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Cycle XXXIV

Assessment of eco-friendly modified asphalt mixtures using Graphene-enhanced polymer compound by dry process

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1 Introduction

The recent warnings about waste pollution and the limits of natural resources are encouraging the development of a circular economy changing the paradigm related to the linear economy, by limiting the environmental impact and waste of resources, as well as increasing efficiency at all stages of the product economy.

For this reason, most country in the word are currently updating their legislation on waste management to promote a shift to a more sustainable model known as the circular economy. In detail, the European Commission presented, under the European Green Deal and in line with a proposed new industrial strategy, the new circular economy action plan that includes proposals on more sustainable product design, reducing waste and empowering consumers (such as a right to repair). Specific focus is brought to resource intensive sectors, such as electronics and ICT, plastics, textiles and construction.

On this way, with the aim to protect the ecosystem and to leave the earth with the same current resources for future generations, in the last decade, human activities have pursued more and more frequently and regularly the concerns regarding Eco-sustainability. Several tools are used to support eco-sustainability, promoting the diffusion of environmental technologies and the development of environmentally friendly products, through the research and the choice of results and solutions that have lower impacts on the environment throughout the entire life cycle.

In this historical context, with reference to asphalt pavements, it should be noted that technologies have been developed towards solutions for enhancing the pavement's service life, which should be considered in Life Cycle Analysis (LCA) too. Hence, to improve the service life of asphalt pavement reflecting the principles of Circular Economy, innovative adaption technologies need to be investigated to design adequate road asphalt pavement in next future. The most innovative technologies are oriented to:

- **extend the service life:** increasing the service life of pavements up to 50 years. “Perpetual Pavements” have been introduced;
- **rejuvenating and reusing** asphalt derived from either demolishing or milling of existing asphalt layers (Circular Economy);
- **reducing the energy consumptions** and consequent emissions.

In any case, if on the one hand the Green and Circular Economy move towards the reuse and recycling of end-of-life products, on the other hand we must not forget that, when it comes to asphalt pavements, safety takes the first place, i.e. the assurance of the work performances. The road therefore should not become a “landfill” or a “repository” of disused materials. This means that, the materials used in the construction must be subjected to an adequate technical-environmental study considering:

- product development;
- verification of the use in asphalt layers by laboratory analysis;
- the execution of real-size trial sections, after prequalification phase of the mix design;
- the post-production verification of the modified asphalt using both laboratory and on site tests;
- monitoring the trial section over time;
- LCA verification, even with on-site surveys on emissions and energy consumptions.

On this way to improve the resistance of asphalt pavement at distress phenomena (rutting, fatigue damage, thermal distress…) in respect of circular economy principles, various types of polymers have been introduced as modifiers for Hot Asphalt Mixture (HMA), by adopting two different methods: wet (PMB technology) and dry (PMA technology) processes. Both modification methods assume that bitumen is a thermoplastic material which shows a viscoelastic behaviour in most operating conditions under road traffic loads; this main property makes the bitumen the most adopted binder in hot asphalt mixture and simultaneously has a significantly influence on their mechanical properties.

Therefore, since the research study conducted is included into the "Programma Operativo Nazionale Ricerca e Innovazione 2014-2020 (CCI 2014IT16M2OP005), Fondo Sociale Europeo, Azione I.1 "Dottorati Innovativi con caratterizzazione Industriale", it represents a research study made as cooperation between universities and road industry. Hence, with the research study conducted during the PhD course, the effect of an innovative product that contains graphene and a selected type of recycled hard plastics, on the mechanical related properties of hot asphalt mixtures, were investigated.

Following the main results available in scientific literature on modified Hot Asphalt Mixtures (HMA) the research was divided into several phases as follows:

a) Firstly, the materials used for producing the asphalt mixtures were investigated in terms of mechanical, rheological, and volumetric properties. Hence, four different sizes of limestone aggregates provided by a local quarry in southern Italy were used to design a dense graded asphalt concrete with maximum aggregates' size of 20mm (AC20) for a binder course. In detail, two coarse (limestone 10/18 and limestone 6/12) and two fine aggregates, i.e., limestone sand (0.25–4 mm) and limestone filler (0.063 – 2 mm), respectively, were used to develop the grading curves of the asphalt mixtures and their main physical properties were investigated in terms of: Los Angeles value, Shape Index, Flat Index, Sand Equivalent; Apparent specific gravity and Bulk specific gravity. Therefore, two types of binders were used: a 50/70 penetration-grade neat bitumen provided by a refinery in southern Italy and a commercially hard modified bitumen, PMB 10/40-70, obtained through the addition of 5% of SBS to a 70/100 penetration-grade neat bitumen. A preliminary evaluation of the collected bitumen samples was conducted through traditional bitumen tests such as, the penetration, ring-and-ball, and viscosity tests, as per the European Standard protocols;

b) Considering the dry modification process, two different asphalt modifiers were investigated consisted of a plastomeric polymer compound and a graphene-enhanced asphalt modifier. The first polymeric compound is composed of a mixture of optimized plastomeric polymers, which was designed to cope with severe rutting distress within flexible pavements either in hot climates or those of heavy-duty highways. The second polymer compound is an innovative product that contains graphene and a selected type of recycled hard plastics, on the mechanical related properties of hot asphalt mixtures.

c) With the aim to ensure the mechanical related properties of modified HMA, a traditional HMA (HMA_{NB}) was designed in terms of the aggregates' grading curve and the OBC, following the Superpave protocol [1]. The resulting asphalt mixture was considered as a reference and compared with a) an HMA manufactured using PMB (HMA_{PMB}); b) an HMA manufactured using the dry process with the introduction of the first polymeric compound (HMA_{PC}) and c) an HMA manufactured using the dry process with the introduction of the graphene-enhanced asphalt modifier (HMA_{GRPC}). All investigated asphalt solutions were designed to be similar in terms of: grading curve, Optimum Bitumen Content (OBC) and volumetric properties (air void content (V_a), voids in the mineral aggregate (VMA), and voids filled with asphalt (VFA));

d) With the aim to work on an integrated laboratory methodological approach for introducing innovative polymer compound as modifier into Hot Asphalt Mixtures and to provide an experimental–methodological approach to analyse the mechanical related properties of hot asphalt mixtures manufactured at a laboratory scale using the dry process, a new mixing procedure was designed to ensure the complete dissolution of polymers compound improving the final properties of the mixture. The research study demonstrate that the innovative mixing procedure could maximize the effect of polymeric compound addition for a laboratory-scale production;

e) With the aim of validating the excellence of the graphene enhanced asphalt modifier, it was verified on a large scale with the execution of trial section. The Pre-production and Post-production laboratory tests were conducted in addition to the periodical monitoring operations.

Therefore, the research study conducted is also strictly connected to the objectives formulated by the European Union in the field of Circular Economy, referring to the request for an efficient collaboration between researchers and companies to design products that can be able to both reduce the consumption of resources and the impact of waste on the environment.

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2 Circular and Green Economy

The circular economy is a model of production and consumption, which involves sharing, leasing, reusing, repairing, refurbishing, and recycling existing materials and products as long as possible. In this way, the life cycle of products can be extended. The circular economy is a framework of three principles, driven by design: Eliminate waste and pollution, Keep products and materials in use and Regenerate natural systems. It is based increasingly on renewable energy and materials, and it is accelerated by digital innovation. It is a resilient, distributed, diverse, and inclusive economic model.

The circular economy encompasses a very large number of sectors of activity and can be broken down in different complementary patterns of production and consumption such as:

- **Sustainable procurement:** development and implementation of a responsible purchasing policy;
- **Eco-design:** process of reducing the environmental impacts of a product or service throughout its life cycle;
- **Industrial and territorial ecology:** search for eco-industrial synergies at the scale of a business area - the waste of one company can become the resources of another one;
- **Economics of functionality:** collaborative economy that favours use over possession and thus tends to sell services related to products rather than the products themselves.

2.1 *From Linear to Circular Economy*

A circular economy is fundamentally different from a linear economy. To put it simply, in a linear economy we mine raw materials that we process into a product that is thrown away after use. In a circular economy, we close the cycles of all these raw materials. Closing these cycles requires much more than just recycling. It changes the way in which value is created and preserved, how production is made more sustainable and which business models are used.

The departure from the traditional, linear economic model is based on a take-make-consume-throw away pattern. This model relies on large quantities of cheap, easily accessible materials and energy. Also, part of this model is planned obsolescence when a product has been designed to have a limited lifespan to encourage consumers to buy it again.

In detail, the circular system and the linear system differ from each other in the way in which value is created or maintained. A linear economy traditionally follows the "take-make-dispose" step-by-step plan. This means that raw materials are collected, then transformed into products that are used until they are finally discarded as waste. Value is created in this economic system by producing and selling as many products as possible. Otherwise, the Circular Economy follows the 3R approach: reduce, reuse and recycle. It implies reducing waste to a minimum. When a product reaches the end of its life, its materials are kept within the economy wherever possible. These can be productively used again and again, thereby creating further value. Hence, the perspective on sustainability is different in a circular economy than in a linear economy. When working on sustainability within a linear economy, the focus is on eco-efficiency, which means we try to minimise the ecological impact to get the same output [2]. Otherwise, within a circular economy, sustainability is sought in increasing the eco-effectiveness of the system. This means that not only the ecological impact is minimized, but that the ecological, economic and social impact is even positive [3].

In order to achieve eco-effectiveness, residual flows must be reused for a function that is the same (functional recycling) or even higher (upcycling) than the original function of the material. As a result, the value is fully retained or even increased. This is different in a linear economy. An eco-efficient system typically works on downcycling: a (part of a) product is reused for a low-grade application that reduces the value of the material and makes it difficult to reuse the material flow again [4]. The main differences between linear and circular economy are synthetically represented in Table 2.1.

Table 2.1 - The main differences between linear and Circular economy

	Linear Economy	**Circular Economy**
Step plan	Take-make-dispose	Reduce-reuse-recycle
Focus	Eco-Efficiency	Eco-Effectivity
System boundaries	Short term, from purchase to sales	Long term, multiple life cycles
Reuse	Downcycling	Upcycling, cascading and high grade recycling.
Business model	Focuses on products	Focuses on services

2.2 *The Circular Economy in European Union (EU)*

The European Commission adopted the new circular economy action plan (CEAP) in March 2020. It is one of the main building blocks of the European Green Deal, Europe's new agenda for sustainable growth. The EU's transition to a circular economy aims to reduce the pressure on natural resources and it goes to create sustainable growth and jobs.

The new action plan announces initiatives along the entire life cycle of products. It targets how products are designed, promotes circular economy processes, encourages sustainable consumption, and aims to ensure that waste is prevented, and the resources used are kept in the EU economy for as long as possible.

The measures that are implies into the action plan mentioned above aims to:

- make sustainable products the norm in the EU
- empower consumers and public buyers
- focus on the sectors that use most resources and where the potential for circularity is high such as: electronics and ICT, batteries and vehicles, packaging, plastics, textiles, construction and buildings, food, water and nutrients
- ensure less waste

- make circularity work for people, regions, and cities
- lead global efforts on circular economy

To make the transition to a circular economy, it is necessary to intervene at all stages of the value chain: from the extraction of raw materials to the design of materials and products, from production to distribution and consumption of goods, from repair regimes, remanufacturing and reuse for waste management and recycling

2.3 *The notion of Waste and the new concept of design*

A key role into the transition to Circular Economy is played by the concept of waste. As definition, a waste is a product or substance which is no longer suited for its intended use. Whereas in natural ecosystems waste (i.e., oxygen, carbon dioxide and dead organic matter) is used as food or a reactant, waste materials resulting from human activities are often highly resilient and take a long time to decompose.

For legislators and governments, defining and classifying waste based on risks related to the environment and human health are therefore important to provide appropriate and effective waste management. For the producer or holder, assessing whether a material is waste or not is important in identifying whether waste rules should be followed. Definitions are also relevant in the collection and analysis of waste data as well as in domestic and international reporting obligations.

The transition from linear to circular economy move to consider the “waste” as an element, that can be introduced in a new production cycle. Consequently, a profound revision of Community legislation begins, in the light of circular economy transition. If the green economy already considered rejection a solution and no longer a problem, even today the rejection itself is subject to meticulous regulation, which significantly limits many of its intrinsic potential, through rules that provide for restrictions in terms of management and handling.

On this way, the transition from a "cradle to grave" economy to the circular economy already represents a moment of strong change in the materials management strategy with the tools available (termination of the qualification of waste and identification of by-products) and represents a strong impulse in the identification of new waste streams to be subjected to "end-of-waste" (EoW) processes and in the recognition of new by-products, especially as a result of the recent enactment of the decree by-products [5]. The new legislative proposals on waste stem from the need to improve resource efficiency and they are also accompanied by an impact assessment evaluation to:

- Reduce the administrative burdens;
- reduce the greenhouse gas emissions;
- reintroduce the secondary raw materials into the EU economy, thus reducing dependence on the import of raw materials.

In this context, the design plays a fundamental role in the development of products that reflect the principles of the circular economy as much as possible. During the conception, design and development phase, decisions are made that can significantly affect the sustainability or otherwise of the product during its life cycle. Hence, design for circular economy is closely linked to design for sustainability because in last decades it has moved beyond a pure environmental focus to also include economic and social aspects. In the new concept of design, the starting point the creation of a product and its eco-impacts, which should be minimized preserving value and human quality.

At the same time, the concept of design for circular economy has a different starting point because it aims to optimize the economic potential of available resources through new business models, while also restoring natural resources and enhancing human health. So, while in the long run the two concepts may amount to the same result, the short-term path is markedly different. The concept of design for circular economy can also be linked to design for recycling, but here the main difference is that the design for sustainability quickly takes a pure material view, while the Design for circular economy looks at extending the life cycle of products, systems and components before going to the material level, preserving the value in the product life cycle. focusing on the development of methods and tools that enable the design of products that are used more than once (i.e. that have multiple lifecycles). The new "designer" explores circular design strategies, such as product life-extension, reuse, remanufacturing and recycling, and the business models that enable these strategies. With this new concept, the researchers and designers try to solve tensions and dilemmas in circular product design, such as between the energy needed for production and energy consumption during lifetime and aims to generate knowledge on consumer attitudes and behaviour related to multiple lifecycle products (for example, how design can help to stimulate acceptance of new product ownership models).

2.4 *Green Public Procurement and Minimum Environmental Criteria*

Minimum Environmental Criteria (MEC) are environmental requirements established for the various phases of the purchasing process, aimed at identifying the best product, service or design solution in environmental terms, throughout its life cycle, taking account of availability on the market. These criteria are defined within the framework of the plan for environmental sustainability of consumption in the public administration sector (Green Public Procurement - GPP). The Green Public Procurement (GPP) is defined as "a process whereby public authorities seek to procure goods, services and works with a reduced environmental impact throughout their life cycle when compared to goods, services and works with the same primary function that would otherwise be procured" [6].

Thanks to the emissions of Minimum Environmental Criteria (MEC), the Green Public Procurement has become one of the main environmental and production policy tools capable of reducing environmental impacts, rationalizing and reducing public spending is able to promote innovative companies from an environmental point of view.

The combined uniform and systematic application of MEC end GPP help spread environmental technologies and the most environmentally favourable products, and by exerting leverage on the market, prompts the less virtuous economic operators to adapt to the new requirements of the public administration. In fact, according to Italian regulations on public contracts, contracting authorities that intend to purchase goods, works and services falling within certain categories, have to include mandatorily in the relevant calls for tenders the technical specifications and contractual clauses identified by the so-called Minimum Environmental Criteria.

This is the clearest example of how the principles of sustainable development embodied in the most recent European regulations on public contracts are concretely applied in the field of public procurement, in the context of the so-called sustainable public procurement and the promotion of the so-called “circular economy”. In this regard, the Italian public contracts code also includes other aspects, such as (i) the focus on the “product/service life cycle’’, which can be a criterion for evaluating the tenders beyond the mere price, (ii) the possibility of choosing flexible procedures, (iii) focus on “innovative solutions”, first and foremost in terms of efficiency within public procurement.

In general, the application of considerations and criteria of environmental aspect, social benefits and Life Cycle Analysis in public administration tenders have a very relevant importance also for economical issues. The application of these criteria, especially in some product areas, allows to guarantee, at the same time, better working conditions in Italy and abroad and the control of the environmental quality of production systems, thus also reducing unfair competition for goods produced thanks to scarce checks on working conditions and polluting emissions from production.

3 Bitumen for road asphalt mixtures

Increasing traffic loads have led researchers to explore different solutions for improving the mechanical performance of the road asphalt materials. Considering that a typical hot asphalt mixture (HMA), is a combination of aggregates, bitumen, and air, it has been established that the performance of an asphalt pavement are affected by the rheological properties of bitumen [7][8][9]. Hence, a comprehensive analysis should be done on to the bitumen production processes before to talk about more complex systems such as Hot Asphalt Mixtures.

3.1 *Bitumen: production processes and constituent elements*

Bitumen is thermoplastic solids at ambient temperature, while at higher temperature they behave as Newtonian liquids since its viscosity decreasing with rising temperature. Bitumen is also a visco-elastic material, so it behaves as elastic solid at short loading times and as viscous liquid at longer loading times. Polar molecules in bitumen lead it to have a good attraction with aggregates, this condition permits to obtain an homogeneous material that can be used for road asphalt pavement. The bitumen specifications focus on defining its physical properties, rather than being based upon chemical composition. The physical properties give a contribute both to determine the appropriateness for a its application and to define the circumstances under which the product must be managed to be placed in the structure in which it is to be used.

It is well known that the bitumen is produced by fractional distillation of crude oil. Referring to the production process, as first the crude oil is heated up to 300-350°C and introduced into an atmospheric distillation column. Hence, lighter fractions (such as naphtha, kerosene and gas oil) are separated from the crude oil at different heights in the column. The long residue is heated up to 350-400°C and introduced into a vacuum distillation column. By using reduced pressure, it is possible to further distillate lighter products from the residue because the equivalent temperature (temperature under atmospheric conditions) is much higher. If second distillation were carried out under atmospheric conditions and by increasing the temperature above 400°C, thermal decomposition/cracking of the heavy residue would occur. The residue at the bottom of the column is called short residue and is the feedstock for the manufacture of bitumen. The viscosity of the short residue depends on the origin of the crude oil, by the temperatures of the long residue and by the pressure in the vacuum column. The amount of short residue decreases and the relative amount of asphaltenes increases with increasing viscosity of the short residue. The differences in properties between high and low penetration grade bitumen are mainly caused by different amounts of molecule structures with strong interactions. Low penetration grade bitumen contains more of these molecule structures.

