

The polymers were introduced in the composition of the alternative binders to improve the elastic response of the final formulations. The powdered rubber from ELTs was supplied by Ecopneus s.c.p.a. The product is a black powder with a maximum size dimension of about 42 μm. Moreover, the introduction of SBS polymer has been considered, since this elastomeric polymer is commonly used in the road sector for the production of modified bitumens. In this study, the amount of SBS used was limited to a maximum of 2% in order to reduce the production costs of the final blends. In addition, it is well-known that SBS polymers work well in combination with rubber from ELTs [12,33]. The SBS polymer was supplied by Kraton Polymers LLC. In order to improve the adhesion of REOBs to the lithic skeleton, an adhesion promoter (AP) has been employed, since it was proven to be effective [34,35]. To modulate the viscosity, various cellulose polysaccharides were used as viscosifier: P2, nano-fibrillated cellulose (CNF), and nanocrystalline cellulose (CNC) [36]. Additionally, to ensure a good workability of the asphalt mix at high temperatures, waxes with melting points of about 100 °C were used, which are commonly used for the production of WMA mixtures [37,38]. In particular, Sasobit waxes (Sb) were employed in this study. Some other issues observed during the blend preparation and analysis have been solved by the aid of other additives such as pine resins (PR) [29,39], which improve the cohesive properties of the REOBs; thickening agents such as Lithium salt (LiS) and nanotubes (Nt) have been used to take advantages of their gelling properties (widely employed in industrial grease production). The PR, AP, and P2 were supplied by Kimical s.r.l. The lithium salt (LiS) was supplied by Sigma Aldrich, while the nanotubes (Nt) were produced in laboratories of the University of Calabria. The nano-fibrillated cellulose (CNF) was supplied by Nanografi Co. Inc., while nano-crystalline cellulose (CNC) was obtained in the laboratories of the University of Calabria from waste papers following the methods reported in the reference [40]. All the supplied products were used without any further treatment. The mean cost of the blends, considering the various additives' prices and percentages used in our blend preparation, is about 350–400 €/ton.

2.3. Alternative Binders

The additives that were used allowed for the definition of final alternative binders similar to the traditional bitumen used for paving. In total, 18 alternative binders were defined and then characterized at the binder and the asphalt mixture levels, which are listed in Table 2. Each alternative binder description consists of all materials that were used in quantity greater than 0%. Hence, each line of Table 2 represents the recipe of one alternative binder. Prior to sample preparation, the various additives underwent thermogravimetric analysis in order to check their stability at the high temperature, i.e., 160 °C. No additives showed considerable weight loss and, consequently, no additives degradation would occur during mixing process.

The preparation of alternative binders required the preliminary heating phase of each specific REOB (V1, V2TQ, V2F and V2D) at about 160 ± 5 °C. Then, the quantity of the chosen additives was gradually added to the warmed REOB (1 g/min). The additives were incorporated at room temperature. All constituents were mixed by means of high-shear mixer (IKA model) with an average speed of about 1400–1600 rpm. Each blend was mixed at 160 °C for 60 min to guarantee an essentially homogenous sample.

Blend	V1	V2TQ	V2F	V2D	PFU	Sb	SBS	AP	P2	CNC	CNF	PR	Nt	LiS
B23 CNC	-	-	60	-	15	10	-	0.3	-	14.7	-	-	-	-
B26	-	-	40	-	10	10	-	-	20	-	-	40	-	-
B27	-	-	60	-	5	10	-	-	15	-	-	10	-	-

B29	-	-	40	-	10	10	-	-	-	-	-	40	-	-
B29V1	40	-	-	-	10	10	-	-	-	-	-	40	-	-
B30	-	-	40	-	-	8	-	-	14.9	-	-	27	0.1	10
B26D	-	-	-	40	10	10	-	-	20	-	-	20	-	-
B27D	-	-	-	60	5	10	-	-	15	-	-	10	-	-
B29D	-	-	-	40	10	10	-	-	-	-	-	40	-	-
B30D	-	-	-	40	-	8	-	-	14.9	-	-	27	0.1	10
B26-1	-	-	60	-	10	10	1	0.3	8.7	-	-	10	-	-
B27-1	-	-	60	-	5	10	1	0.3	13.7	-	-	10	-	-
B29-1	-	-	50	-	10	10	0.5	0.3	-	-	-	29.2	-	-
B31	-	-	60	-	15	10	2	0.3	7.7	-	-	5	-	-
B31V1	60	-	-	-	15	10	2	0.3	7.7	-	-	5	-	-
B32	-	-	60	-	15	5	-	0.3	-	-	14.7	5	-	-
B32V1	60	-	-	-	15	5	-	0.3	-	-	14.7	5	-	-
B33TQ	-	60	-	-	19.7	13	2	0.3	-	-	-	5	-	-

Table 2. Type and percentage of constituent materials of the 18 alternative binders.

2.4. Asphalt Mixtures

The asphalt mixes with the alternative binders were produced using RAP aggregates only. The recycled aggregates consisted of milled asphalt concrete from existing pavements of highways. The grading distribution and the binder content were designed in order to produce a traditional wearing course asphalt mixture. The grading distribution of the RAP aggregates met the Italian technical specifications. Based on the aged bituminous binder content already present in the recycled aggregates and on previous studies based on Cantabro test (EN 12697-17) [41], the optimum binder content was selected as equal to 2.5% of the total weight of aggregates. The innovative asphalt mixtures were compared with samples of a traditional wearing course layer made of 90% virgin aggregates and 10% RAP and Pen 50/70, which was considered as a reference mix, and a mix consisting of 100% RAP aggregate and Pen 50/70. Moreover, the limits of the Italian technical specifications for wearing course layers were considered as reference for comparisons.