A second distillation can be used to cut off additional amounts of the more volatile products and create vacuum residues of the desired consistency. These one-stage and two-stage distilled asphalt fractions are referred to as straight-run bitumen, because the bitumen is separated from the crude oil while preserving its chemical properties.

Starting from this assumption, it is easy to understand how different crude oils contain different quantities of vacuum bottom and require specific refining techniques to produce the desired bitumen. Oxidized bitumen from the bottom of the reactor is sent to the separator, where bitumen vapours are separated which are returned to reactor and then to storage Straight-run bitumen, constitutes oxidized bitumen, the basic material that may be tailored for specific paving or industrial demands. Because oxidized bitumen is a viscous, semisolid material, it is difficult to mix with other substances at ambient temperatures. By heating it, the oxidized bitumen may be made more liquid and can coat aggregates to produce hot mix paving materials.

Other methods to reduce oxidized bitumen’s viscosity are to disperse particles of it in water (emulsified bitumen) or to dissolve it in petroleum solvents (cutbacks bitumen).

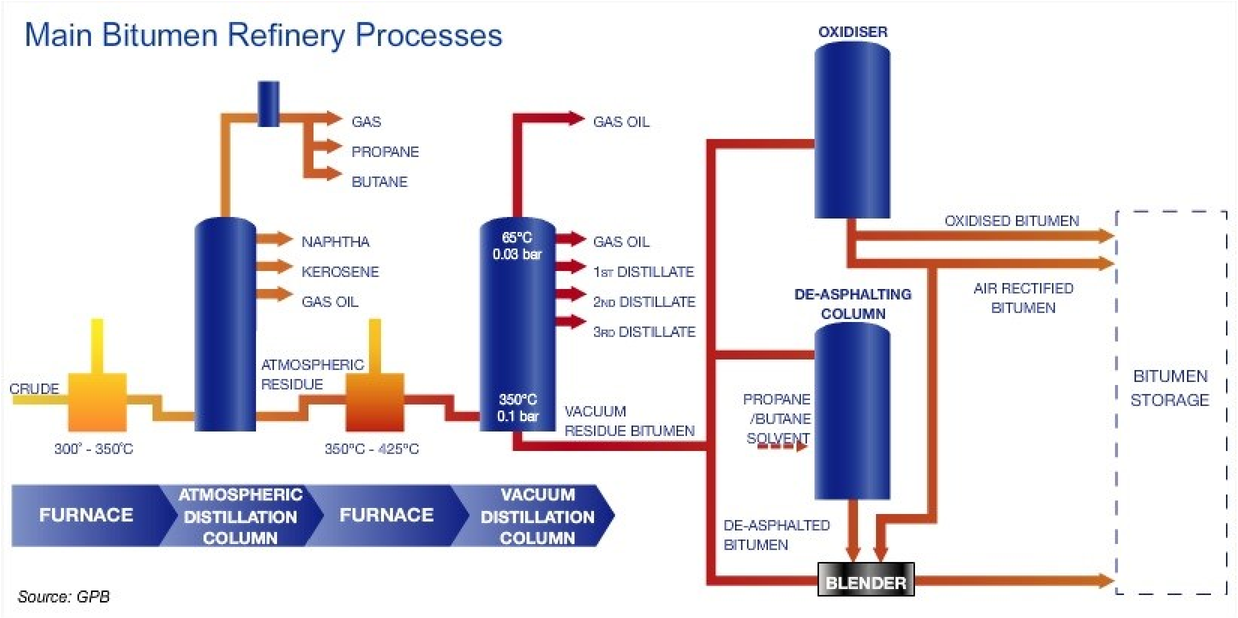


Figure 3-1: Typical bitumen production scheme [10]

3.1.1 *Chemical components of bitumen*

The chemical bitumen components are normally comparable, but some variation can be observable depending on the properties of original crude oil and on the production processes adopted. Bitumen can generally be described as complex mixtures of hydrocarbons containing many different chemical compounds of relatively high molecular weight. There is considerable uncertainty as to the molecular weight distribution of bitumen. The smallest size, approximately 300 Dalton, is determined by the distillation ‘cut point’ during the manufacture of the bitumen. The largest size has not been finally concluded; earlier research suggested that molecular weights up to 10000 Dalton are present, while some research indicates that there are probably very few if any, molecules larger than 1500 in bitumen. The molecules present in bitumen are combinations of alkanes, cycloalkanes, aromatics, and hetero molecules containing sulphur, oxygen, nitrogen, and metals. The bitumen components are classified into four classes of compounds:

- **Saturates,** saturated hydrocarbons, the % saturates correlates with a softening point of the material;

- **Naphthenic aromatics**, consisting of partially hydrogenated polycyclic aromatic compounds;
- **Polar aromatics**, consisting of high molecular weight phenols and carboxylic acids;
- **Asphaltenes**, consisting of high molecular weight phenols and heterocyclic compounds;

The naphthenic aromatics and polar aromatics are typically the majority components. Additionally, most natural bitumen contains organosulfur compounds, resulting in an overall sulphur content of up to 4%. Nickel and vanadium are found in the < 10 ppm level, as is typical of some petroleum. The substance is soluble in carbon disulphide. It is commonly modelled as a colloid, with asphaltenes as the dispersed phase and maltenes as the continuous phase. and it is almost impossible to separate and identify all the different molecules of asphalt because the number of molecules with different chemical structure is extremely large.

Bitumen functionality relates to how molecules interact with each other and/or with other materials, e.g. aggregate surfaces and water. The content of sulphur, nitrogen, oxygen, and metals in some molecules makes them slightly polar. The significance of molecules containing heteroatoms in bitumen chemistry is the ability to form molecular associations, which strongly influence the physical properties and performance of bitumen.

The components containing the heteroatomic compounds can vary in content and characteristics in bitumen obtained from different crude sources.

Table 3.1: Elemental analysis of bitumen from various sources [10]

Element	Unit	Range
Carbon	%w	80.2-84.3
Hydrogen	%w	9.8-10.8
Nitrogen	%w	0.2-1.2
Sulphur	%w	0.9-6.6
Oxygen	%w	0.4-1.0
Nichel	ppm	10-139
Vanadium	ppm	7-1590
Iron	ppm	5-147
Manganese	ppm	0.1-3.7
Calcium	ppm	1-335
Magnesium	ppm	1-134
Sodium	ppm	6-159

The sulphur content may be 1-7% by mass in bitumen and can consist of many different sulphur compounds such as thiophenes and sulphides Although nitrogen compounds are not as common, pyrrole, indole and carbazole groups are found in some bitumen. Oxygen is mainly present in functional groups as carboxylic acids and esters. The metals appear mainly in porphyrin-like structures. Bitumen is a viscoelastic material; therefore, chemical polarity is an important property to measure. The most polar components create structural components which give bitumen stiffness (modulus) properties. Whereas the least polar components give asphalt its flexibility and low-temperature properties, the intermediate polarity components in bitumen compatibilized the least and most polar components. Since bitumen contains a continuous range of molecules it is impractical to analyse each individual compound. Common practice is, therefore, to divide bitumen into four broad, increasingly polar fractions (Figure 3-2): saturates, aromatics, resins, and asphaltenes (SARA). The asphaltenes are usually separated using solvent precipitation while the three other fractions are defined by using chromatography. There are several standard methods available for separation of bitumen into these four fractions and the naming of the fractions, which is not descriptive of the chemical composition, which may vary.

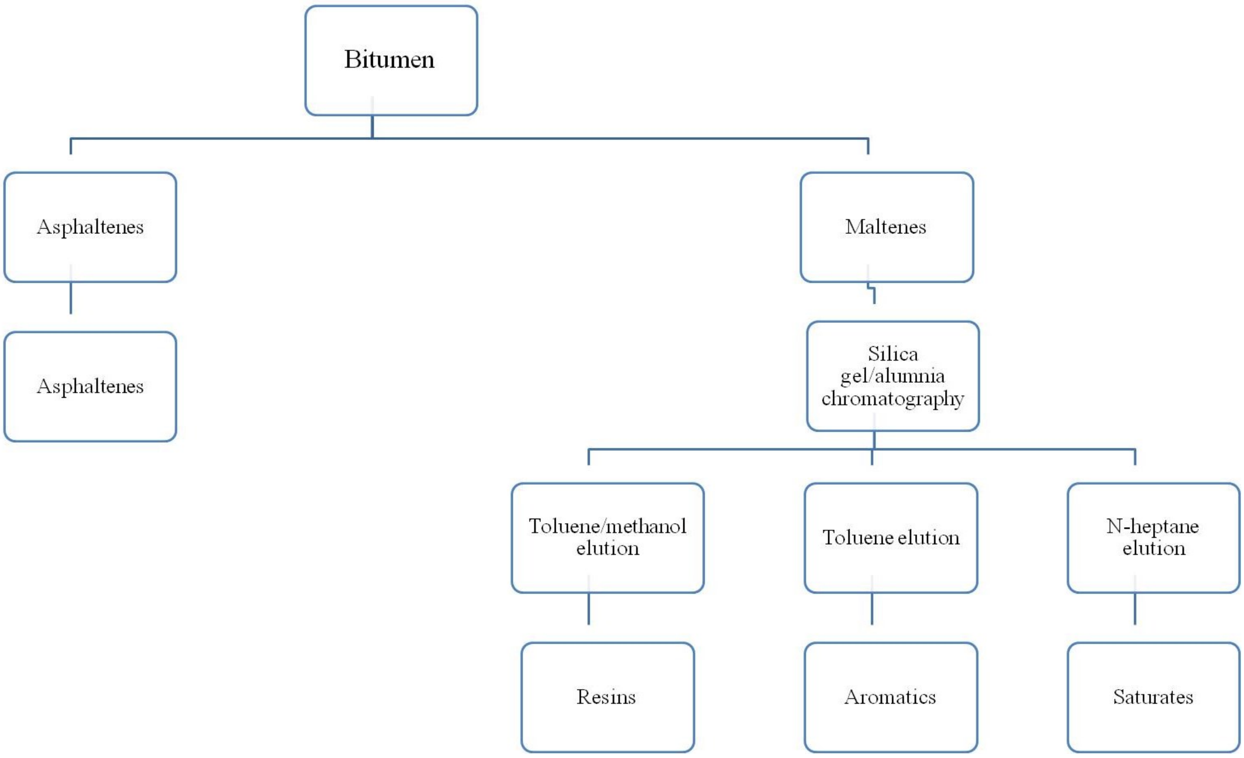


Figure 3-2: Schematic for the separation of chemical constituent in bitumen

Other important chemical bitumen constituent that are noteworthy are the Polycyclic Aromatic Hydrocarbons (PAH). PAH is a subset of a broader group of polycyclic aromatic compounds (PACs) which may also contain other atoms, such as sulphur, oxygen, and nitrogen. Crude oils contain low levels of polycyclic aromatic hydrocarbons, which partly end up in bitumen at ppm levels. The maximum temperatures involved in the production of bitumen, <385°C (725°F), are not high enough to initiate significant PAH formation, which requires pyrolysis or combustion and typically takes place at temperatures above 500°C (930°F).The principal refinery process used for the manufacture of bitumen, vacuum distillation, removes the majority of PAHs. Also, as noted above, oxidation has also been shown to reduce overall concentrations of PAHs in bitumen. When bitumen is further processed such as in air rectification and oxidation the SARA analysis shows a shifting of Resins being converted to Asphaltenes and Aromatics being converted to Resins. Overall the bitumen becomes stiffer and more elastic compared to the starting bitumen. During oxidation, the primary oxidative process is carbon-carbon bond formation via oxidative condensation. Asphaltene content is increased, while the content of naphthenic and polar aromatics is decreased As the asphaltene concentration increases beyond a certain point, the ambient temperature flow properties of the modified bitumen product change from visco-elastic to nearly pure elastic behavior at ambient temperature. Oxygen that is added to the bitumen in the air-blowing appears to reside in the hydroxyl, peroxide, and carbonyl functional groups (ketones, acids, acid anhydrides, and esters) Small amounts of volatile components of the bitumen are also removed during the oxidation process. As a result of these reactions, the polycyclic aromatic hydrocarbon (PAH) content of the bitumen is reduced.

The 85 % of bitumen production (on the average about 90 mln. tons of bitumen per year) is used as a binder in road construction. However oxidized and residual bitumen does not have the necessary properties to meet modern requirements to the pavement. The most common way to increase the performance properties of oil bitumen (primarily, oxidized bitumen) is the use of various polymers as modifiers.

3.2 *Modified Bitumen*

Polymer modified bitumen compared to conventional bitumen has several significant advantages. They are more elastic, flexible, and durable, less sensitive to the temperature changes and aging, have better adhesive and cohesive properties.

Bitumen modified in this manner is known as polymer-modified bitumen (PMB), and the modification process is known as the “wet process.” This process requires two different plants: one to mix the neat bitumen with modifiers (i.e., the PMB plant) and another one to mix the modified bitumen with the aggregates (i.e., the asphalt plant) to manufacture the final asphalt mixture. The PMB is transported from the PMB plant to the asphalt plant using trucks equipped with blenders to maintain the temperature ranging between 160°C - 180 °C; then, the PMB is transferred into dedicated storage tanks equipped with a mixer to maintain similar temperatures. This condition is maintained until the PMB has been added to the aggregates at the asphalt plant to produce the final asphalt concrete mixture, which is then transported to the road construction site.

The physical properties of a specific polymer are determined by the sequence and chemical structure of the monomers from which it is made. The addition of polymers to asphalt has been shown to improve the performance of binder; when polymers are added to asphalt, the properties of the modified asphalt concrete depend on various things as: polymer characteristics, bitumen characteristics, mixing condition and compatibility of polymer with bitumen. Generally, pavement with polymer modification exhibits greater resistance to rutting and thermal cracking, and decreased fatigue damage, stripping and temperature susceptibility [11][12]. The main reasons to modify asphalts with polymers could be summarized as follows:

- To obtain softer blends at low service temperatures and reduce cracking;
- To reach stiffer blends at high temperatures and reduce rutting;
- To reduce viscosity at layout temperatures;
- To increase the stability and the strength of mixtures:
- To improve the abrasion resistance of blends;
- To improve fatigue resistance of blends;
- To improve oxidation and aging resistance;
- To reduce structural thickness of pavements;
- To reduce life costs of pavements.

The rheological behaviour of asphalt-polymer blends is of great interest because it is closely related to the performance of pavements. Furthermore, the addition of small amounts of polymer dramatically changes the rheological properties of the asphalt. The addition of polymer introduces an additional difficulty to the asphalt complexity, because of its high molecular weight. The formation of a homogeneous system is not easy and incompatibility problems arise.

The used of synthetic polymers to modify bitumen started after World War II ended. Over the years, researchers developed various polymer modifiers. Today, widely used polymers for bitumen modification can be classified into two categories: plastomers and thermoplastic elastomers [13]

- Plastomers have little or no elastic component, usually resulting in their quick early strength under load and the following permanent deformation or brittle failure;
- Thermoplastic elastomers soften on heating, harden on cooling and are able to resist permanent deformation by stretching under load and elastically recovering once the load is removed, which leads to their greater success than plastomers as bitumen modifiers.

The graph in Figure 3-3 shows some typical stress-deformation curves for different types of polymers.

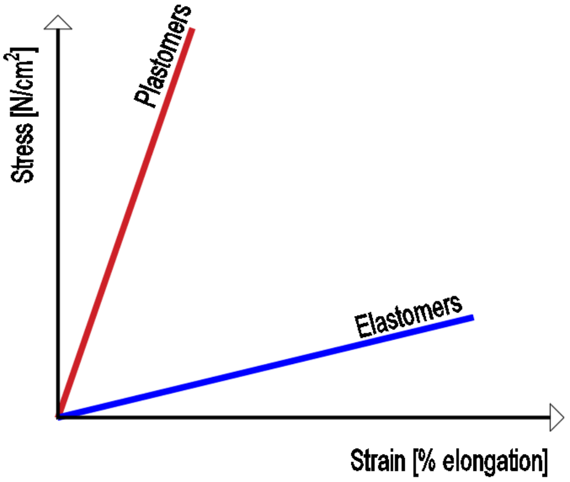


Figure 3-3: Stress-deformation curves for different types of polymers

Some popular polymers for bitumen modification are listed in **Table 3.2** with their advantages and disadvantages. Among them, SBS attracted the most attention due to its relatively good dispersibility (or appropriate solubility) in bitumen as well as the relatively excellent properties and acceptable cost of SBS modified bitumen. Of course, besides these listed polymers, some others like styrene-butadiene rubber (SBR, random copolymers), styrene-butadiene diblock copolymers (SB) and ethylene-propylene-diene monomer rubber (EPDM) were also popular for bitumen modification. . In addition, some small molecule organic materials, such as PPA and paraffin wax, were also widely used as modifiers for bitumen.

Before reviewing the most popular polymer modifiers, it is worth to note that even for a given polymer modifier, selection of base bitumen still has some important effects on the resulting PMB, as each bitumen has its own specific chemical composition and structure. Additionally, base bitumen usually composes over 90% of the PMB by weight, which could introduce overriding influences on the final properties of the PMB. Good-quality base bitumen helps to enhance the effects of polymer modification, while poor-quality one may make the modification futile. Regarding the compatibility between polymer and bitumen, selection of base bitumen is usually completed by laboratory experiments. However, some theoretical trends were also highlighted based on the SARA (saturates, aromatics, resins and asphaltenes) fractions of bitumen.

Table 3.2: *Popular polymers for bitumen modification*

Categories	Examples	Advantages	Disadvantages
Plastomers	Polyethylene (PE)	Good high-temperature properties	Limited improvement in elasticity
	Polypropylene (PP)	Relatively low cost	Phase separation problems
	Ethylene-vinyl acetate (EVA)	Relatively good storage stability	Limited improvement in elastic recovery
	Ethylene-butyl acrylate (EBA)	High resistance to rutting	Limited enhancement in low-temperature properties
Thermoplastic elastomers	Styrene-Butadiene-Styrene (SBS)	Increased stiffness	Compatibility problems in some bitumen
	Styrene-Isoprene-Styrene (SIS)	Reduced temperature sensitivity	Low resistance to heat, oxidation and ultraviolet
		Improvement elastic response	Relatively high cost
	Styrene-ethylene/butylene styrene (SEBS)	High resistance to heat, oxidation and ultraviolet	Storage instability problems
			Relatively reduced elasticity
			High cost

3.2.1 Plastomers

These polymer additives improve strength and deformation characteristics of bitumen and asphalt:ì. Generally, they are used to increase the resistance to rutting phenomena, to reduce the risk of cracking at low temperatures and fatigue cracking of asphalt under prolonged stress. Polymers which are quite often used now: polyvinyl acetate, polystyrene, polyisobutylene, polyethylene, polypropylene, atactic polypropylene, polypropylene, polyvinyl chloride, Viskoplast-S, EVA, ethylene methyl acrylate.

As an important category of plastomers, polyolefin is one of the earliest used modifiers for bitumen. Various polyolefin materials, including high-density polyethylene (HDPE), low density polyethylene (LDPE), linear low-density polyethylene (LLDPE), IPP and APP, have been studied for application in bitumen modification due to the relatively low cost and the benefits they might bring. After polyolefin materials are added into bitumen, they are usually swollen by the light components of bitumen and a biphasic structure is formed with a polyolefin phase (dispersed phase) in the bitumen matrix (continuous phase). As the polyolefin concentration increases, phase inversion occurs in the modified bitumen. Two interlocked continuous phases are ideal for polyolefin modified bitumen, which could improve the properties of bitumen to some extent. Those used materials were usually found to result in high stiffness and good rutting resistance of modified bitumen, although they are quite different in chemical structure and properties. However, those used polyolefin materials failed to significantly improve the elasticity of bitumen. In addition to this, the regular long chains of those polyolefin materials give them the high tendency to pack closely and crystallize, which could lead to a lack of interaction between bitumen and polyolefin and result in the instability of the modified bitumen. Furthermore, some researchers claimed that the compatibility of polyolefin with bitumen is very poor because of the non-polar nature of those used materials. As a result, the limited improvement in elasticity and potential storage stability problems of polyolefin modified bitumen restrict the application of polyolefin materials as a bitumen modifier, whereas they are popular in production of impermeable membranes [15].

More used plastomers in bitumen modification are ethylene copolymers, such as EVA and EBA: EVA copolymers are composed of ethylene-vinyl acetate random chains. Compared with PE, the presence of polar acetate groups as short branches in EVA disrupts the closely packed crystalline microstructure of the ethylene-rich segments, reduces the degree of crystallization and increases the polarity of the polymer, which were both believed to be beneficial to improving the storage stability of modified bitumen by some researchers. However, the properties of EVA copolymers are closely related to the vinyl acetate content. When the vinyl acetate content is low, the degree of crystallization is high, so the properties of EVA are quite similar to those of LDPE. As the vinyl acetate content increases, EVA tends to present a biphasic microstructure with a stiff PE-like crystalline phase and a rubbery vinyl acetate-rich amorphous phase. The higher the vinyl acetate content, the higher the proportion of amorphous phase. But the degree of crystallization should be controlled carefully when EVA is used as a bitumen modifier, because neither too low (getting easy to be disrupted) nor too high (causing the lack of interactions with bitumen) degree of crystallization is good for bitumen modification. After EVA copolymers are added into bitumen, the light components of bitumen usually swell the copolymers. At low EVA concentrations, a dispersed EVA-rich phase can be observed within a continuous bitumen-rich phase. As the EVA concentration increases, phase inversion occurs in modified bitumen and the EVA-rich phase becomes a continuous phase. If two interlocked continuous phases form in the modified bitumen, the properties of bitumen could be improved to a large extent. EVA was found to form a tough and rigid network in modified bitumen to resist deformation, which means that EVA modified bitumen has an improved resistance to rutting at high temperatures. Although some properties of bitumen are enhanced by EVA modification, there are still some problems limiting its application. One large limitation is the fact that EVA cannot much improve the elastic recovery of bitumen due to the plastomers nature of EVA. Furthermore, the glass transition temperature (Tg) of EVA copolymers, which strongly depends on the vinyl acetate content, is not low enough to significantly improve the low-temperature properties of bitumen. As a result, EVA's ability to improve the low-temperature properties of bitumen is rather limited, especially at high EVA concentrations. Additionally, the melting temperature of ethylene-rich segments in EVA copolymers is much lower than the usual preparing temperature of modified bitumen. Those rigid crystalline domains could be partially broken by the applied shear forces during the preparation.

3.2.2 Elastomers

This type of modifiers includes polymers, rubbers and rubber polymers [15]. For the bitumen polymer composition rubber imparts a new property – flexibility, which is typical of natural rubber in a wide temperature range. The new rheological state provides composition deformation at low temperatures, despite the lack of plastic properties of bitumen. In other words, this additive in bitumen improves its extensibility and elasticity at low temperatures, improves thermal and crack resistance, strength, deformation resistance, water resistance, frost resistance, durability, resistance to aging. Rubber can be introduced into bitumen by direct fusion, or in the presence of a solvent [16].

The main disadvantage of elastomers is their poor dispersion in bitumen, so special measures are needed to obtain homogeneous modified bitumen (fusing, special solvents, etc.). Moreover, phase separation between polymer and bitumen in a liquid phase takes place, especially during storage. To avoid this phenomenon complicated devices that can support high temperatures and PMB continuous mixing are needed.

Rubber crumb is a promising product to be used for the modification. The main advantages are low cost and possibility of tires and other waste rubber products recycling. Despite the obvious advantages over other modifiers, using crumb rubber in road building is also limited because of the technological difficulties that arise when they are mixed with bitumen.

Thermoplastic elastomers are usually more effective than plastomers for bitumen modification. There are three types of styrene block copolymers: styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), styrene-ethylene / butylene-styrene (SEBS). The content of polymers in PMB can reach 3–10 wt %. Thermoplastic elastomers (TE), compared to thermoplastics, are characterized by higher elasticity [15]

3.2.3 Styrene – Butadiene - Styrene (SBS)

Styrene‑butadiene‑styrene (SBS) is a block copolymer that increases the elasticity of asphalt. It is probably the most appropriate polymer for asphalt modification, although the addition of SBS type block copolymers has economic limits and can show serious technical limitations. Although low temperature flexibility is increased, some authors claim that a decrease in strength and resistance to penetration is observed at higher temperatures. Styrene block copolymers of SBS type are mostly used for bitumen modification due to their ability to increase the strength of bitumen, and to provide polymer-bitumen compositions with elasticity, including that at low temperatures. Thermoplastic elastomer of SBS type is a linear polymer, which provides elasticity (ability to initial distortion) for bitumen-polymer system due to its structure (styrene units are linked by butadiene "flexible" blocks). Block copolymers of butadiene and styrene of SBS type are well combine with bitumen because polystyrene and polybutadiene are swelled in paraffin-naphthenic and aromatic hydrocarbons of bitumen and partially dissolved in them at 423 K. To improve polymer dissolution in bitumen the plasticizers are used (usually a mixture of aromatic based hydrocarbons). Plasticizer significantly improves the polymer solubility in bitumen, but slightly decreases the adhesive properties of the resulting binder compared to the original bitumen [16]

4 Literature review

In the last 40 years, more solutions have been sought progressively, and various types of polymers such as polyethylene (PE), ethylene vinyl acetate (EVA), ethylene butyl acrylate (EBA), and thermoplastic elastomers such as styrene–butadiene–styrene (SBS) and styrene–ethylene–butylene–styrene (SEBS) have been adopted as modifiers to enhance the physical and rheological properties of bitumen [17][18][19][20][21].

4.1 *The PMB modified asphalt mixtures (wet process)*

Ahmed et al. [22]compared the properties of asphalt mixtures made with three different types of binders: two neat bitumens (60/70 and 80/100) and a PMB (60/70 neat bitumen mixed with 1.3% Elvaloy® polymer by the total weight of the bitumen). The OBC was 4.55% for all three mixtures. The results showed that the asphalt mixture with PMB had the highest indirect tensile strength (10.97 MPa vs 9.32 MPa of HMA with 60/70 neat bitumen and 6.60 MPa of HMA with 80/100 neat bitumen) and the highest resilient modulus (4,645 MPa vs 3,142 MPa of HMA with 60/70 neat bitumen and 1,405 MPa of HMA with 80/100 neat bitumen).

Khodaii and Mehrara [23] compared the permanent deformation resistance of two dense asphalt mixtures made up using two types of bitumen: 60/70 neat bitumen and PMB with 5% of SBS by total weight of the neat bitumen. The OBC of the unmodified mixture was determined using the Marshall method and was found to be 5.2%. The same bitumen content was adopted for the PMB solution. Dynamic creep test showed that, at a 200-kPa stress level, the unmodified mixture exhibited the highest permanent deformation at both 50 °C (30,000 μs at 6,000 load cycles vs 5,000 μs at 10,000 load cycles) and 40 °C (10,000 μs at 10,000 load cycles vs almost 3,000 μs at 6,000 load cycles).

Gorkem and Sengoz [24] investigated the properties of asphalt mixtures whose binder was modified on the one hand with 2%, 3%, 4%, and 5% of SBS (by total weight of neat bitumen) and on the other, with 3%, 4%, 5%, 6%, and 7% of EVA (by total weight of neat bitumen) . The OBC of the asphalt mixture with neat bitumen was determined by the Marshall method to be 4.73% (by the total weight of aggregate); while it was found to be equal to 4.82% (by the total weight of aggregate) for both PMB asphalt mixtures. The ITS was 1,118.16 kPa for the mixture without polymer and it was highest at a 5% SBS content (1,708.32 kPa) and a 7% EVA content (1,529.16 kPa) for the PMB mixtures. Similarly, the ITSR values were higher for the SBS and EVA mixtures, with the greatest values obtained in correspondence of 6% modifier: 96.55% for SBS mixture and 95.62% for EVA mixture versus 86.02% for unmodified mixture.

Becker et al. [12] draw attention to the difficulties into producing homogeneous modified asphalt mixtures because, to be effective, a polymer must be blended with the bitumen and increase its rutting resistance at high temperatures without rendering it too viscous for the mixing procedure or too brittle at low temperatures [25]. However, ensuring this compatibility is a very difficult task because the constituents of PMB are highly dissimilar in terms of molecular properties (i.e., structure and weight), viscosity, and density [26]. Additionally, the components of bitumen can differ depending on the production process as well as the quality of the original crude oil. The type of polymer that can be used is strongly related to the bitumen components, which act as solvents or swelling agents for the modifier [27]. Other factors that affect the performance of PMB include the nature of the polymer [28][29], its physical form (powder, crumbs, pellets) and the type of mixing equipment (high-shear and low-shear mixing) used [13][30].

The difficulties to obtain a stable PMB are confirmed by Zani et al [31] who have studied five PMBs in terms of physical (softening point, penetration grade, elastic recovery, viscosity), chemical (SARA analysis) and rheological properties (frequency sweep test) making an advanced storage stability analysis using DSR frequency sweep tests on bottom and top samples of cigar tuben samples stored for 3, 5 and 7 days (180 °C), respectively. Authors proved that the chemical incompatibility between the neat binder and polymer could cause instability during storage; in detail it has been demonstrated that only three of the five binders tested were able to bear storage periods longer than three days without losing their initial rheological properties, while all binders showed reduced rheological properties between three and five days of storage.

Moreover, the modified polymer must be cost effective, so the polymer content has been reduced to 2 or 3%. Sometimes waste materials (due to their low cost they might be added in higher proportions), or mixes of two different polymers (as mentioned before) are being used [13][14]. On this way, Zhu et al. [15] shows as for PMB, the cost is quite relevant in dependence of the dosage of the added polymer that can be estimated around 3.5% by weight in the final product for a typical SBS polymer.

4.2 *The PMA modified asphalt mixtures (dry process)*

In recent years, another material—polymer-modified asphalt (PMA)—has been investigated by researchers. The procedure adopted to introduce fibers and polymers into the asphalt mixture is defined as the “dry process.” The concept of PMA is considerably different from that of the PMB because the former does not require any modification of the bitumen properties to improve the mechanical properties of the asphalt mixture; rather, PMA is produced by directly introducing fibers and polymers into the asphalt mixture during the mixing process at the asphalt plant [32]. The dry process is simpler because it requires only one plant (asphalt plant) to mix neat bitumen with aggregates and polymer compounds, without the need to maintain a high temperature for the bitumen. Thus, this technique can allow for improving the performance of HMA [33] without the risk of the bitumen/polymers splitting while ensuring a lower environmental impact owing to the absence of one plant in this case. This technique has been widely used to recycle materials such as tire rubber and plastic wastes as partial substitutes as aggregates for bitumen, which has led to obtaining encouraging results [34][35][36][37].

Movilla-Quesada et al.[38] investigated the effects of adding coarse (5–10 mm) and fine (0.25–2 mm) particles of crushed scraps of plastics, such as polyethylene terephthalate (PET), high-density polyethylene (HDPE), and polyvinyl chloride (PVC), to AC16S asphalt mixtures designed with 4.7% OBC by the total weight of the mixture. Four solutions were prepared using 10% and 20% (by the total weight of the mixtures) both of coarse and fine plastic particles in the mixtures. The results showed that increasing the percentage of plastic scrap the air void content and voids in the mineral aggregate (VMA) increase but decreased the bulk specific gravity and voids filled with asphalt (VFA), because the plastic scrap partially surrounded the aggregates in the mix. The Marshall stability of the reference solution was 13 kN, while that for the mix with 20% plastic fine particles was 15 kN, and that for the mix with 10% plastic coarse particles was 16 kN. At 60 °C, the rut depth was 3.301 mm for the reference mixture but 1.410 mm and 0.712 mm for the mixes with 10% and 20% fine plastic scrap, respectively, and 1.534 mm and 0.704 mm for the mixes with 10% and 20% coarse scrap plastic, respectively.

Tahami et al. [39] evaluated the properties of mixes with 1.4%, 2.8%, and 4.2% by the total weight of the mixture of crumb rubber powder (CRP) as filler (corresponding to 20%, 40%, and 60% substitutions of mineral filler with CRP). The OBC of an HMA reference mixture (5.5% by the total weight of the mixture) was determined by the Marshall procedure, and the same bitumen content was used for all three mixtures made with CRP. The results showed that the HMA mixture with 20% CRP, which was initially subjected to a 2-h curing time, exhibited the highest stiffness modulus (7,301 MPa at 5 °C), and its stiffness modulus (3,778 MPa) at 25 °C was higher than that for the reference mixture (2,694 MPa) under the same conditions. The ITS increased when the CRP mixtures were subjected to an initial curing process; for example, for the 20% CRP mixture, the ITS improved from 756 kPa (in the absence of curing) to 810 kPa and 840 kPa after 1 and 2 h of curing time, respectively.

4.3 *The use of graphene in asphalt mixtures*

Besides polymers, Nanotechnology showed promising achievements in bitumen and asphalt modification in recent years [40]. Basically, Nano rubber, Nano silica, different kinds of Nano clays, and Nano graphene are most of Nano materials, investigated and designed in the asphalt industry. It has been shown that using Nano clay as the second modifier in SBS polymer modified asphalts can improve the storage stability and the aging resistance of polymer-modified asphalts [41]. Different types of Nano carbons, including Carbon Nano Tube (CNT), Graphene Oxide (GO) and Graphite Nano Platelets (GNPs) are other technologies, have shown advantages in asphalt modification. Among these Nanomaterials probably Nano graphene with outstanding cold temperature mechanical properties [42]. Recent studies have shown that a moderate addition of GNP to bitumen can lead to about 130% increase to the flexural properties. In addition, compared to CNTs, in which a homogeneous dispersion of it into the modified material is considered a big challenge [43][44] it is much easier to disperse the GNPs into asphalt binders. Due to its relatively low aspect ratio, no potential clustering was observed during the mixing [44]. Researchers at the University of Minnesota also found that that the addition of graphene Nanoplatelets significantly reduces the compaction effort required to prepare asphalt mixtures [44]. However, the lake of knowledge regarding the Nanomaterial cost considerations, lack of technology in the application of materials in such geometries, and compatibility with other polymers and additives are some of the obstacles in the use of Nanomaterials in the asphalt industry.

4.4 *Literature gap*

From literature review analysis it is possible to find how:

a) Owing to the aforementioned advantages, PMB is widely used to enhance the mechanical properties of the asphalt concrete mixtures. However, PMB has certain significant drawbacks as well, e.g., a) complex operating procedures need to be performed in order to ensure an affinity between the bitumen and polymer, b) PMB becomes highly viscous during the mixing phase (the mixing temperature is usually around 170–180 °C), and c) PMB is expensive and not environment-friendly [45].

b) Referring to the dry modification process, a standard laboratory equivalent is yet to be established for the modification of asphalt mixtures with the dry process. Moreover, in several cases, the mixture cannot be produced at a laboratory scale, because the short mixing times involved, and the low quantity of materials added can affect the final performance of the mixture. For instance, Sarang et al. [46] observed that a stone matrix asphalt (SMA) mixture produced in a laboratory with 16% plastic waste (mainly polyethylene) with respect to the total weight of 50/70 neat bitumen (with optimum bitumen content (OBC) 5.88% of the total weight of aggregate) failed to achieve the Marshall stability of an SMA mixture prepared using PMB (with OBC = 5.90% of the total weight of aggregate); specifically, the Marshall stability of the PMB-based mixture was 19% greater than that of the PMA-based mixture (19.63 kN for the PMB mixture vs 16.41 kN for the PMA mixture).

c) more studies were conducted introducing the plastics waste materials as aggregates or binder substitutes and as asphalt mixtures modifiers [47][48]. These research studies have demonstrated that waste plastic can act as a partial aggregate replacement in bituminous mixes, and a binder extender without having any significant influence on the properties of the asphalt mix. However, it should be noted that not all the plastics are applicable in asphalt modifications.

d) No research studies have been conducted both using graphene nano platelets and recycled plastics as asphalt modifier to improve the mechanical related properties of road asphalt mixtures.