All alternative binders were used for producing 18 different asphalt mixtures. Per each asphalt concrete mix, three samples were manufactured. The cylindrical samples had diameter of 100 mm and were 55 mm tall, approximately. The correct amount of recycled aggregates and the alternative binders were preliminarily heated in an air-forced oven before being mixed and compacted. Per each asphalt mix, 3000 g of RAP aggregates were heated at 150 °C for 2 h and 75 g of the prepared blends (i.e., 2.5%wt.) at 150 °C for a minimum of 1 h. The samples underwent compaction by means of a gyratory compactor applying 100 gyrations at 600 kPa [42].

3. Test Methods

In order to preliminarily assess the feasibility of using alternative binders for road construction materials, the 18 new binders underwent rheological analysis. Then, the mechanical response of all asphalt mixtures, those containing an alternative binder and the reference mixes, were investigated. Since these were binders without bitumen as the main constituent, the basic tests were planned with the aim of assessing a possible relationship, if any, between the behaviour of binders and that of mixtures as they exist for traditional bituminous materials.

3.1. Rheological Measurements

A dynamic shear rheometer (SR5000, Rheometric Scientific, Piscataway, NY, USA) was used to perform the rheological tests on the various alternative binders. The con- trolled shear stress rheometer was used in a plate–plate configuration. Plate tools of ϕ = 25 mm diameter were used for testing in the temperature range of 25–120 °C. The gap was set equal to 2 mm. A Peltier system (±0.1 °C) controlled the test temperature. The rheological responses of Pen 50/70 and alternative binders were determined under the kinematics of both steady and oscillatory simple shears. In steady-shear experiments, the viscosity of blend samples was determined from the ratio of measured shear stress to applied shear rate, as a function of shear rate that varied from 1 to 100 s^{-1}. Steady states were previously checked by transient experiments (step-rate test). For all samples, it was observed that 10 s was a sufficient scanning time to ensure the steady-state condition. All samples showed a Newtonian behaviour in the investigated shear rate range. Dynamic tests were carried out in conditions of linear viscoelastic (LVE) region, where measured material features do not depend on the amplitude of applied load and are related to materials microstructure only. With the aim of investigating the material viscoelastic phase transition, dynamic temperature ramp tests (DTRT) were performed both at 1 Hz and temperature rate of 1°C/min from 25 °C to 120 °C by applying the proper stress values—previously determined by stress sweep tests—to guarantee linear viscoelastic conditions at all tested temperatures.

3.2. Mechanical Analysis

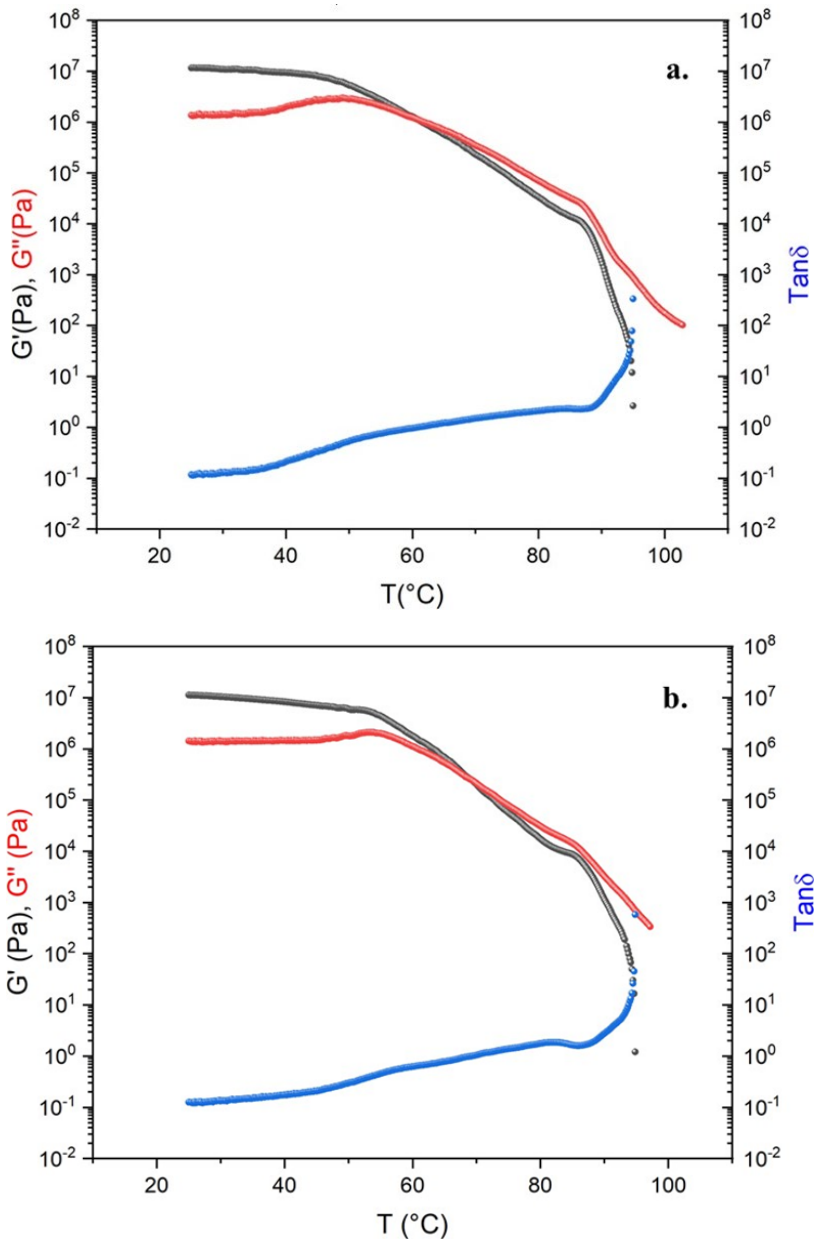
The resulting 18 asphalt mixtures were subjected to dynamic and static mechanical characterizations. The asphalt concrete samples underwent mechanical tests after being cured for a minimum of 24 h. Dynamic tests were used to determine the Indirect Tensile Stiffness Modulus (ITSM) at 20 °C of all samples by using a servo-pneumatic testing ma- chine. The ITSM values were determined according to EN 12697-26 standard [43], in the indirect tensile configuration (IT-CY). A pulse loading was applied with a 124 ms rise time to generate a horizontal deformation of 5 ± 2 μm. Two static mechanical characterizations were used to measure the Indirect Tensile Strength (ITS) and the Indirect Tensile Strength Ratio (ITSR) of all mixes according to the EN 12697-23 [44] and EN 12697-12 [45] standards, respectively. The tensile resistance of asphalt concretes was determined by applying a compression load with a constant speed rate of 51 mm/min. The ITS test was performed at 25 °C. The latest characterization, i.e., the ITSR ratio, aimed to assess the durability of the wearing course samples, as it determines the effect of water conditioning. This investigation quantifies the ratio between the ITS values of an asphalt mix after water conditioning and those of dry specimen. According to standard method A, the samples were saturated while stored in a water bath at 40 °C for three days. Successively, the samples were removed, dried, and conditioned at 25 °C in a climate chamber to further undergo ITS testing. The two static characterizations applied a load until failure; hence, two samples were used to evaluate the average ITS values, while the third specimen of each asphalt mix was used to determine the corresponding ITSR value. Before being tested, all samples were kept in a climate chamber at the test temperature for at least 4 h.