5 Experimental investigation

To fill the literature gaps previously described, in the research here presented four hot asphalt mixtures for binder layer were designed and compared between them in terms of mechanical and environmental performance. In detail, three mixtures were designed, in turn, through cold-addition of a plastomeric polymer compound (PC) and a graphene-enhanced recycled plastic compound (GRPC) to a traditional HMA with a neat bitumen 50/70 penetration grade. For comparison, an HMA made up with PMB 10/40-70 was adopted as the control mixture, parallel to a traditional one containing a neat bitumen 50/70 penetration grade.

The same Optimum Bitumen Content (OBC) was adopted for all investigated mixtures; however, an innovative mixing processes and compaction efforts were designed for HMA_{PMB}, HMA_{PC} and HMA_{GRPC} to achieve the same volumetric properties as those of the reference mixture in terms of the air void content (V_a), voids in the mineral aggregate (VMA), and voids filled with asphalt (VFA). This innovative mixing procedure was designed to maximize the effect of polymeric compound addition for a laboratory-scale production.

The performance-related properties of the HMAs were investigated considering the main causes of damage, such as moisture damage, cracking, and rutting. In detail:

a) The indirect tensile strength ratio (ITSR) was determined in accordance with EN12697-12 to ascertain the moisture damage resistance of the investigated mixtures.
b) The cracking failure mechanism during dynamic loading was investigated through fatigue tests, specifically, indirect tensile tests, in accordance with EN 12697-24 – ANNEX E, to analyze the crack-initiation phase (Phase 1). Semi-circular bending (SCB) tests were conducted to determine the crack-propagation resistance of the

asphalt mixtures which represents the second part of the failure mechanism (Phase 2). Both tests were conducted at 10 °C.

c) The rutting resistance was investigated in terms of the behavior of the asphalt under a vertical compressive stress; accordingly, the stiffness of the designed bituminous mixtures was evaluated in terms of the indirect tensile stiffness modulus (ITSM) at 10, 20, and 40 °C, in accordance with EN 12697-26 – Annex C. Subsequently, the susceptibility of the designed materials to permanent deformations was ascertained through the wheel tracker tests conducted at 60 °C, as per EN 12697-22.

In addition, the retainment of the conventional properties was assured through the indirect tensile strength (ITS) tests conducted at 10 °C [49].

For each group of mechanical related properties investigated, at least one test was conducted with the indirect tensile load configuration at 10 °C since correlations among the different parameters were sought to find a common link between the causes of damage, mechanical performance tests, and test temperatures.

The third main phase of research program refers to the application of LCA methodology to the life cycle of the four designed solutions, involving all the unit processes associated with asphalt mixture production and road pavement construction operations up until the end of the service life of the pavement, expressing the effect of the environment through 18 midpoint impact category indicators of the ReCiPe impact assessment method [50].

In the last phase, a test track was built to evaluate the response of the innovative polymer compound introduced in a real scale application. To ascertain this Pre and post-production laboratory tests were conducted in addition to the periodical monitoring operations made on site.

Figure 5-1 shows a summary graph of the main phases conducted in the present research.

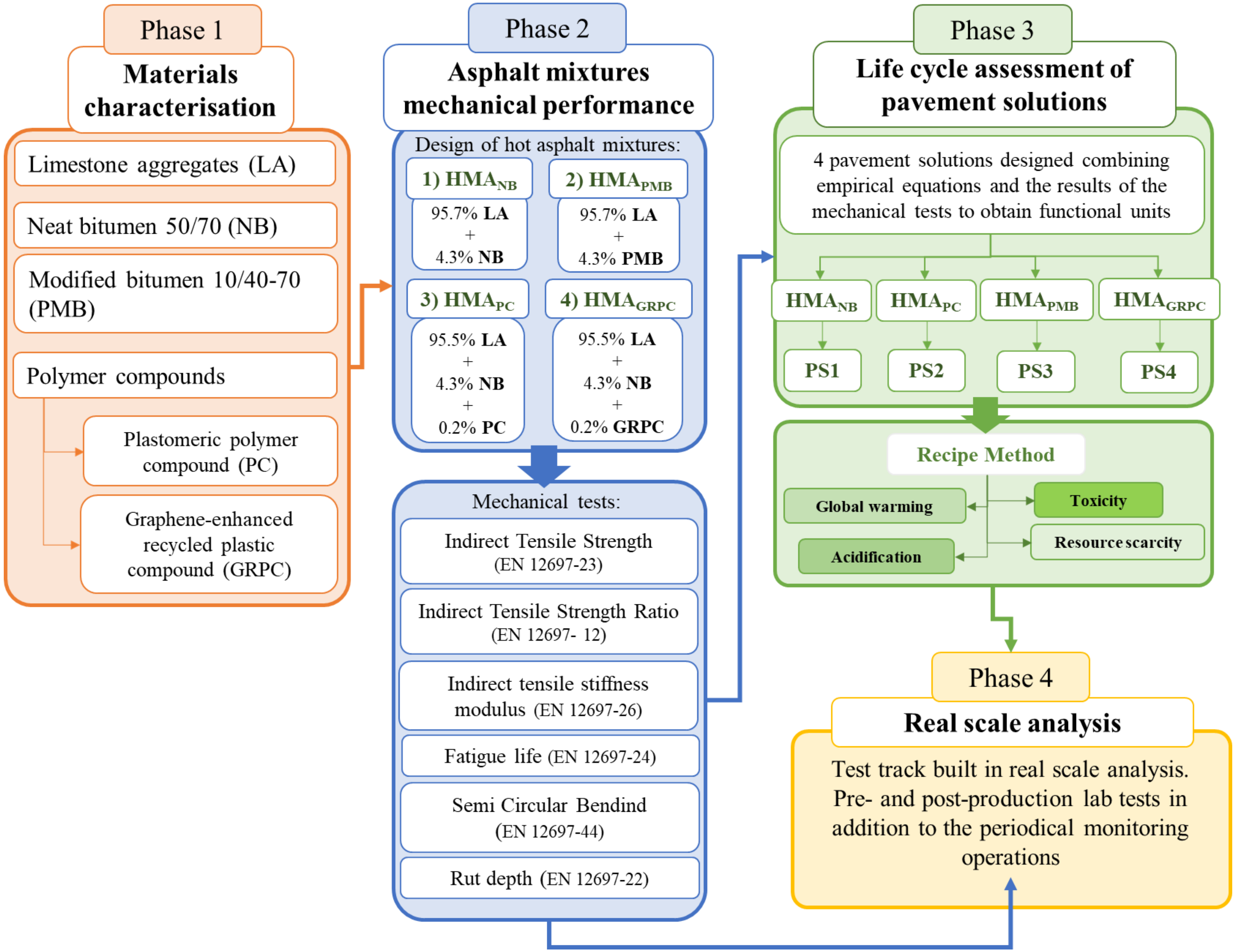


Figure 5-1 Overview of the research main steps

5.1 ***Materials characterization***

5.1.1 Limestone aggregates

A dense graded asphalt concrete with maximum aggregates' size of 20mm (AC20) for a binder course was designed with four different sizes of limestone aggregates provided by a local quarry in southern Italy (Figure 5-2). Two coarse (limestone 10/18 and limestone 6/12) and two fine aggregates, i.e., limestone sand (0.25–4 mm) and limestone filler (0.063 – 2 mm), respectively, were used to develop the grading curves of the asphalt mixtures.

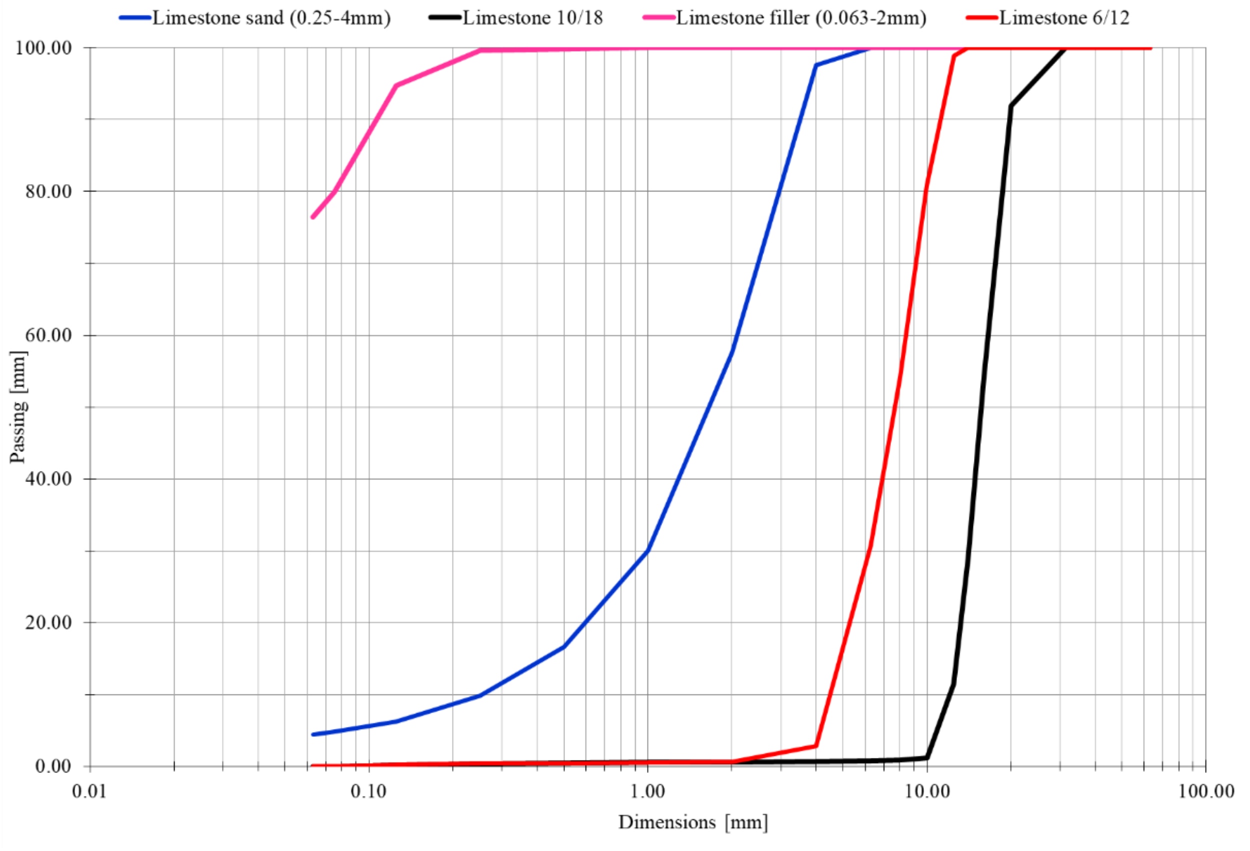


Figure 5-2 - Particle size distribution of limestone materials

On each particle size, the main physical and volumetric properties were investigated according to European Standard as shown in

Table 5.1 - Main properties of limestone aggregates

	Test					
Aggregate-particle size	**Los Angeles value,** % (EN1097-2)	**Shape index,** % (EN933-4)	**Flat index,** % (EN933-3)	**Sand equivalent,** % (EN933-8)	**Apparent specific gravity,** gr/cm^3 **[G$_{sa}$]** (EN1097-6)	**Bulk specific gravity,** gr/cm^3 **[G$_{sb}$]** (EN1097-3)
Limestone 10/18	20.6	4	8	-	2.694	2.686
Limestone 6/12	20.1	8	11	-	2.713	2.685
Limestone Sand (0.25–4 m)	-	-	-	95.3	2.718	2.689
Limestone Filler (0.063–2 mm)	-	-	-	-	2.737	2.737

5.1.2 Neat and PMB modified bitumen

Two types of binders were used: a 50/70 penetration-grade neat bitumen provided by a refinery in southern Italy and b) a commercially hard modified bitumen, PMB 10/40-70, obtained through the addition of 5% of SBS to a 70/100 penetration-grade neat bitumen. Assured the different type of bitumen adopted, the mixing and compaction temperatures for each one of them were selected after a preliminary analysis of their viscosity at four test temperatures (60 °C, 100 °C, 135 °C, and 150 °C), conducted in accordance with EN 13702. A Dynamic shear rheometer (Figure 5-3) was used, with a cone-plate geometric configuration with a 35-mm diameter and a 4° angle for measuring the viscosity.

a) *b)*

Figure 5-3 - Dynamic shear rheometer: a) geometric configuration; b) bitumen sample preparation

Based on the temperature (t) – viscosity (η) diagrams (see Figure 5-4), the best mixing and compaction temperatures for the neat bitumen were determined in light of the values η = 0.28 ± 0.03 Pa·s and η = 0.17 ± 0.02 Pa·s, respectively [1], while the mixing and compaction temperatures for the PMB were derived from the technical data sheets (see Table 5.2).

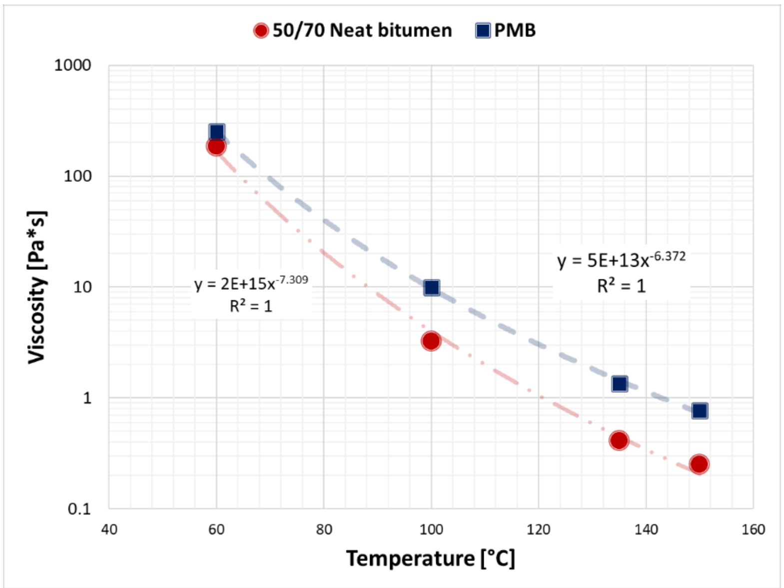


Figure 5-4 - Temperature vs viscosity diagram

The results in Figure 5-4 and Table 5.2 show that the PMB displays a higher viscosity than the neat bitumen at the test temperatures considered. Consequently, the asphalt mixture made with PMB required higher mixing temperatures and compaction temperatures than the traditional HMA.

Table 5.2 - Mixing and compaction temperatures

Test	Unit	Neat Bitumen 50/70	PMB
Viscosity at 60 °C	Pa·s	186	251
Viscosity at 100 °C	Pa·s	3.220	9.967
Viscosity at 135 °C	Pa·s	0.413	1.340
Viscosity at 150 °C	Pa·s	0.250	0.769
Mixing temperature	°C	156-161	170 – 185
Compaction temperature	°C	146-150	160 - 175

The complex shear modulus G* was determined by performing a frequency sweep (FS) test using a dynamic shear rheometer (DSR) at different test temperatures (0 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C) over a frequency range of 0.1 Hz to 10 Hz (EN 14770). A plate–plate DSR configuration with a 25-mm diameter and 1-mm gap was used for test temperatures greater than or equal to 30 °C, while an 8-mm diameter with a 2-mm gap was used for test temperatures less than 30 °C.

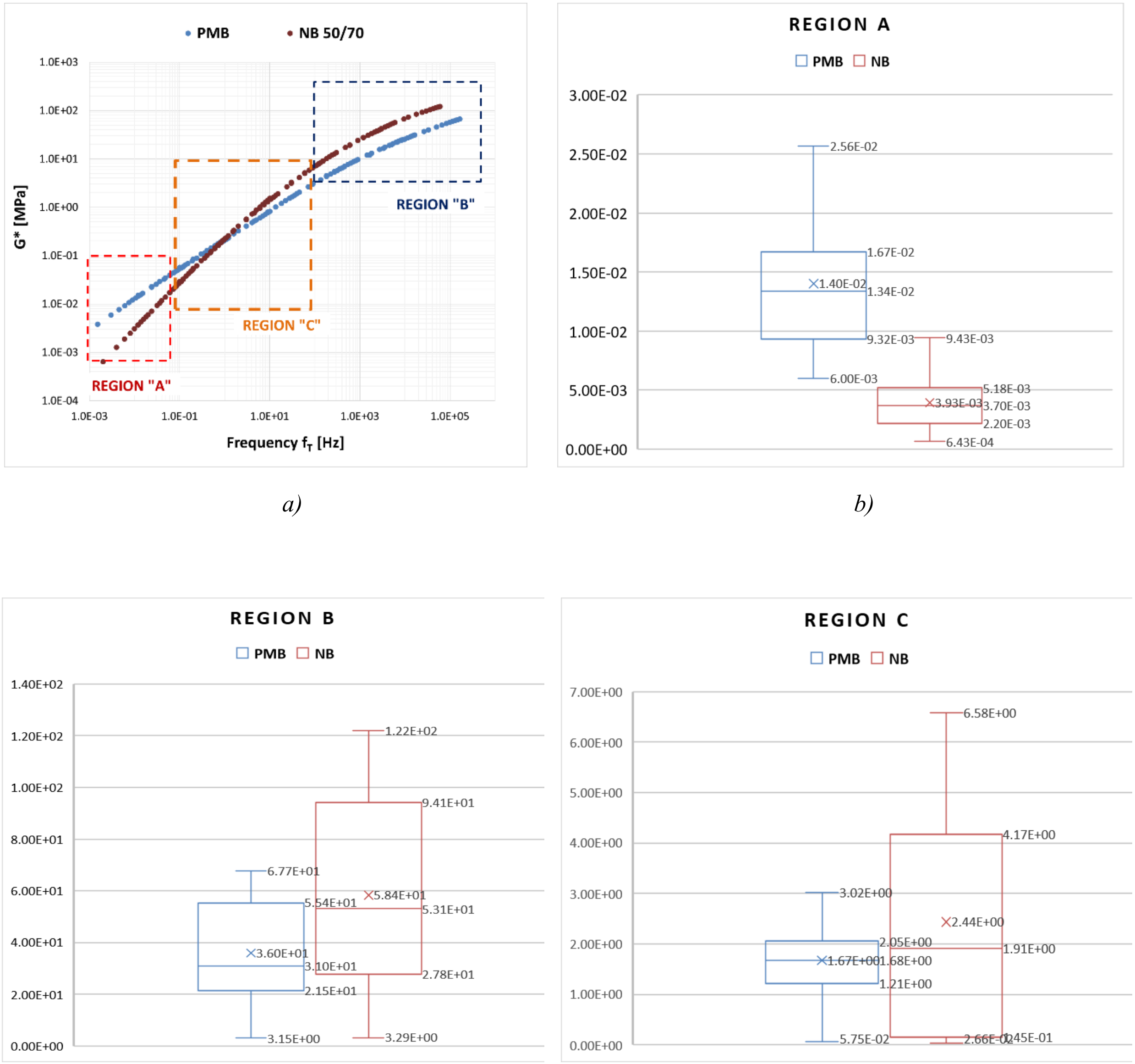
In compliance with UNI EN 14770, before the FS was conducted, the viscoelastic linear region (LVE) was established on the basis of the following three conditions: a) a strain sweep conducted using the 25-mm plate–plate geometry configuration at 50 °C and a 0.1-Hz frequency, b) a strain sweep conducted using the 8-mm plate–plate geometry configuration at 0 °C and a 10-Hz frequency, and c) verification that the difference between G′ (the storage modulus) and G″ (the loss modulus) did not differ by more than 5% from the initial value, to ensure that fell within the LVE region. For the purpose of effective comparison among all of the bituminous samples, the smallest shear strain sweep values, 0.1% for the 25-mm plate–plate configuration and 0.05% for the 8-mm plate–plate configuration, were selected and used for all specimens.