4. Results and Discussion

4.1. Rheological Analysis

Figure 2 shows the results of the DTRT obtained from the blends B26-1, B27-1, B29-1, and B32V1. Among all alternative binders, these four blends were selected because they exhibit good

rheological and mechanical responses, as can be seen by comparing the DTRT of our blends with that of a 50/70 bitumen reported in Figure 3. The remaining blends that were prepared show good rheological behaviour, but they do not behave as expected from a mechanical point of view (the DTRT of the other blends can be found in the Supplementary Information Figure S1). The DTRT of virgin REOBs (V2F, V1, V2D, V2TQ) are reported in Figure 3. Figures 2 and 3 shows that alternative binders strongly enhance the rheological properties of both REOBs and bitumen. Moreover, by comparing the DTRT of the alternative binders—even those reported in the Supplementary Information—with that of an SBS-modified bitumen (PmB) reported in Figure 4, it can be concluded that the alternative binders resemble the behaviour of a polymer-modified bitumen.



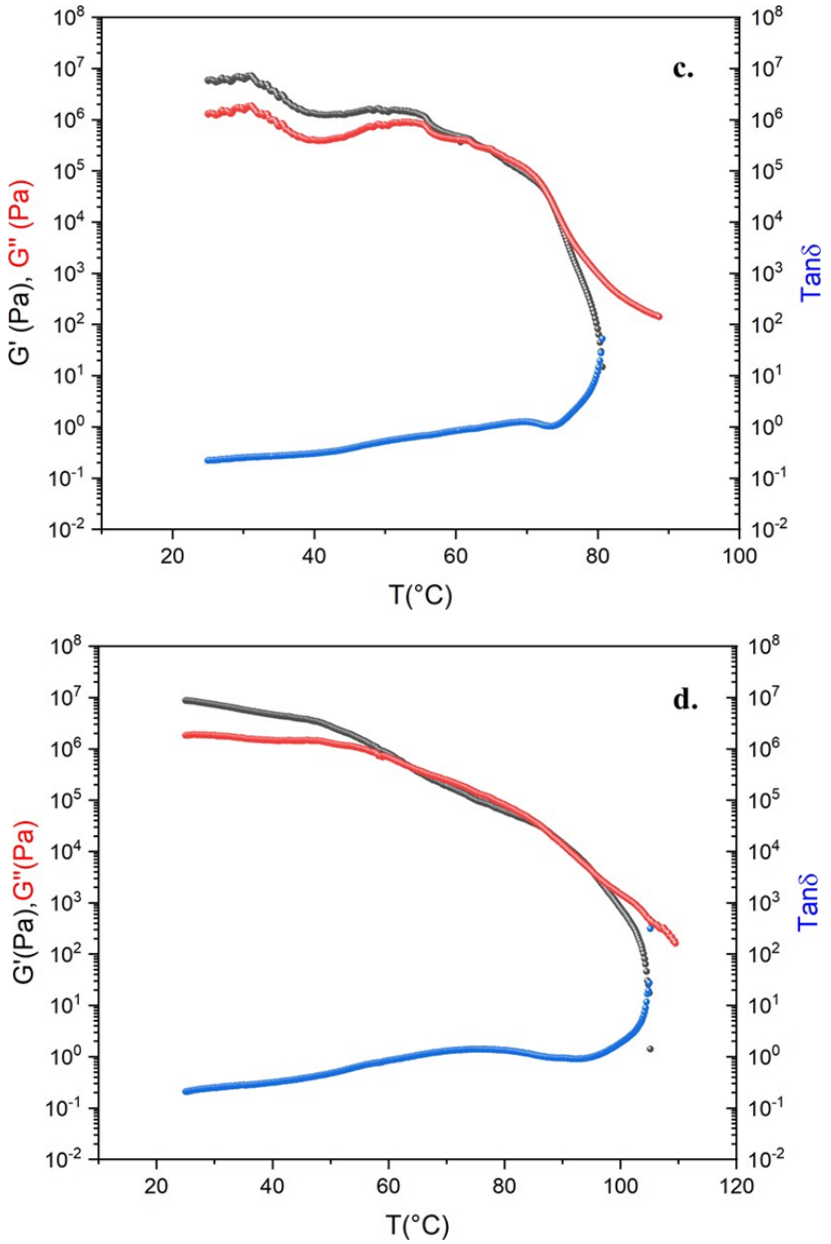
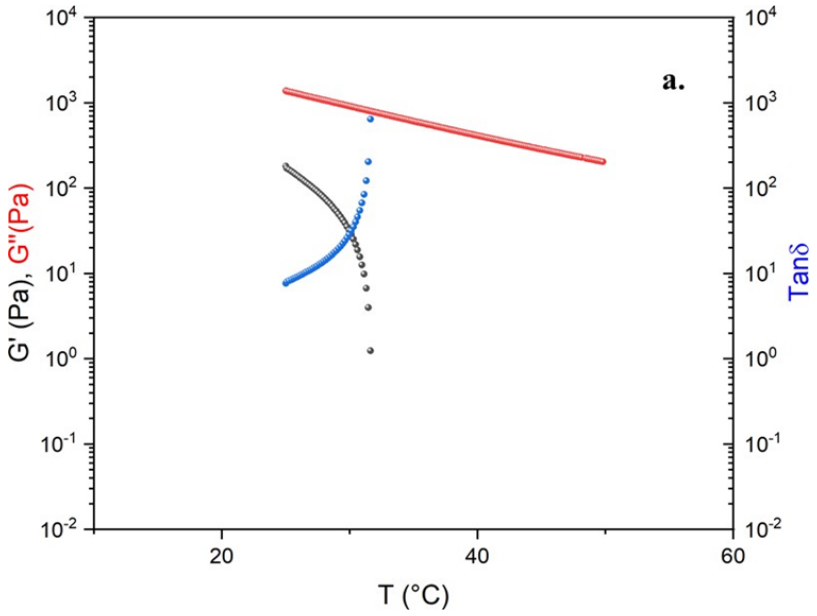
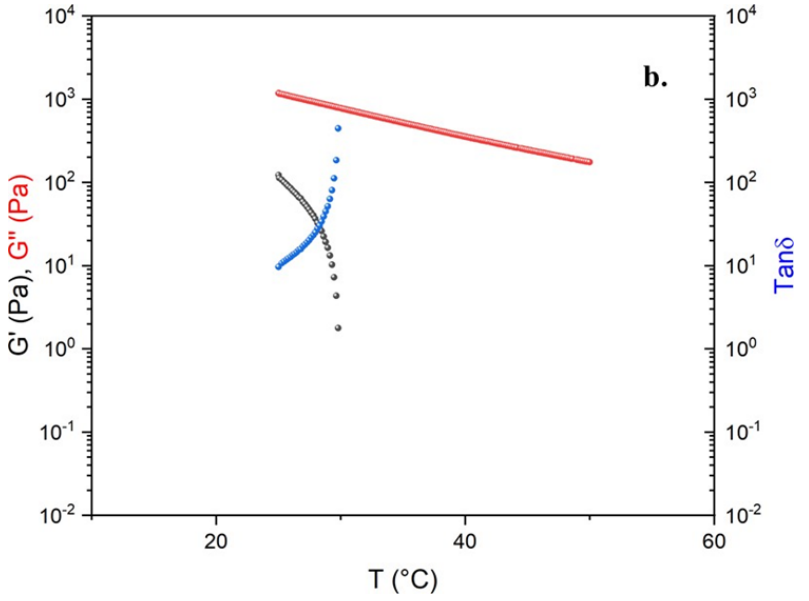
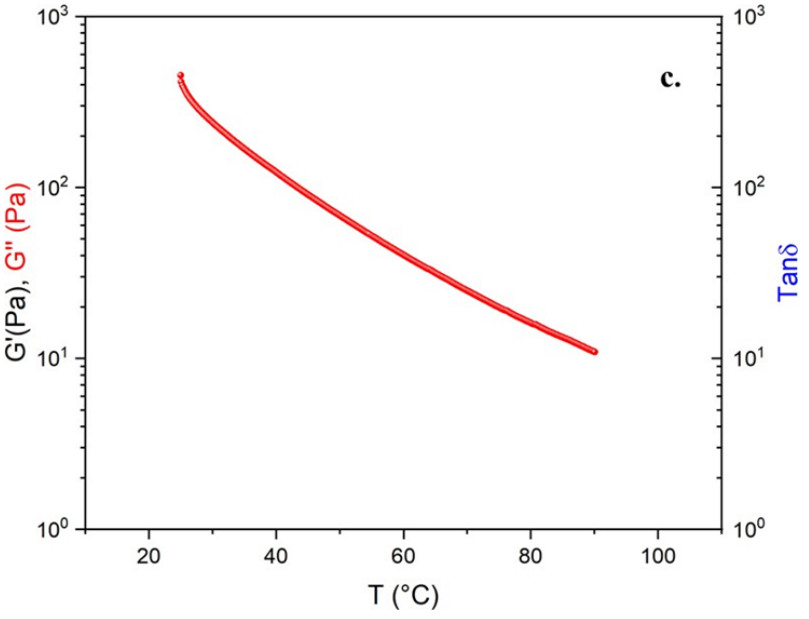


Figure 2. Dynamic Temperature Ramp Test (DTRT) of (a) blend 26-1, (b) blend 29-1, (c) blend 27-1, (d) blend 32V1.


a.
G' (Pa), G''(Pa)
Tanδ
T (°C)


b.
G' (Pa), G'' (Pa)
Tanδ
T (°C)


c.
G'(Pa), G'' (Pa)
Tanδ
T (°C)

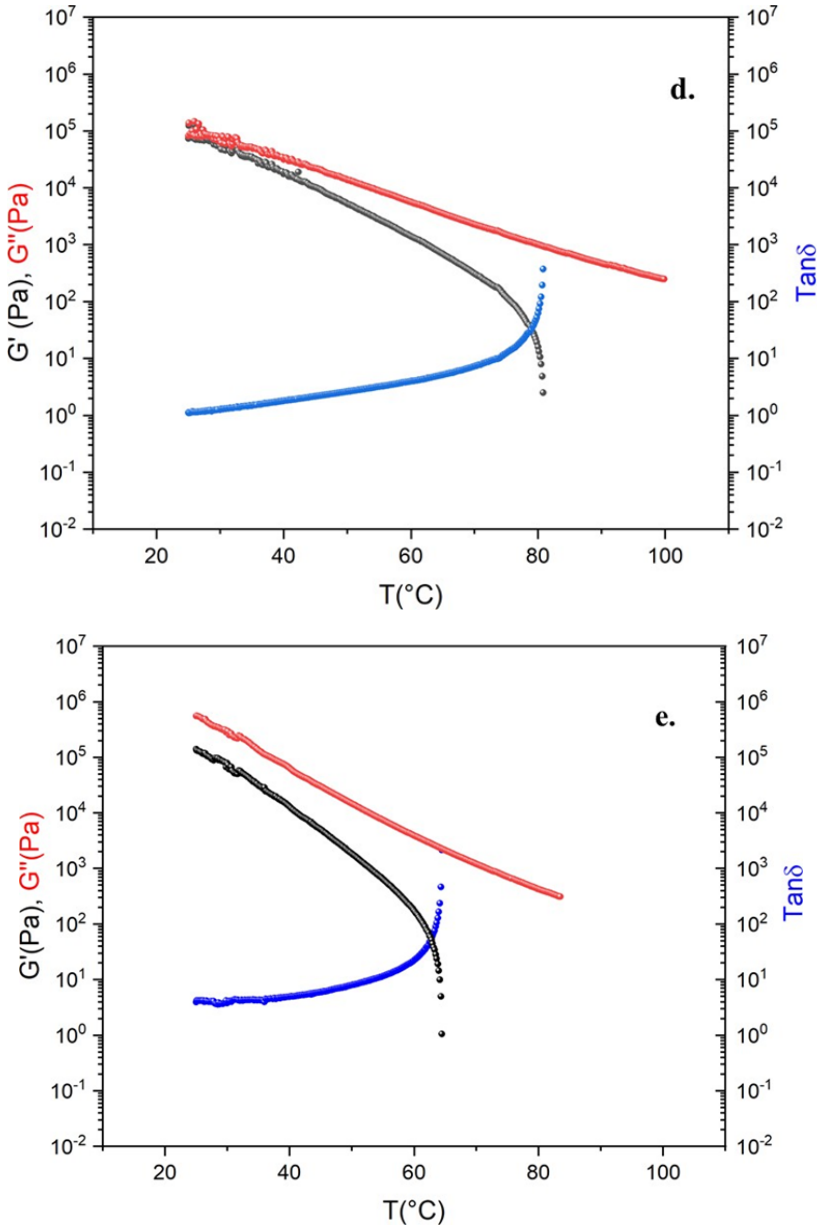


Figure 3. Dynamic Temperature Ramp Test of (a) V2F, (b) V2D, (c) V1, (d) V2TQ, (e) Pen 50/70.

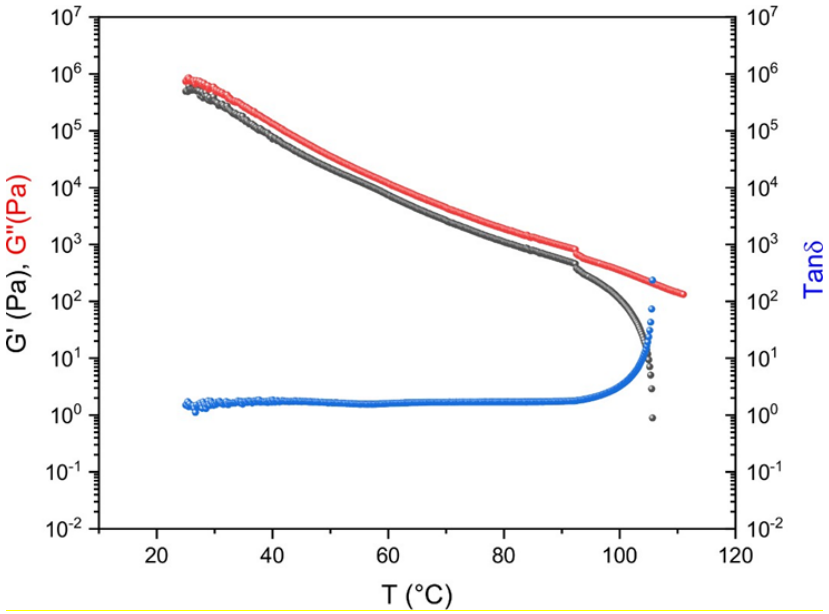


Figure 4. Dynamic Temperature Ramp Test of an SBS-modified bitumen (Pen 50/70 + 3% SBS).

4.2. Mechanical Analysis

The dynamic mechanical characterization of the asphalt mixtures manufactured with the 18 alternative binders and Pen 50/70 is reported in Figure 5. The asphalt mixes exhibit high variability in the ITSM results, which can be ascribed to the constituent materials used. The mixture with B23CNC shows the lowest stiffness modulus, while the mixture containing B29D has the highest stiffness. In general, the asphalt mixes containing the V2D show higher stiffness than the corresponding asphalt concrete mixtures with V2F. The higher presence of low-molecular-weight oil in the alternative binders lead to soften the final materials as expected. Hence, the type of REOB affects the final ITSM values. Additionally, the combination of specific additives permits alternatively increasing or decreasing the stiffness modulus of the corresponding asphalt mixture. In fact, the B33TQ mix has lower ITSM value than the B29D asphalt concrete. In general, the minimum ITSM values at 20 °C of a traditional wearing course layer made with virgin materials only are 3000 MPa and 3500 MPa for samples produced with unmodified and polymer-modified bitumens, respectively. Previous studies on the reference mix that contains 10% of RAP and Pen 50/70 have assessed an average ITSM value equal to 5500 MPa at 20 °C, which can be used for comparing the stiffness modulus of the innovative asphalt mixtures with the alternative binders. Among all tested asphalt materials, the mixtures manufactured with B26-1, B27, B27-1, B31, B31V1, B32, and B32V1 have similar stiffness to the reference mixture that mainly contains virgin materials. Most of the recycled asphalt mixtures with alternative binders have higher stiffness than the samples of the reference mix, which can be mainly related to the presence of RAP and to the addition of PR. In general, the use of recycled aggregates has been found to stiffen the final asphalt concretes; indeed, the mixture with 100% RAP and Pen 50/70 is stiffer than the reference one. The introduction of PR in the bituminous binders improve the cohesion properties, which turn in higher ITSM values. Indeed, the alternative binders with a high content of PR are very stiff. However, the use of asphalt mixtures with a very high stiffness is disadvantageous, as the resulting asphalt pavement may be more prone to fatigue and thermal cracking.