Master curves were plotted for both the neat bitumen and PMB, as shown in Figure 5-5a, assuming a reference temperature (T_0) of 30 °C and computing the shift factor using the William–Landel–Ferry equation.

Examining the G* curves, the following three main regions can be identified that make it possible to delineate some main performance features of the investigated binders: a) Region A, which contains data related to high test temperatures (40 °C and 50 °C) and low frequencies ($f_t < 0.1$ Hz); b) Region B, which contains data related to low test temperatures ($T \leq 10$ °C) and high frequencies ($f_t > 90$ Hz); and c) Region C, which contains data astride the borders of the two other regions (20 °C ≤ T ≤30 °C and $0.1 < f_t < 90$ Hz).

In Region A (see Figure 5-5b), the PMB is stiffer than the neat bitumen (mean G* of 1.40E-02 MPa for PMB vs 3.93E-03 MPa for NB). In Region B (see Figure 5-5c), at low test temperatures and high frequencies, the opposite is true (G* for NB is 62% higher on average than for PMB). Regions A and B return a homogeneous distribution of the points than corresponding mean values.

In the transition zone Region C, the point cloud reveals a nonuniform data trend of PMB and neat bitumen measurements, respectively, that becomes steady in the two border regions (see Figure 5-5d). In this region, the mean G* is almost the same for the PMB and the neat bitumen (1.68 MPa for PMB vs 1.91 MPa for NB).



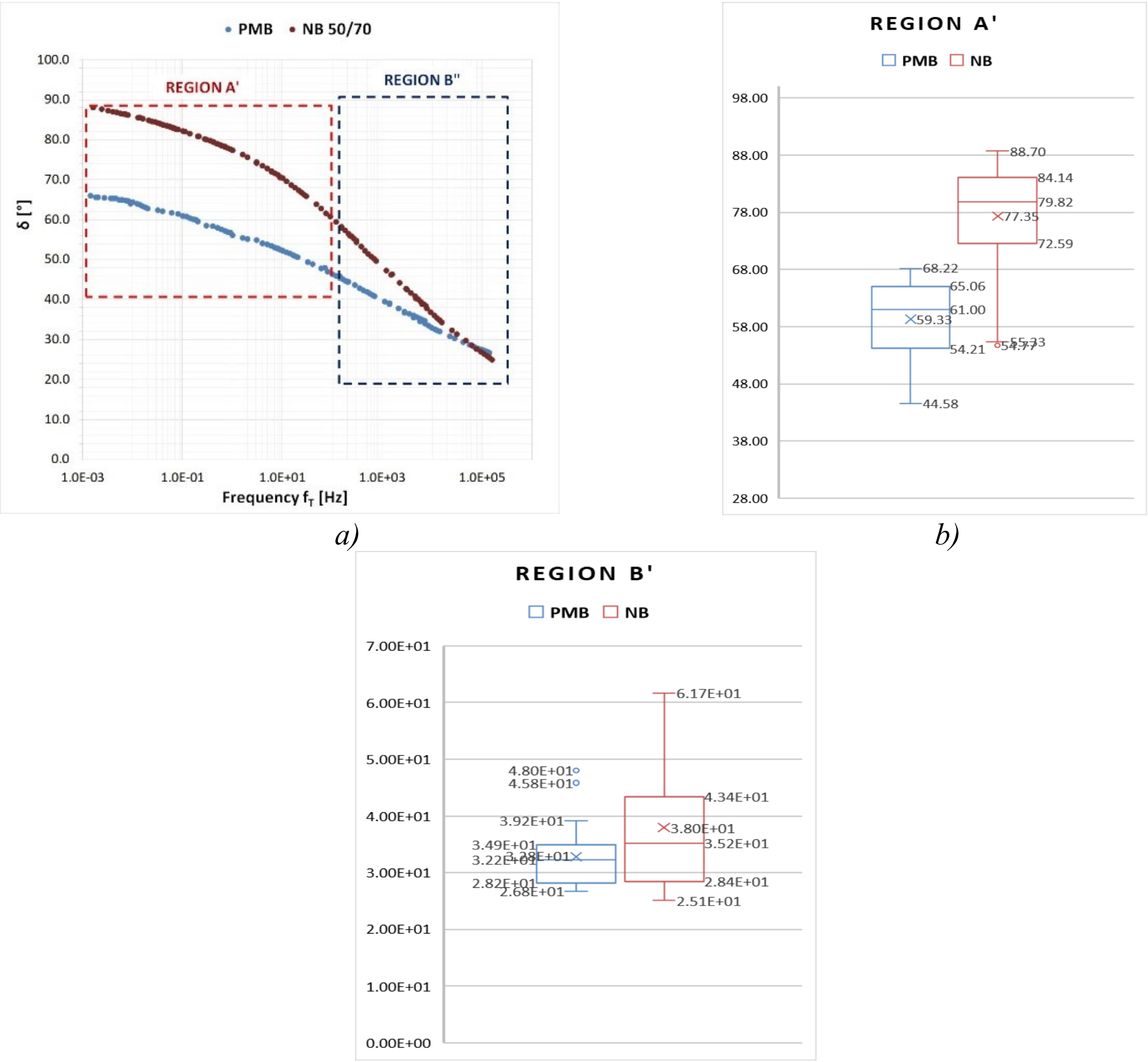
a) *b)*

c) *d)*

Figure 5-5 - Neat bitumen vs PMB: a) master curves; box and whisker plots for b) Region A, c) Region B, and d) Region C.

From the analysis of the phase angle (δ) variation (shown in Figure 5-6) two main regions were identified as useful in describing the δ behavior of the neat bitumen and PMB: Region B′ encompasses δ values observed at low test temperatures (T ≤10 °C) and high frequencies (f_t > 90

Hz), while Region A′ encompasses δ values observed at T > 20 °C and $f_t < 90$ Hz. Figure 5-6b shows that values falling within the Region A′ that are associated to the measurements of PMB and neat bitumen differ statistically; specifically, the region A’ contains PMB δ values lower (by an average of 23%) than those associated with the neat bitumen and illustrates that PMB exhibits better elastic performance at mid-to-high test temperatures than the neat bitumen (as indicated by a mean δ of 59.33° for PMB and 77.35° for NB). A close examination of Region B′ (see Figure 5-6c), shows that the phase angles for PMB and neat bitumen do not significantly differ for various frequency values at low test temperatures (mean δ of 32.2° for PMB vs 35.2° for NB).



a)

b)

c)

Figure 5-6: Neat bitumen vs PMB: a) phase angle variation; box and whisker plots for b) Region A′ and c) Region B′.

5.1.3 Polymer compounds

As mentioned before, two polymeric compounds were cold-added to two additional HMA_{NB}, namely: a) a plastomeric polymer compound (PC) and a graphene-enhanced recycled plastic compound (GRPC) industrially-produced through a palletisation process.

5.1.3.1 Plastomeric polymer compound (PC)

The Plastomeric polymer compound (PC) consists of a mixture of plastomeric polymers with low molecular weight (mainly polyethylene) and medium melting point (falling within a range from 160 to 180 °C), smashed to obtain flexible semi-soft granules. In detail, the PC was composed of a) polypropylene (PP), polyethylene (PE) and polyethylene terephthalate (PET) recycled plastics subjected to a crushing treatment process to achieve final dimensions lower than 2 mm; b) a mixture of optimized plastomeric polymers and copolymers such as Low-Density Polyethylene (LDPE) and EVA and c) additives of different types to ensure that the final polymer compound would be in the form of semi-smooth and flexible granules. The main physical properties of the polymer compound are shown in Table 5.3.

Figure 5-7 - Plastomeric polymer compond (PC)

5.1.3.2 *Graphene-enhanced recycled plastic compound (GRPC)*

As the innovative part of this study, the graphene and waste-hard-plastic asphalt modifier also contained graphene nano platelets was investigated. This new product is composed of specific polymers and graphene.

Figure 5-8: Graphene and Waste hard Plastic polymer compound (GRPC) asphalt modifier at ambient temperature

This super modifier is in the form of grey-black coloured granules with an average diameter of 1.0-4.0 mm (Figure 5-8) and is composed of:

a) selected recycled plastics: deriving from the recovery of objects composed of "hard plastics" (for example toys, bins, boxes, tubes, tables and chairs, etc.). They are industrially treated according to a patented process that also includes the techno-selection depending on the specific physical-chemical characteristics (however, not all hard plastics can be used, but only part of them). The techno-selected hard plastics are therefore selected from the traditional disposal circuit, which ends at the waste-to-energy plants. The techno-selection allows the recycling of hard plastics that are usually considered non-recyclable and non-reusable, avoiding their disposal at waste-to-energy plants;
b) functional base: is composed of additives of different nature, which are a part of the super modifier. The physio-chemical composition is protected by industrial secrecy;

c) graphene: the one that was used is G+ (named ITC1) and is composed of extremely pure nanoplatelets of graphene that is produced without solvents or other chemical products (production with plasma);

Table 5.3 - Main properties of PC and GRPC

Properties	**Units**	**PC**	**GRPC**
Colour	-	Grey	Black
Pellet size	mm	2–4	2-4
Softening point (ISO 306)	°C	160	180
Melting point (ISO 3146)		180–190	190-200
Apparent density at 25 °C (ISO 1183-2)	g/cm^3	0.40–0.60	0.5-0.7

Technically, the immense specific surface area of the nano graphene is extended throughout the binder and results in asphalt reinforcement. To demonstrate this, the morphology of the innovative polymeric compound was studied using a Scanning Electron Microscope (SEM) using the Hitachi TM3000. From the analysis of the SEM results (see Figure 5-9) it is possible to observe how the dimension of the graphene particles have a dimension between 1 and 5 microns; while, the polymer compound is composed by many overlapping layers of graphene particles, well distributed and dispersed within the polymer matrix.

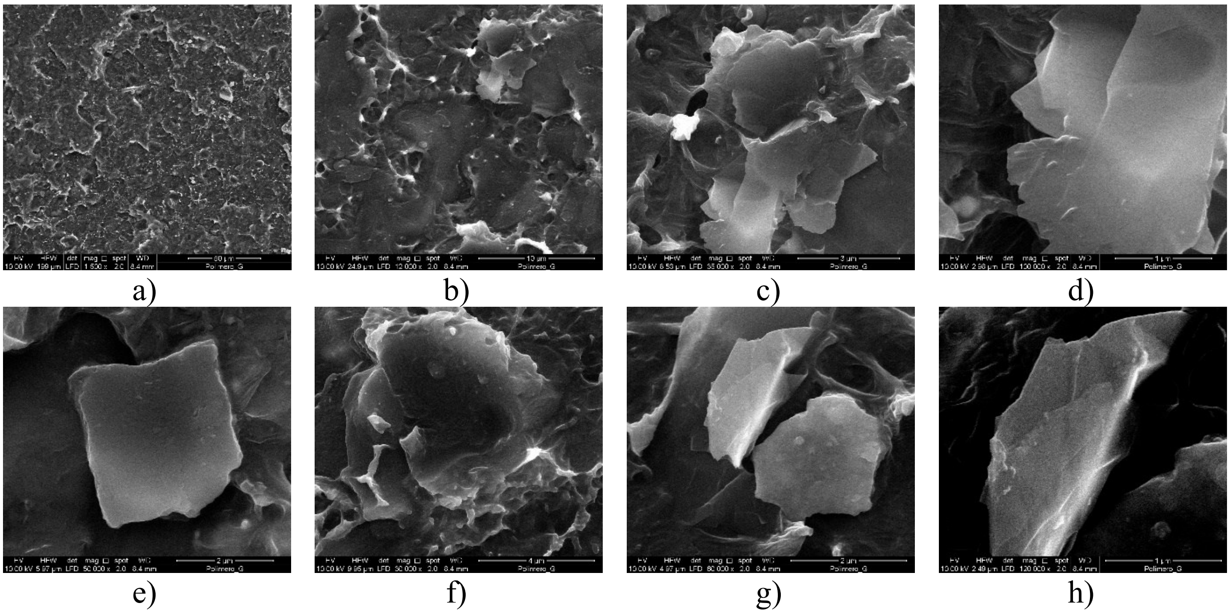


Figure 5-9: SEM image of polymer compound at: a) 1500x mag; b) 12000x mag; c) 35000x mag; d) 100000x mag; e) 50000x mag; f) 30000x mag; g) 60000x mag; h) 120000x mag

This additive has been developed to cope with severe rutting distress of flexible pavements either in hot climates and/or those subjected to heavy-duty traffic passing. However, thanks to its recycled-waste plastic base, it is also considered a sustainable solution for asphalt modification with less environmental impact.

5.2 ***Design of Hot Asphalt Mixtures***

Four Hot Asphalt Mixtures for AC 20 dense-graded binder layers were designed to meet the goals listed in the first section. The Superpave procedure was used to design first of all the traditional HMA_{NB} mix, and when the OBC was determined the same value was used in developing two other mixtures through the cold-addition of a plastomeric polymer compound (PC) and a graphene-enhanced recycled plastic compound (GRPC) to a traditional HMA with a neat bitumen 50/70 penetration grade. For comparison, an HMA made up with PMB 10/40-70 was adopted as the control mixture.

5.2.1 Mix design

The gradation curve for each mixture mentioned above was defined according to the following European Standard and Technical local Requirements, using locally available aggregates:

- EN13108-1 (see Table 1 in EN 13108-Overall limits of target composition – basic sieve set plus set 2);
- Technical Specifications on Road Maintenance issued by National Italian Autonomous Roads Corporation that meet EN 13108-1 but requires lower passing through some specific sieves (0.063 mm, 0.25 mm, 0.50 mm, 2.00 mm, 4.00 mm, 8.00 mm, 12.50 mm, 16.00 mm and 22 mm);
- Superpave requirements consisting on the identification of a) control points (determined for a nominal maximum aggregate size of 19 mm) and b) a sand restricted zone that helps to reduce compaction problems during placement of the mixtures; and

- Maximum-density gradation according to the Fuller and Thompson equation to be avoided (n = 0.45) [51].

$$P = 100\left(\frac{d}{D}\right)^{n} \tag{1}$$

where: P is the percentage of passing corresponding to dimension d; D is the maximum size of the aggregate; n is a constant.

Three trial HMA_{NB} blends (see Figure 5-10) were studied to identify which could best meet the listed requirements.

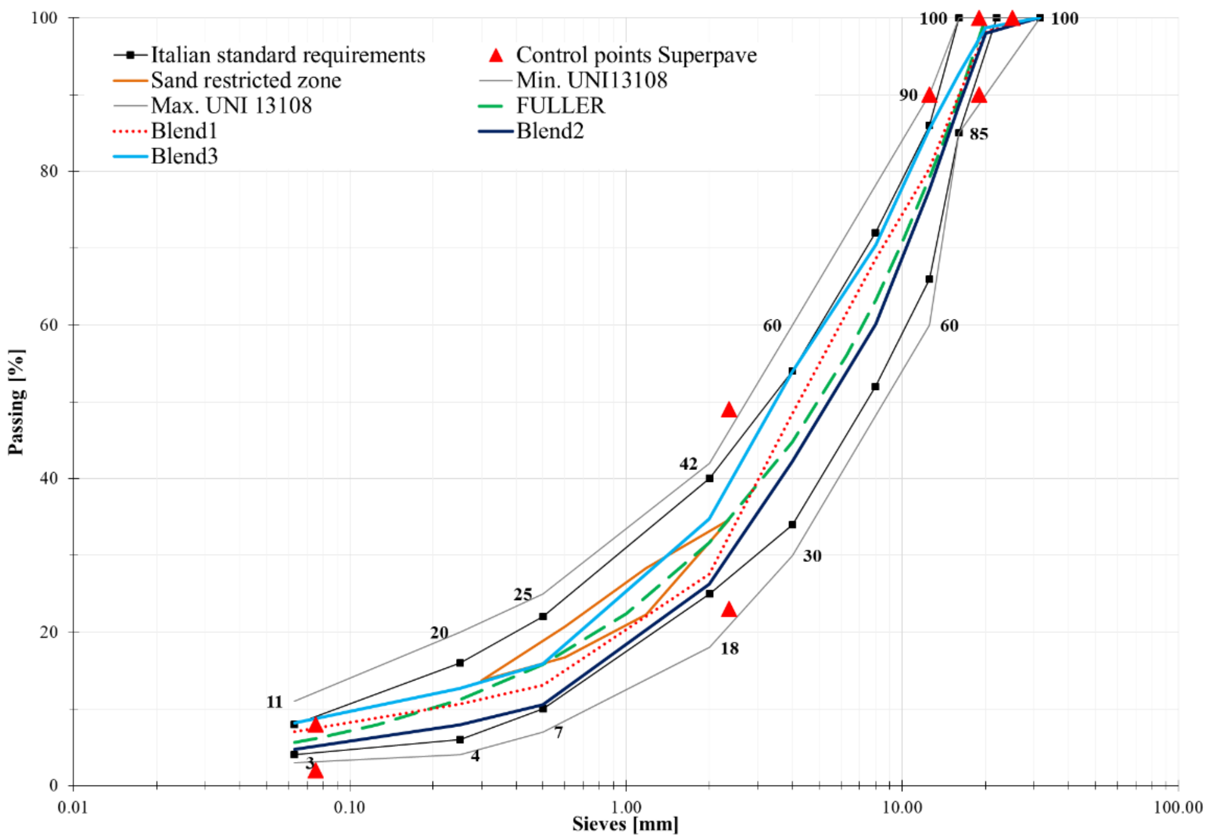


Figure 5-10 - Trial gradation curves in compliance with technical requirements

Two cylindrical specimens (150 mm in diameter) were prepared under gyratory compaction for each of three trial blends using a trial bitumen content (P_{bi} see Eq. 5) defined according to Superpave equations (see Table 5.4). The value of P_{bi} was the same for all of the trial blends, as shown in Table 5.5, because a) the aggregate type was the same for all of the blends, b) no significant differences existed in terms of the effective specific gravity (G_{se}), c) the nominal maximum sieve size of the aggregates was the same, d) no differences existed in terms of V_a = 4%, and e) the percentages of aggregates (P_s = 0.95) and binder (P_b = 0.05) were identical for all three blends and were fixed in accordance with the Superpave procedure.