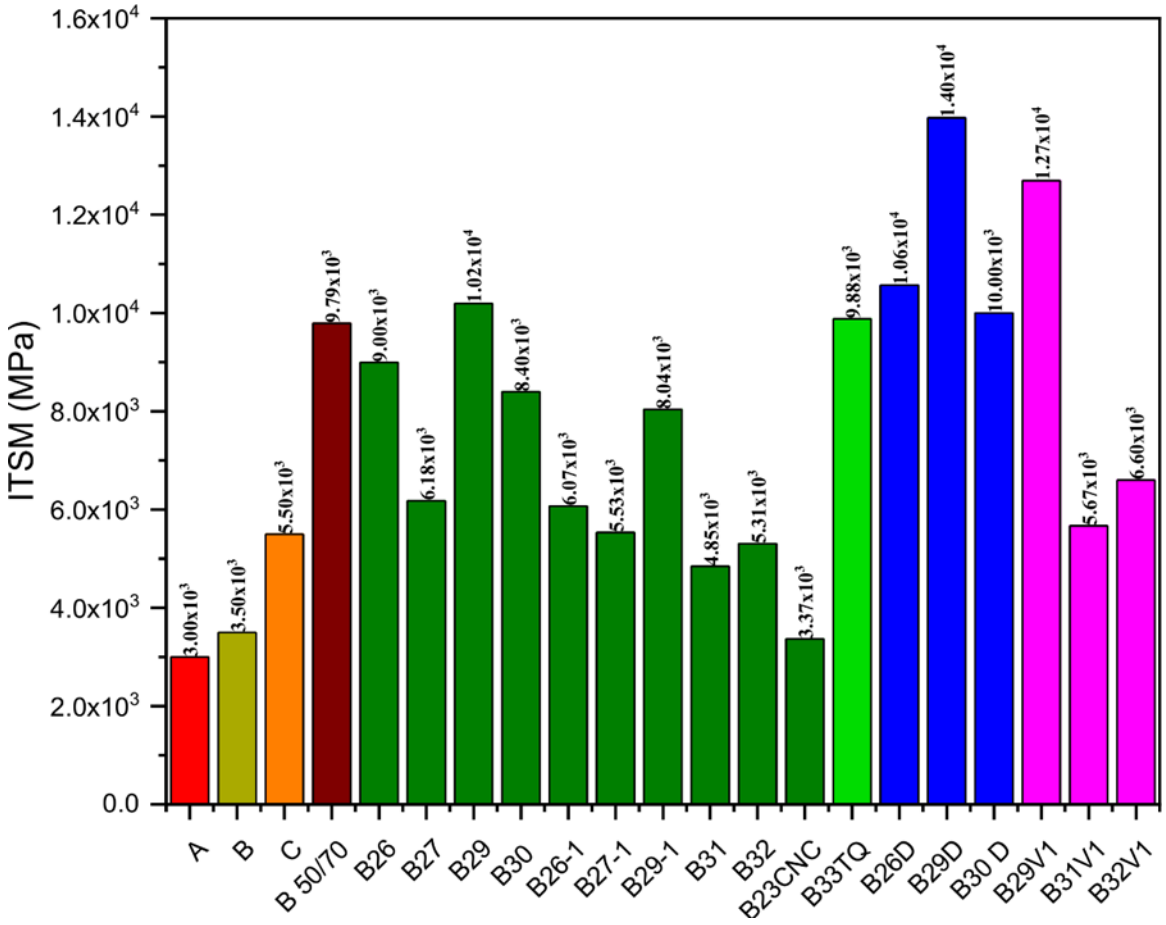


Figure 5. Results of the ITSM values at 20 °C of the recycled asphalt mixtures produced with 100% RAP and the alternative binders. Legend: Asphalt concrete with virgin bitumen and aggregates (A); Asphalt concrete with virgin polymer- modified bitumen and aggregates (B); Reference mix (C); 100% RAP asphalt concrete with Pen 50/70; 100% RAP asphalt concrete with alternative binders containing V2F; 100% RAP asphalt concrete with B33TQ; 100% RAP asphalt concrete with alternative binders containing V2D; 100% RAP asphalt concrete with alternative binders containing V1.

Figure 6 shows the indirect tensile resistance of the innovative asphalt mixtures produced with RAP and alternative binders. The Italian technical specifications require a minimum ITS value equal to 0.72 or 0.95 MPa for asphalt concrete with unmodified and polymer-modified bitumens, respectively. Almost all innovative mixtures meet the requirement; only the innovative mixtures with B23CNC, B27-1, and B29-1 show insufficient tensile resistance. The recycled mix with Pen 50/70 exhibits the highest tensile resistance. For bituminous materials, the tensile resistance and stiffness values are directly related to each other, and this correlation is also confirmed in the present study. The innovative asphalt mixes with the highest ITSM values exhibit the highest ITS results. However, the ITS values close to or higher than 2.0 MPa may reflect a very high stiffness, which may turn into brittle asphalt pavements. As a consequence, the Italian technical specifications limit the tensile resistance of the asphalt mixes, and the ITS values of the asphalt mixtures with neat and polymer-modified bitumen have to be lower than 1.60 and 1.90 MPa, respectively. In this regard, the samples manufactured with B26, B26D, B26-1, B27, B27-1, B29V1, B29-1, B30, B30D, B31, B32, and B32V1 meet the required specifications for mixtures with unmodified bituminous binders. These innovative mixes have a similar response to the reference mix with virgin materials, as their ITS values are equal to 1.2 MPa on average.

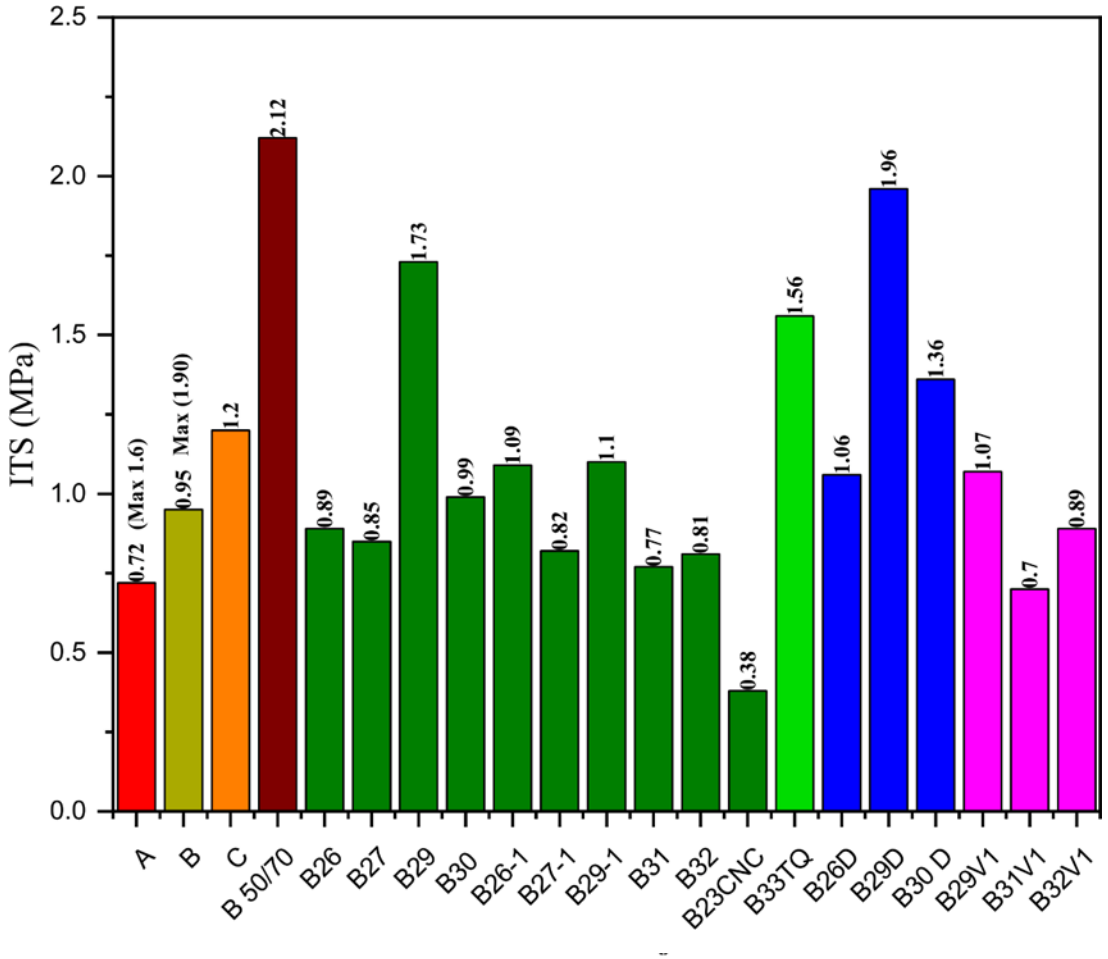


Figure 6. Results of the ITS values at 20 °C of the recycled asphalt mixtures produced with 100% RAP and the alternative binders. Legend: Asphalt concrete with virgin bitumen and aggregates (A); Asphalt concrete with virgin polymer- modified bitumen and aggregates (B); Reference mix (C); 100% RAP asphalt concrete with Pen 50/70; 100% RAP asphalt concrete with alternative binders containing V2F; 100% RAP asphalt concrete with B33TQ; 100% RAP asphalt concrete with alternative binders containing V2D; 100% RAP asphalt concrete with alternative binders containing V1.

The results of measuring the water susceptibility for the innovative asphalt mixtures are reported in Figure 7. The type of REOB significantly affect the resistance of asphalt concrete, as the use of V1 decreases the water damage resistance of the mixes when com- pared to the corresponding mixtures with one of the V2s. The minimum ITSR value required by the Italian technical specifications is about 90% when unmodified bitumens are used. Among the innovative asphalt mixtures, almost all mixes that contain V2F (except for B26 and B23CNC) and the mixtures made with B33TQ, B29D, B30D, and B32V1 show good resistance against water damage, or they do not even show any water susceptibility, as the ITSR results are greater than 100%. This behaviour can be ascribed to the presence of a very high quantity of RAP aggregates. The abovementioned asphalt concrete mixes behave similarly to the reference mix mainly produced with virgin aggregates. On the other hand, the ITS value of the 100% RAP mix with Pen 50/70 is considerably reduced after water conditioning, and its ITSR ratio is about 89%.