Table 5.4 - Volumetric property equations for the asphalt mixtures

Equation	Eq. Number	Variables
$G_{se} = G_{sb} + 0.8 \cdot (G_{sa} - G_{sb})$	(2)	G_{se} = effective specific gravity [g/cm^3] G_{sb} = bulk specific gravity of aggregate [g/cm^3] (see Table 1) G_{sa} = apparent specific gravity of aggregate [g/cm^3] (see Table 1) V_{ba}= Volume of binder absorbed [cm^3/cm^3] P_b = percent of binder (assumed to be 0.05) P_s = percent of aggregate (assumed to be 0.95) G_b = specific gravity of binder (assumed to be 1.02 g/cm^3) V_a = volume of air voids (assumed to be 4%) V_{be} = Volume of the effective binder[cm^3/cm^3] S_n = nominal maximum sieve size of the aggregate blend [mm] P_{bi} = initial trial binder content [%] W_s = mass of aggregate [g]
$V_{ba} = \dfrac{P_s \cdot (1 - V_a)}{\left(\dfrac{P_b}{G_b} + \dfrac{P_s}{G_{se}}\right)} \times \left(\dfrac{1}{G_{sb}} - \dfrac{1}{G_{se}}\right)$	(3)	
$V_{be} = 0.176 - 0.0675 \cdot \ln(S_n)$	(4)	
$P_{bi} = \dfrac{G_b \cdot (V_{be} + V_{ba})}{\left[G_b \cdot (V_{be} + V_{ba})\right] + W_s} \times 100$	(5)	
$W_s = \dfrac{P_s \cdot (1 - V_a)}{\left(\dfrac{P_b}{G_b} + \dfrac{P_s}{G_{se}}\right)}$	(6)	

Table 5.5 - Design parameters of trial blends

	G_{se}	G_b	P_b[1]	P_s	V_a	V_{ba}	S_n	W_s	V_{be}	P_{bi} [2]
	[g/cm^3]	[g/cm^3]	[%]	[%]	[%]	[-]	[mm]	[g]	[-]	[%]
Blend 1	2.709	1.02	5	95	4	0.006	19	2.281	0.095	4.307
Blend 2	2.706	1.02	5	95	4	0.006	19	2.280	0.095	4.303
Blend 3	2.709	1.02	5	95	4	0.006	19	2.282	0.095	4.310

[1] *P_b is the initially assumed binder percentage by total weight of the mixture (5%)*

[2] *P_{bi} is the initial trial asphalt binder content, calculated according to Eq. 5 in Table 5*

Two cylindrical 4500 gr. specimens were prepared for each trial HMA_{NB} blend (a total of six specimens) by mixing aggregates and neat bitumen at 160 °C (the mixing temperature shown in Table 5.2). Each specimen was placed in a flat pan and into a forced-draft oven for 2 h at 150 °C (neat bitumen's compaction temperature in Table 5.2) for making the short-term ageing process. Then, the compaction phase was initiated using a gyratory compactor applying a pressure of 600 kPa at an external angle of 1.25° (EN 12697-31). Each specimen was compacted at N_{max} = 160 gyrations, and all corresponding volumetric features were determined; volumetric properties were also calculated at N_{ini} = 8 gyrations and N_{des} = 100 gyrations that were established on basis of the design high temperature of the paving location and the traffic level.

The ratio of h_{min} (the minimum specimen height at N_{max} corresponding to a zero-air void content) to D (the specimen diameter) was fixed to 0.68 (within the range of 0.66–1.05 recommended in EN 12697-31).

At the end of the compaction phase, each specimen was extruded from the mold and allowed to cool. Then, the compaction grade was determined according to the following six steps:

1. Determination of the estimated bulk specific gravity ($G_{mb(estimated)}$) at all numbers of gyrations, using Eq. 8;
2. Determination of the measured bulk specific gravity ($G_{mb(measured)}$) after 24 h of curing, using Eq. 9;
3. Determination of the maximum specific gravity of each specimen (G_{mm}), using Eq. 10;
4. Comparison of $G_{mb(estimated)}$ at N_{max} and $G_{mb(measured)}$ at N_{max}, using a correction factor (Eq. 11);
5. Adjustment of the bulk specific gravity (G_{mb}) by a correction factor (C) and assessing $G_{mb(correct)}$ for all numbers of gyrations (from 1 to 160), using Eq. 12; and
6. Determination of the compaction level for all numbers of gyrations (% G_{mm}) for each specimen.

Table 5.6 - Equations for assessing the compaction grade of the specimens

Equation	**Variables**	**Equation Nr**
$V_{mx} = \frac{\pi d^2 h_x}{4}$	• $\pi = 3.14$ • d = mold diameter [mm] • h_x = height of the specimen at a specific number of gyrations [mm]	(7)
$G_{mb(estimated)} = \frac{W_m / V_{mx}}{\gamma_w}$	• W_m= specimen mass [g] • V_{mx} = volume of the mold [cm^3] • Υ_w = water density [g/cm^3]	(8)
$G_{mb(measured)} = \frac{m_1}{m_3 - m_2} \cdot \rho_w$	• m_1 = dry specimen mass [g] • m_2 = mass of the specimen in water [g] • m_3 = mass of the saturated surface-dried specimen [g]	(9)
$G_{mm} = \frac{100}{\frac{P_S}{G_{sb}} + \frac{P_b}{G_b}}$	• P_s= percent aggregate • G_{sb}= bulk specific gravity of the aggregates [g/cm^3] • P_b =percent binder • G_b = specific gravity of binder (assumed to be 1.02 g/cm^3)	(10)
$C = \frac{G_{mb(measured)}}{G_{mb(estimated)}}$	• $G_{mb(measured)}$ = measured bulk specific gravity [g/cm^3] • $G_{mb(estimated)}$ = estimated bulk specific gravity [g/cm^3]	(11)
$G_{mb(correct)} = C \times G_{mb(estimated)}$	• $G_{mb(correct)}$ = adjusted bulk specific gravity [g/cm^3] • C = correction factor • $G_{mb(estimated)}$ = estimated bulk specific gravity [g/cm^3]	(12)
$\%G_{mm} = \frac{G_{mb(correct)}}{G_{mm}}$	• $G_{mb(correct)}$ = adjusted bulk specific gravity [g/cm^3] • G_{mm} = maximum specific gravity [g/cm^3] • $\%G_{mm}$= compaction grade	(13)
$V_a = 100 - \%G_{mm} @ N_{des}$	• $\%G_{mm}@N_{des}$ = compaction grade at N_{des} (100 gyrations) • V_a = air voids content	(14)
$VMA = 100 + \left(\frac{\%G_{mm} @ N_{des} \times G_{mm} \times P_s}{G_{sb}} \right)$	• $\%G_{mm}@N_{des}$ = compaction grade at N_{des} (100 gyrations) • G_{mm} = maximum specific gravity [g/cm^3] • P_s= percent aggregate • G_{sb}=bulk specific gravity of aggregate [g/cm^3]	(15)
$VFA = 100 \cdot \frac{VMA - V_a}{VMA}$	• VMA = voids in the mineral aggregate [%] • V_a = air void content [%]	(16)

Figure 5-11 shows the compaction grade results for the investigated trial blends, with the number of gyrations plotted on the x axis and % G_{mm} plotted on the y axis. As the figure shows, Blend 3, which is characterized by the highest sand and filler percentages (see Figure 5-10), exhibited a higher compaction grade and lower air voids content than the other two blends. Figure 5-11 also shows that the compaction curve for Blend 2, which is characterized by the lowest percentages of sand and filler, was lower than those of the other trial blends, while the compaction curve for Blend 1 falls between those of the other two blends.

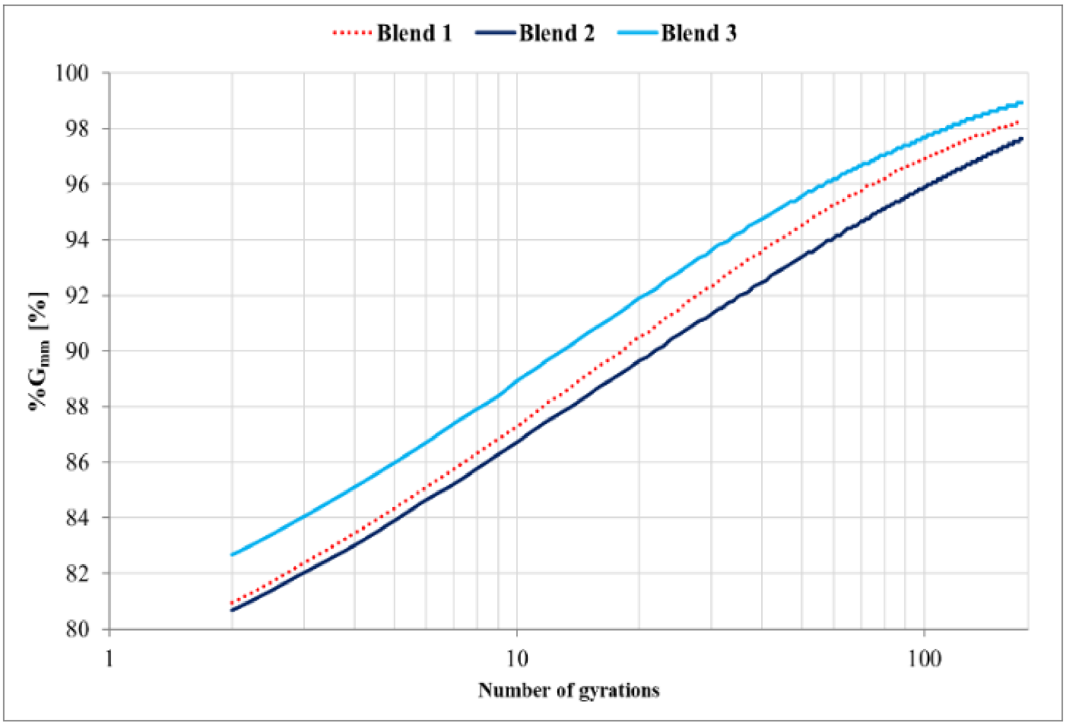


Figure 5-11: Compacting curves for three trial blends

Table 5.7 shows that Blend 2 met all the Superpave requirements. It was therefore selected as the best design blend for the HMA$_{NB}$ mix. The OBC of Blend 2 was 4.30% by total weight of the mixture.

Table 5.7 - Volumetric properties of the trial blends, based on Superpave criteria, ESALs <30 million and nominal maximum aggregate size = 19 mm

Blend/ Design Criterion	**P_{bi}**	**Va**	**VMA**	**VFA**	**$\%G_{mm}$ @N_{ini}**	**$\%G_{mm}$ @N_{max}**	**DP**
	[%]	**[%]**	**[%]**	**[%]**	**[%]**	**[%]**	**[-]**
Blend 1	4.307	3	13.40	70.14	85.14	97.20	1.75
Blend 2	4.303	4	14.12	71.67	85.62	97.41	1.13
Blend 3	4.310	2	12.69	68.47	86.14	96.86	2.37
Superpave Requirements		4	> 13	65–75	< 89	< 98	0.6÷1.2

Starting from these results and consideration, four mixtures were designed as follow:

Table 5.8 - Composition of designed asphalt mixtures

Features	**Units**	**HMA$_{NB}$**	**HMA$_{PMB}$**	**HMA$_{PC}$**	**HMA$_{GRPC}$**
Limestone 10/16 mm ^{a}	%	23.9	23.9	23.9	23.9
Limestone 6/12 mm ^{a}		31.6	31.6	31.5	31.5
Limestone sand 0.25/4 mm ^{a}		36.4	36.4	36.3	36.3
Limestone filler 0.063/2 mm ^{a}		3.8	3.8	3.8	3.8
NB ^{a}		4.3	-	4.3	4.3
PMB ^{a}		-	4.3	-	-
PC $^{a, b}$		-	-	0.2	-
GRPC ^{a,b}		-	-	-	0.2

^{a} percentage by the total weight of the mixture
^{b}The dosage of the plastomeric compound was in accordance with the manufacturer's recommendations (4% to 6% by total weight of the bitumen).

5.2.1.1 *Mixing procedures*

Once the OBC had been determined for all investigated mixtures, 32 cylindrical specimens (eight for each HMA) were prepared based on the following mixing procedure to ascertain the optimum mixing process and compaction effort for each HMA. As mentioned earlier, an innovative mixing procedure was considered to address the main issues associated with maximizing the effect of polymer addition for a laboratory-scale production. The main steps are synthetically depicted in Figure 5-12 and listed below as well:

a) For HMA_{NB} and HMA_{PMB}, the same procedure was adopted, as shown in Figure 5-12a. The only difference was in terms of the operating temperatures and compaction efforts (see Table 5.2); since the viscosity of the PMB binder was greater than that of the neat bitumen, HMA_{PMB} required higher mixing and compaction temperatures (see Table 5.2) and a greater number of gyrations than HMA_{NB}.

b) For HMA_{PC} and HMA_{GRPC} (Figure 5-12**b**), an internal protocol (Figure 5-12) was followed:

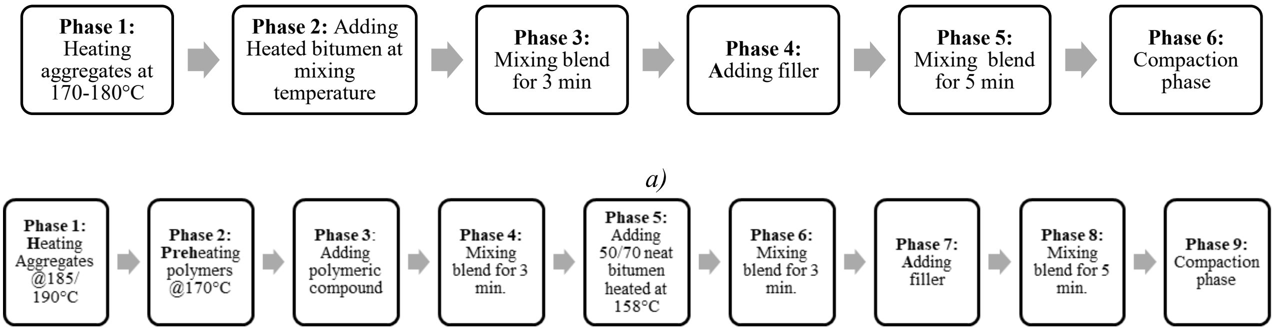
   I. The aggregates were preheated for 4 h at 185–190 °C.

   II. The polymer compound was added before the introduction of neat bitumen. In the first phase, the compound was added as per the procedures adopted for large-scale mixture production (asphalt plant). The compound was stored at room temperature and added directly to the aggregates immediately, before the bitumen. However, this procedure led to an incomplete dissolution of the compound inside the asphalt mixture (Figure 5-13e). To overcome this, the polymer compound was preheated at 170 °C for 1 h and then blended with the aggregates for 1 min using the Controls Automatic Laboratory Mixer BITUMIX (see Figure 5-13b). The obtained result (Figure 5-13f) demonstrates how the moving from the large-scale to the laboratory-scale different procedure should be adopted for production of HMA_{PC} and HMA_{GRPC}, to ensure dissolution of the polymer compound. Thus, the proposed mixing procedure improved the effect of polymer addition in laboratory-scale production.

III. The next steps (see Figure 5-13**c**) involved the addition of the neat bitumen (preheated for 1 h at 158 °C) and further mixing (for approximately 3 min) until the aggregate was fully coated with bitumen (see Figure 5-13**d**)

IV. The filler was then added, and further mixing was performed (for 5 min).

It is necessary to clarify that into the asphalt plant the polymers compound is usually added at the air temperature, without any pre-heating phase or longer mixing times, and the melting process is successfully achieved. This difference that occurs between situ and laboratory scale should be due to the different force applied by the asphalt plant/laboratory mixer during the mixing process. In fact, while the force applied to the asphalt plant is very high; in laboratory scale, the mixer adopted cannot have the same "mixing force", so the melting process of modifiers needs to be helped with a pre-heating step as described

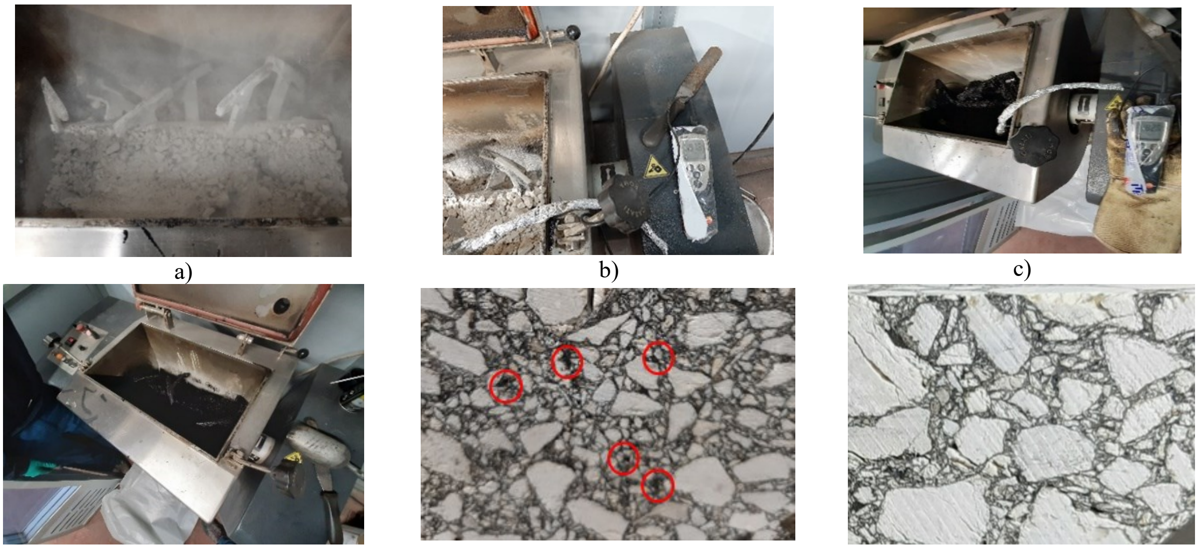


a)

b)

Figure 5-12:. Steps in preparation of HMA specimens: a) HMA_{NB} and HMA_{PMB}; b) HMA_{PC} and HMA_{GRPC}

Before compaction phase the short-term aging of all investigated solutions was performed by placing the loose mix in a flat pan inside a forced-draft oven at the compaction temperature of the neat/PMB bitumen, as shown in Table 5.2 for two hours.



a) b) c)

d) e) f)

Figure 5-13. Preparation of HMA$_{PC}$ and HMA$_{GRPC}$ specimens. a) Aggregate introduction into the mechanical mixer, b) adding polymeric compound and checking mixing temperature, c) adding neat bitumen and checking mixing temperature, d) asphalt mixture at the end of the mixing process, e) unmelted polymeric compound in cut specimen, f) melted polymeric compound in specimen after preheating of compound

5.2.1.2 Compaction effort

After being prepared, each of the 32 specimens was compacted using a gyratory compactor; a pressure of 600kPa was applied combined with an external angle of 1.25°. All specimens were compacted using a mould with 150mm diameter because the designed asphalt mixture have the maximum aggregate size greater than 16 mm. Two key parameters were considered to determine the adequate compaction effort for each investigated asphalt mixture[52][53]: a) the compaction level and the number of gyrations and b) the energy distribution during the compaction phase.

The first parameter is a key factor for ensuring that the nontraditional mixtures (HMA$_{PMB}$, HMA$_{PC}$ and HMA$_{GRPC}$) achieve the same volumetric properties as those of the reference HMA$_{NB}$. Thus, eight specimens were prepared for each mixture, and their mean %G$_{mm}$ values were plotted against the number of gyrations (Figure 5-14) to determine the appropriate compaction effort. From the analysis of the compaction curves shown in Figure 5-14, some relevant observations can be made:

a) During the initial compaction phase (less to 40 gyrations), all asphalt mixtures designed exhibits almost the same densification curves as demonstrated by the air voids values shown at 8 gyrations number (N_{ini}) displayed in Table 5.9.

b) During the final compaction phase (over 40 gyrations) all modified asphalt solutions display the same compaction curves between them, but a different trend than the traditional mixture prepared with neat bitumen. In detail, from the analysis of Figure 5-14, it is possible to observe how higher compaction effort is required by the asphalt mixtures prepared with PMB/ recycled polymers, since lower compaction curves are obtained.

Considering this, it is clear that the investigated asphalt solutions do not exhibit the same volumetric properties between them, since different air voids values was observed during compaction. Thus, they did not satisfy the Superpave requirement for an air voids value of 4% at N_{des}, as shown in Figure 5-15. Almost the same condition can be found at 160 gyrations where the air voids are equal to 3.7% for traditional asphalt mixture, to 4.1% for the solution modified using PMB and to 3.0% for both asphalt mixture modified by dry process.

Hence, the number of gyrations used for HMA_{PMB}, HMA_{PC} and HMA_{GRPC} was changed. As observable from Figure 5-14, the appropriate N_{des} for these mixtures was determined by drawing a horizontal line at the $\%G_{mm}$ value of the HMA_{NB} mixture (96%) and determining where that line intersected the densification curves previously plotted for HMA_{PMB}, HMA_{PC} and HMA_{GRPC} (the green, violet and red curves, respectively, in Figure 5-14). In this manner, 112 was found to be the appropriate N_{des} for HMA_{PMB}, HMA_{PC} and HMA_{GRPC} to achieve the same $\%G_{mm}$ as that calculated for HMA_{NB} at 100 gyrations. The results are shown in Table 5.9.

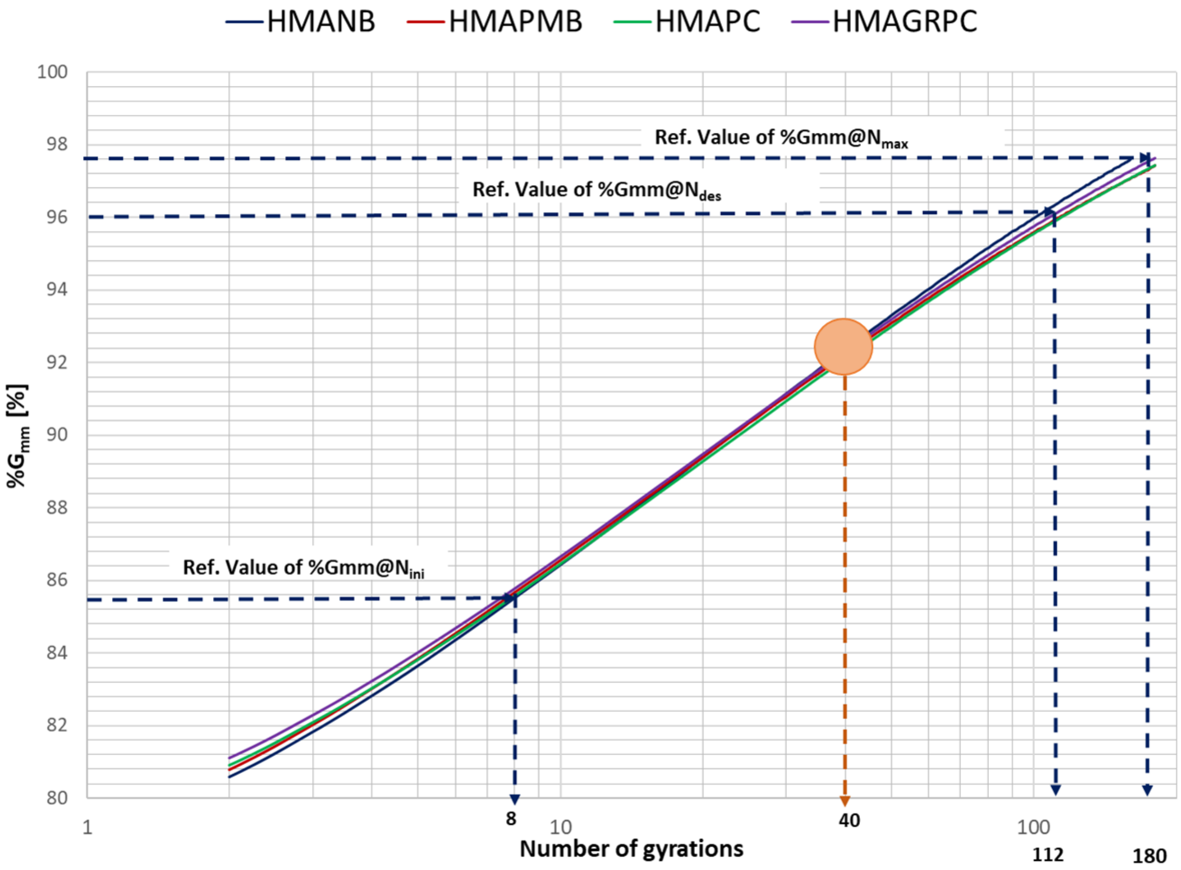


Figure 5-14: Compaction results the %Gmm vs number of gyrations

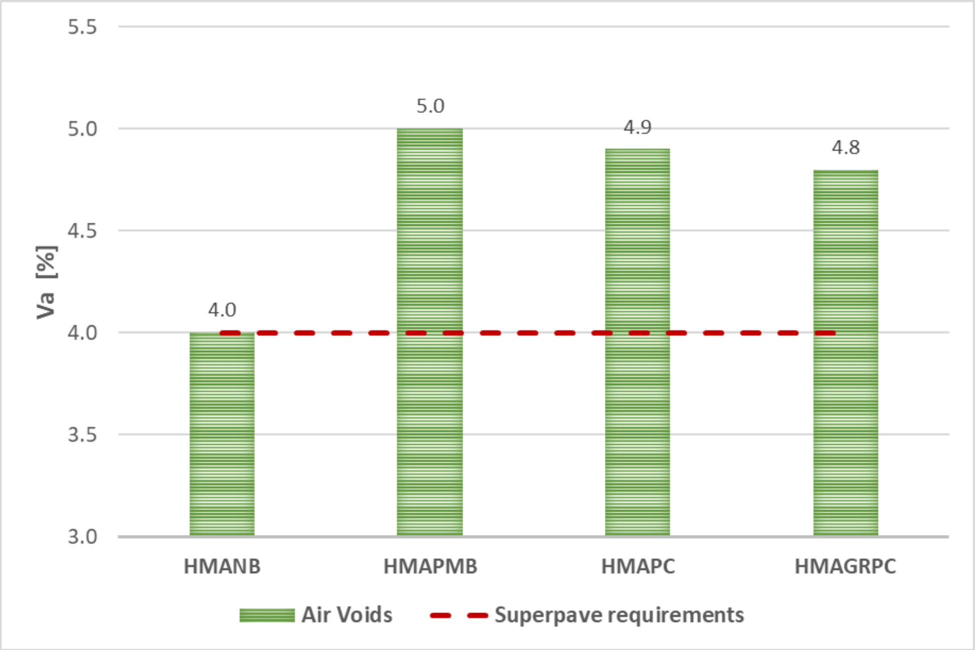


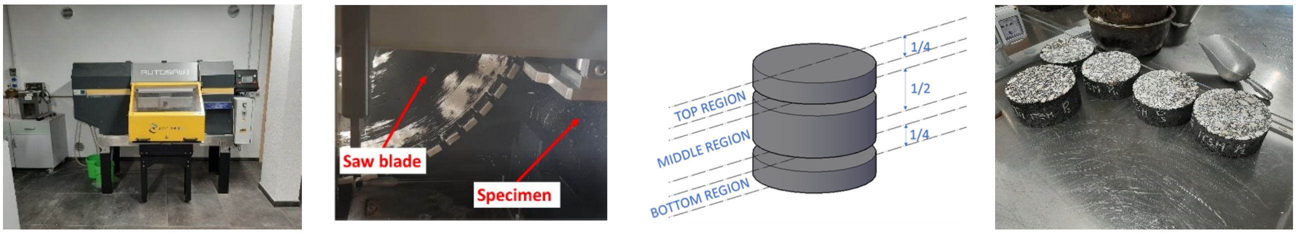
Figure 5-15: Compaction results air values at 100 gyration number

Table 5.9: Design compaction levels for all three mixtures

	$\mathbf{HMA_{NB}}$	$\mathbf{HMA_{PMB}}$	$\mathbf{HMA_{PC}}$	$\mathbf{HMA_{GRPC}}$
$\mathbf{N_{ini}}$	8	8	8	8
$\mathbf{N_{des}}$	100	112	112	112
$\mathbf{N_{max}}$	160	180	180	180
$\mathbf{\%G_{mm}@N_{ini}}$	85.4	85.7	85.5	85.6
$\mathbf{\%G_{mm}@N_{max}}$	97.7	97.4	97.4	97.3
$\mathbf{\%G_{mm}@N_{des}}$	96.0	95.9	96.1	95.8

Regarding the energy distribution during the compaction phase, the literature review well clarifies that the during the compaction phase if a gyratory compaction is used, the energy applied on specimen has a cone-shaped distribution [54]. The compaction energy is highest close to the top and bottom plates and decreases toward the middle, until it reaches its lowest level at the tip of the cone. Consequently, a non-uniform distribution of V_a is usually observed from the top plate to the bottom plate and close to the mold [55][56].

Accordingly, the mean volumetric properties of the three mixtures were assessed with a focus on the central part of each specimen, where the height varied from 48.92 to 54.96 mm. A sawing system (Figure 5-16a) equipped with automated clamps and a 650-mm-diameter blade (Figure 5-16b) was used to cut each specimen into three sections, as shown in Figure 5-16c and Figure 5-16d. No coring operations were performed since no coring machine was available during the testing phase.



a) *b)* *c)* *d)*

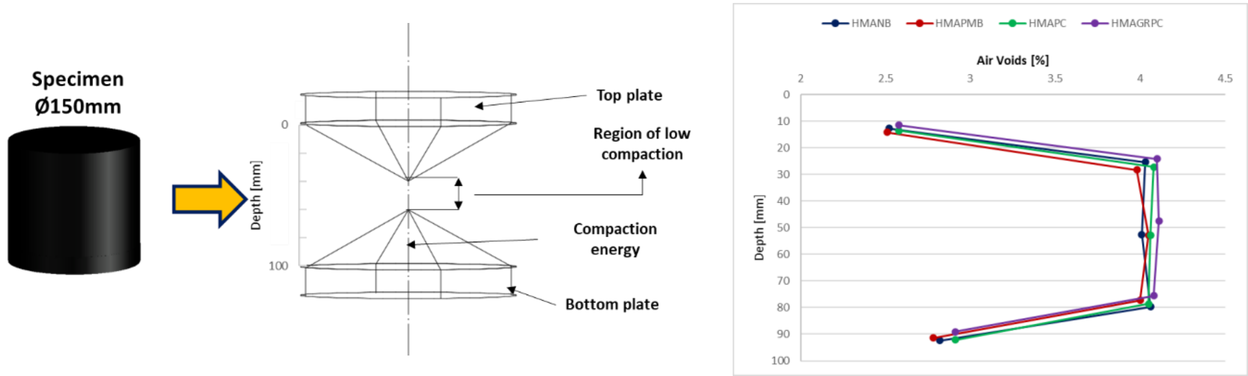
Figure 5-16. Cutting process. a) sawing system, b) blade, c) specimen sections, d) cut specimen sections

Table 5.10 and Figure 5-17 show the mean values of the volumetric properties measured at the central sections of the specimens. Evidently, the values did not differ significantly among the three mixtures.

Table 5.10 - Volumetric properties of the asphalt mixtures

Mixture	V_a	VMA	VFA	$\%G_{mm}$ @N_{ini} (8 gyrations)	$\%G_{mm}$ @ N_{max}	Dust Portion
	[%]	[%]	[%]	[%]	[%]	[-]
HMA$_{NB}$	4.0	14.2	70.6	85.4%	97.7%	1.1
HMA$_{PMB}$	4.1	14.4	71.8	85.7%	97.4%	1.1
HMA$_{PC}$	3.9	14.1	71.6	85.5%	97.4%	1.1
HMA$_{GRPC}$	3.8	14.2	71.4	85.6%	97.3%	1.1

Starting from these results, it is possible to confirm the hypothesis made above, since Table 5.10 validate the necessity to design different procedures between traditional and modified asphalt solution to reach comparable volumetric properties between them.



a) *b)*

Figure 5-17: Gyratory compaction effects over the height of cylindrical specimens: a) conical distribution of the energy; b) V_a variation

5.3 ***Mechanical related properties investigation***

5.3.1 Indirect Tensile Strength

The ITS is the maximum calculated tensile stress applied to a cylindrical specimen loaded diametrically until breakage occurs at the test temperature and speed of displacement. Three specimens of each of the four mixtures (a total of 12 specimens) were prepared for ITS testing according to the procedures described in above. Each specimen was stored for 4 h in an air chamber for conditioning at a test temperature of 10 °C (EN 12697-23) before testing. The temperature was controlled using a dummy specimen equipped with a built-in temperature indicator. At the end of the conditioning phase, the specimens were aligned on the lower loading strips of the test apparatus and loaded diametrically at a constant speed of deformation (50 ± 2 mm/min), after a transitory period lasting less than 20% of the loading time, until the peak load was reached. The ITS was calculated according to the following equation:

$$ITS = \frac{2P}{\pi DH} \tag{17}$$

where ITS is the indirect tensile strength in GPa, P is the peak load in kN, D is the diameter of the specimen in mm, and H is the height of the specimen in mm.