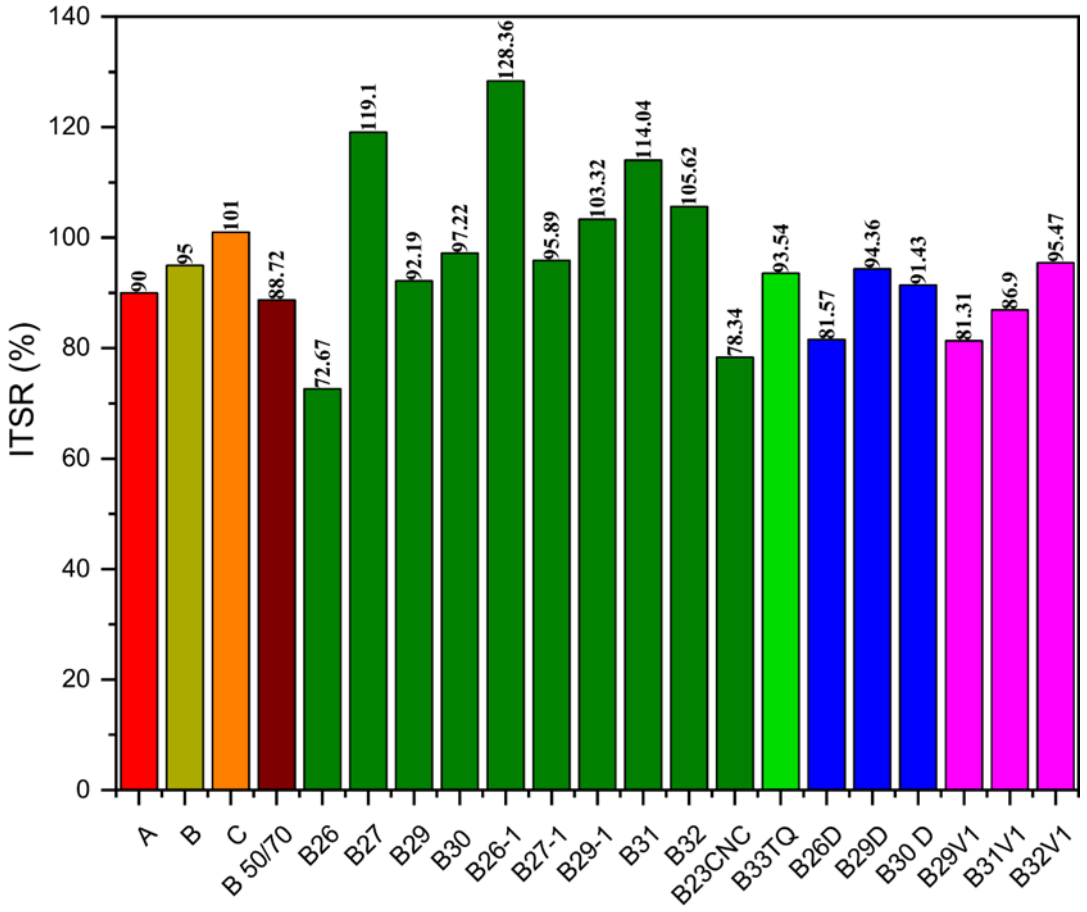


Figure 7. Results of the ITSR values at 20 °C of the recycled asphalt mixtures produced with 100% RAP and the alternative binders. Legend: Asphalt concrete with virgin bitumen and aggregates (A); Asphalt concrete with virgin polymer- modified bitumen and aggregates (B); Reference mix (C); 100% RAP asphalt concrete with Pen 50/70; 100% RAP asphalt concrete with alternative binders containing V2F; 100% RAP asphalt concrete with B33TQ; 100% RAP asphalt concrete with alternative binders containing V2D; 100% RAP asphalt concrete with alternative binders containing V1.

Among all analysed asphalt mixtures, those containing the blends B26-1, B27, B27-1, B31, B32, and B32 V1 exhibit good mechanical properties in terms of stiffness, tensile resistance, and water susceptibility. Although the results obtained with the alternative binders are promising, further specific rheological and mechanical tests have to be carried out in order to assess the feasibility and the durability of these road materials that do not contain standard bitumen. For instance, testing fatigue (mechanical), ageing susceptibility (rheological and mechanical), and low-temperature behaviour of the final alternative binders and asphalt mix will be crucial to establish the performances of these innovative asphalt products. In particular, the ageing tendency of the alternative binders, and consequently of asphalt concrete, has to be evaluated, since an aged material is used, i.e., REOB. Some of the abovementioned tests are ongoing and are showing promising results.

5. Conclusions

In this work, the potential reuse of waste products that were opportunely treated to produce new possible petroleum-based binders starting from REOBs is proposed. In addition, the use of 100% recycled aggregates (RAP) together with alternative binders can represent a good alternative to the

current use of virgin materials at the binder and asphalt mixture levels. During this study, rheological and mechanical tests were carried out to preliminarily assess the mechanical properties of these innovative binders. From a rheological point of view, the alternative binders exhibit similar behaviour to polymer-modified bitumen (3%wt. of SBS). The type of REOB, the chosen additives, and the combination of constituent materials are found to be crucial to the final responses of the innovative petroleum-based binders and asphalt mixes. In particular, the introduction of low-molecular-weight oils by REOB products softens the resulting alternative binders and, consequently, the asphalt mixtures, resulting in lower ITSM and ITS values. In addition, the use of recycled mixture with 100% of RAP and alternative binders confers good water damage resistance to the corresponding asphalt mix. In general, various eco-friendly asphalt mixtures show promising results in terms of stiffness, tensile resistance, and water susceptibility. In detail, among all tested materials, the asphalt concretes that contained the alter- native binders B26-1, B27, B27-1, B31, B32, and B32V1 meet the requirements of the Italian technical specifications for wearing course samples produced with virgin materials. Hence, these innovative mixtures satisfy the basic mechanical performances. However, limited recipe adjustment may allow the stiffness reduction of the abovementioned asphalt mixtures without compromising the cohesion and water sensitivity of the final road materials. Even though the results of the present study are promising, they represent a preliminary evaluation of the performances of the alternative binders, and further rheological and mechanical analyses are necessary. In particular, the durability of the asphalt concrete has to be investigated, considering the natural ageing process of petroleum- based product and the use of an aged material for the production of the alternative binders (i.e., REOB). The determination of eco-friendly road materials is still ongoing, and the responses of the low-temperature DTRT and fatigue tests are under investigation.

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