a) *b)* *c)*

Figure 5-18: ITS loading test configuration

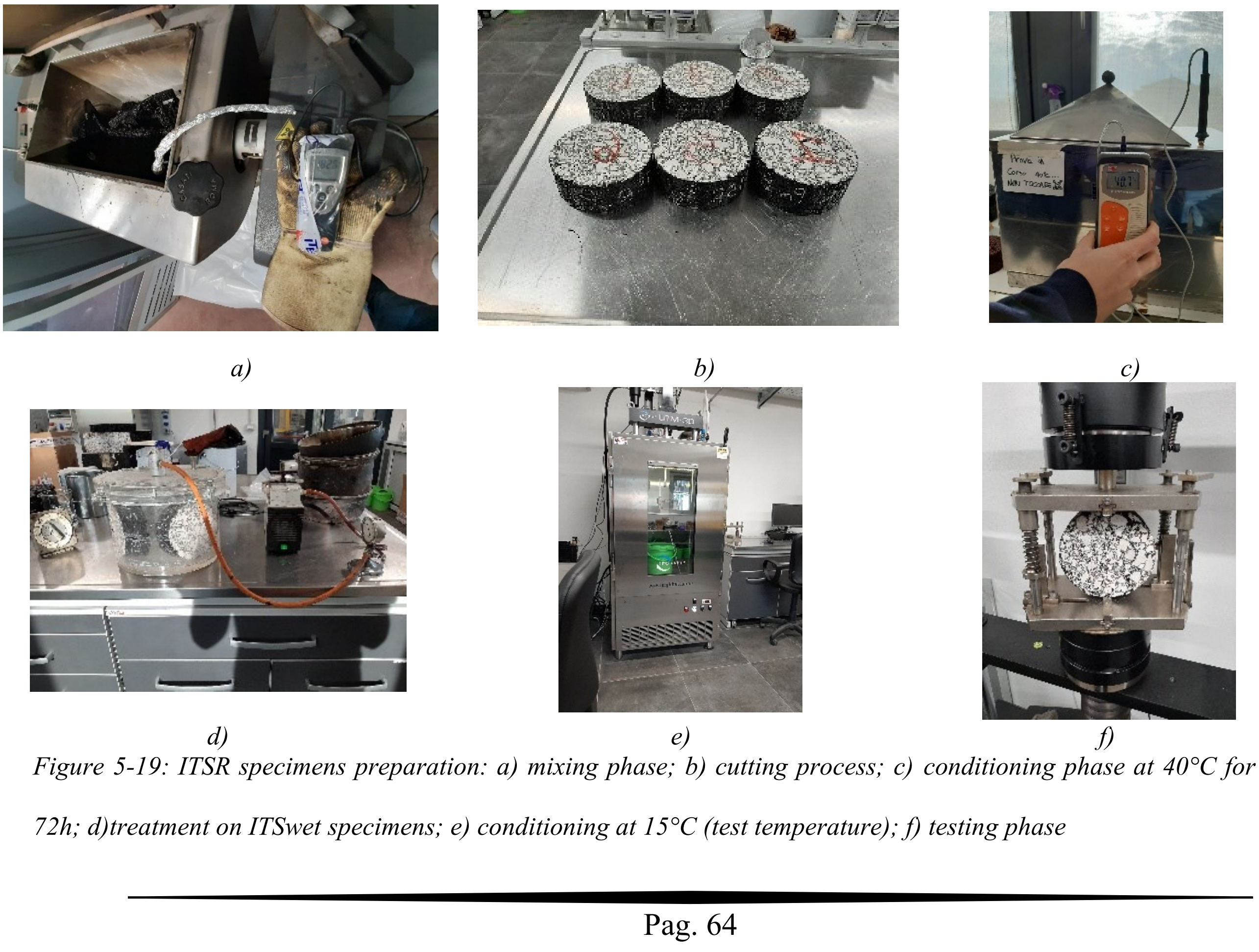
5.3.2 Indirect Tensile Strength Ratio

The moisture sensitivity of each of three mixtures was assessed in accordance with EN 12697-12 (summarized in Figure 5-20). Six cylindrical specimens of each mixture were prepared (a total of 24 specimens) and then subjected to 50 gyrations, before being cut into sections according to the procedure described before (Figure 5-19b). The number of gyrations was less than for the other mechanical tests conducted (ITS and ITSM) to maximize the influence of the water conditioning effect, since lower compaction effort results in a higher air void content in a specimen.

Three of the six specimens for each of the three mixtures were used to determine the ITS_{dry} value. These specimens were maintained in dry conditions at room temperature (20 °C) for 72 h (see Figure 5-19b) and then conditioned for a total of 4 h at 15 °C in an air chamber. The remaining three of the six specimens for each mixture were used to determine the ITS_{wet} value. These specimens were saturated (see Figure 5-19d), stored in a water bath at 40 °C for a total of 72 h (see Figure 5-19c), and then conditioned for another 4 h at 15 °C in a water bath (Figure 5-19e). At the end of the conditioning process, the ITS value was calculated (see Figure 5-19f) as described in previous section. The test temperature was fixed at 15 °C ± 1 °C. The mean ITSR for each mixture was calculated from the following equation 18.

$$ITSR = \frac{ITS_{WET}}{ITS_{DRY}} \times 100 \tag{18}$$

where ITS_{wet} and ITS_{dry} are the mean ITS values under wet and dry conditions, respectively, in kPa.



a) b) c)

d) e) f)

Figure 5-19: ITSR specimens preparation: a) mixing phase; b) cutting process; c) conditioning phase at 40°C for 72h; d)treatment on ITSwet specimens; e) conditioning at 15°C (test temperature); f) testing phase

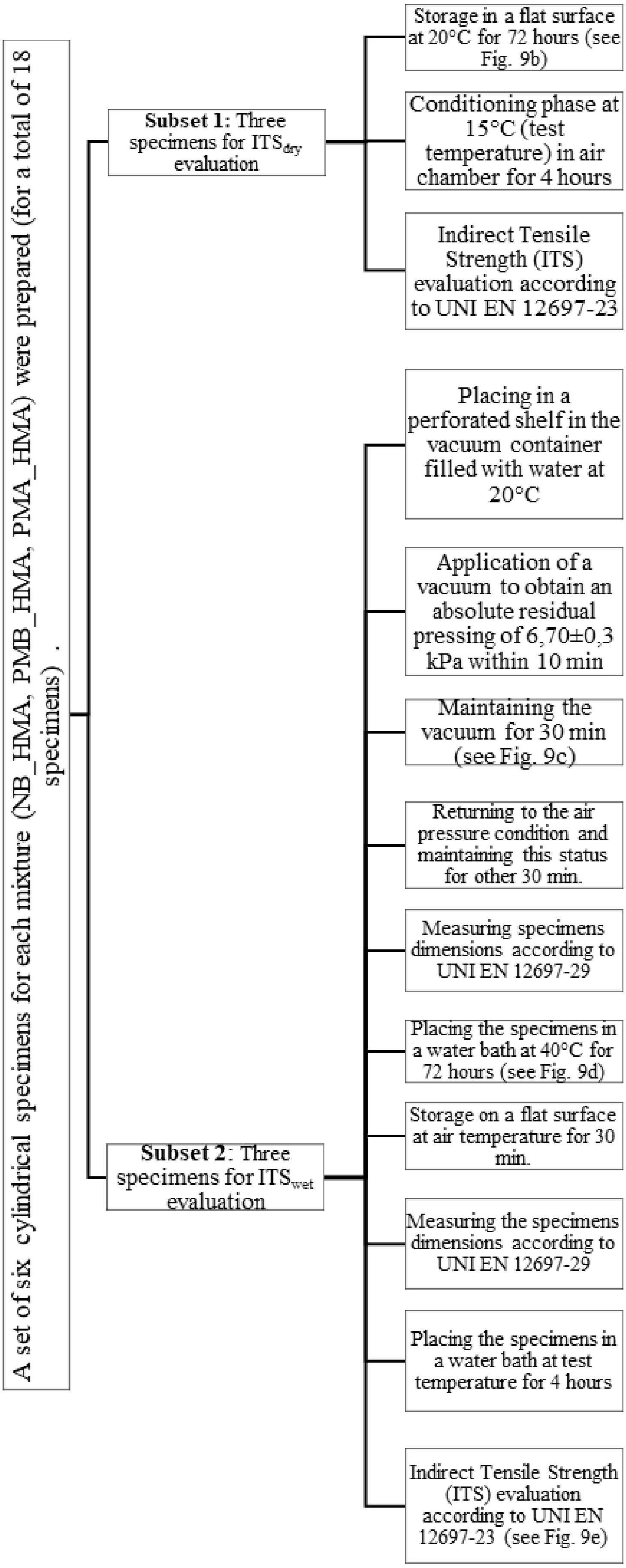
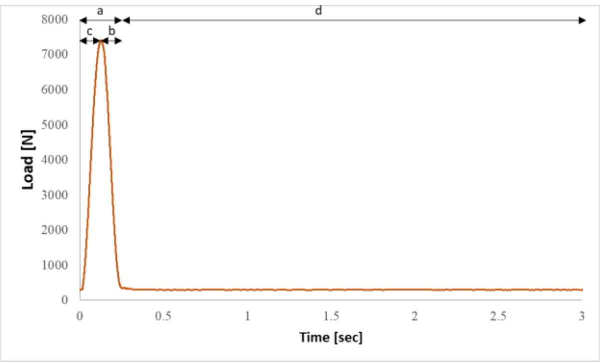
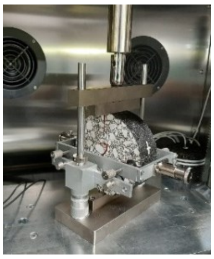


Figure 5-20 Evaluation of ITSR a) overview of the procedure

5.3.3 *Indirect Tensile Stiffness Modulus*

The resilient stiffness modulus was calculated using an indirect tensile load configuration (see Table 5.11), in accordance with EN 12697-26 ANNEX C, by preparing a total of twenty specimens (five specimens for each asphalt mixtures), according to the procedure described in previously. Table 5.11 shows the pulse load configuration adopted, which includes a loading time of 240 milliseconds (part *a* in the graph), divided in two equal parts, the rise time (part *c* of the graph) and the unloading time (part *b* of the graph). The load pulse was followed by a rest period (part *d* of the graph).

Table 5.11- ITSM load configuration

Parameters	**Unit**	**Value**	**Load configuration model**	**ITSM laboratory evaluation**
Waveshape		Haversine		
Loading pulse rise-time [a]	[ms]	240		
Rise time [c]	[ms]	120		
Unloading time [b]	[ms]	120		
Rest period [d]	[ms]	2760		
Pulse repetition period	[ms]	3000		
Number of conditioning pulses	[-]	10		
Estimated Poisson's ratio	[-]	0.35		

The tests were carried out under strain control to ensure a strain level lower than 50 με (EN 12697-26 – Annex C). For this reason, to define an adequate peak load, ten conditioning pulses were applied, followed by a further five pulses for the purpose of stiffness measurement, according to following equation:

$$ITSM = \frac{F \times (\nu + 0.27)}{z \times h} \tag{19}$$

where F is the peak value of the applied vertical load in N, z is the amplitude of the horizontal deformation obtained during the load cycle in mm, h is the mean thickness of the specimen in mm and ν is Poisson's ratio (assumed to be equal to 0.35).

ITSM values were determined at three test temperatures (10 °C, 20 °C, and 40 °C). The 10 °C temperature was selected to match that used for ITS assessment. The 20 °C temperature was used to investigate the mechanical properties of the mixtures at intermediate temperatures close to the test temperature used for assessing ITS_{dry} and ITS_{wet} (15 °C). The 40 °C temperature was used to investigate the mechanical responses of the asphalt mixtures under typical local spring and summer temperatures in the binder layers of roads in southern Italy.

5.3.4 Fatigue life

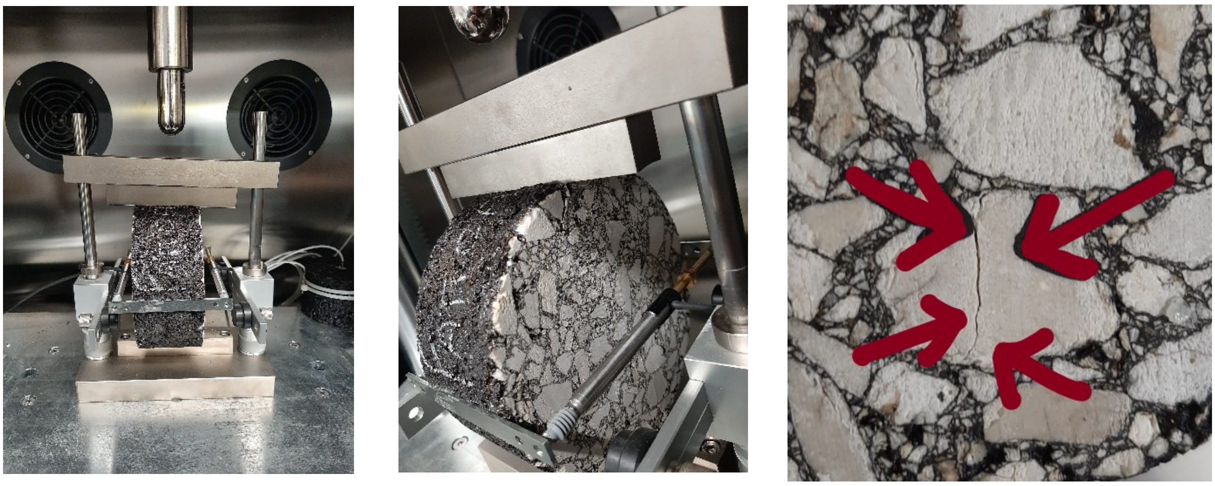
The behaviour of bituminous mixtures under repeated load fatigue testing was evaluated using an Indirect Tensile Test (see Figure 5-21a) according to EN 12697-24 – ANNEX E applying a haversine load repeatedly with 0,1 s loading time and 0,4 s rest time. The test was carried out on a total amount of 15 cylindrical specimens (5 for each HMA designed) manufactured in laboratory according to the procedures described above. The test temperature was fixed to 10°C in line with ITS test (the specimens were placed in the thermostatic chamber and exposed to the specified test temperature for 4 h before testing) and an initial tensile strain range of approximately 70 μm/m to 400 μm/m was considered. The specimens were positioned in the loading device so that the axis of the deformation strips is (90 ± 5)° to the axis of the loading strips (see Figure 5-21b).

The fracture life was determined according to Method 2 (energy ratio) proposed by the EN12697-24 – Annex E so it was obtained from the relationship between decimal logarithm of the number of load cycles and the energy ratio. The fracture life was obtained at the maximum energy ratio:

$$w_n = \frac{n}{\varepsilon_{R,n}} \cdot 10^6 \qquad (20)$$

Where n is the number of the cycles and $\varepsilon_{R,n}$ is the resilient strain.

At the end of the fatigue test a line of fracture can be defined on the tested samples as shown in Figure 5-21c.



a) b) c)

Figure 5-21 - Fatigue test procedure a) Indirect Tensile Test configuration b) Specimens position in loading device c) Line of fracture on tested specimens

5.3.5 Semi Circular Bending Test

The Semi-Circular Bending (SCB) test method was used to determine the tensile strength and fracture toughness of an asphalt mixture for the assessment of the potential for crack propagation (See Figure 5-22e). The test was conducted on a total of 20 specimens (five for each investigated HMA) according to EN 12697-44. The specimens were prepared according to the procedure proposed reaching a final thickness of the specimen within 50 ± 3 mm and then a further cutting process was conducted to a have a final height of the specimen within 74 ± 1 mm (Figure 5-22a). On this way the specimens reach a half cylinder form with a centre crack that was manually created (see Figure 5-22b) to achieve a notch with a width of (0,40 ± 0,20) mm and a depth of (10,0 ± 1,0) mm (see Figure 5-22c). Each prepared specimen was loaded in three-point bending (see Figure 5-22d) in such a way that the middle of the base of the test piece was subjected to a tensile stress. During the test, the deformation rises at a constant rate of 5 mm/min since the corresponding load reach to a maximum value (Fmax) which is directly related to the fracture toughness (Eq. 22) of the test sample by the maximum stress failure (Eq. 21) as shown in following equations:

$$\sigma_{\max} = \frac{F_{\max}}{Dt} \left[\frac{N}{mm^2}\right] \tag{21}$$

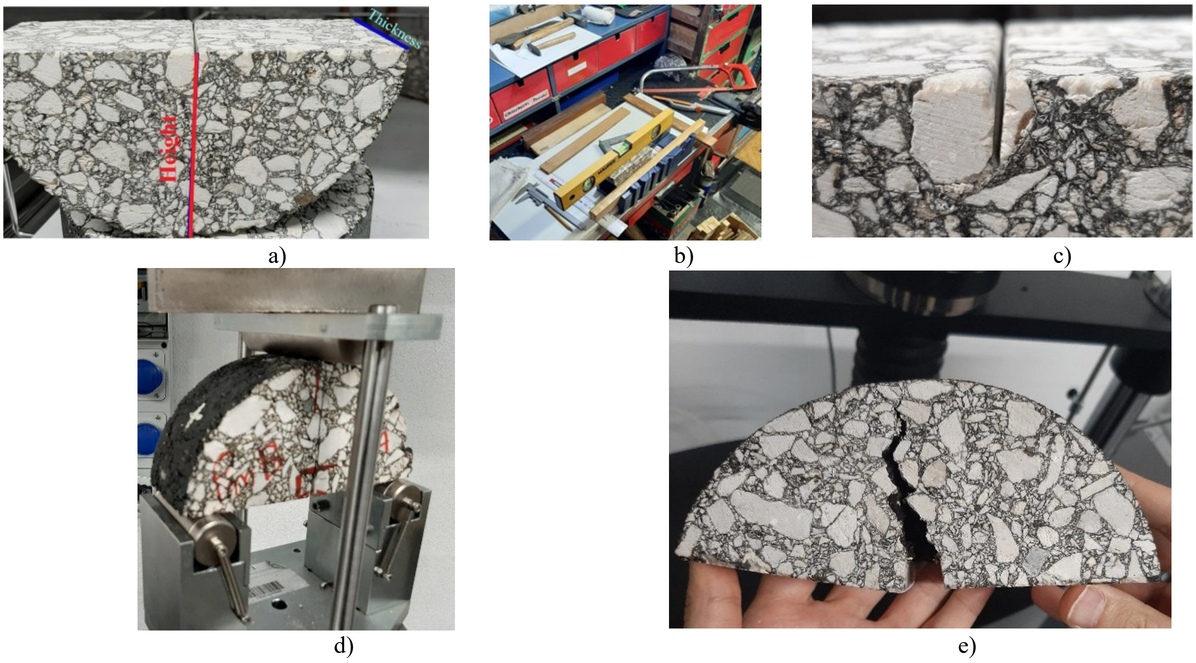
Where D is the diameter of specimen in millimetres (mm); t is the thickness of specimen, in millimetres (mm); F_{max} is the maximum force of specimen, in newtons; σ_{max} is the stress at failure of specimen in newtons per metre squared (N/mm^2).

$$K_{IC} = \sigma_{max} Y_1 \sqrt{\pi a} \left[\frac{N}{mm^{1.5}}\right] \tag{22}$$

where a is the notch depth of specimen, in millimetres (mm) and Y_1 is the normalised mode I stress intensity factor (see Eq. 23);

$$Y_1 = 4.782 - 1.219\left(\frac{a}{r}\right) + 0.063exp\left[7.045exp\left(\frac{a}{r}\right)\right] \tag{23}$$

Where r is the is the radius of height of the specimen in millimetres (mm) and a is half of the distance between the centre of the rollers in millimetres (mm). Since the SCB test is a method to determine the resistance to crack propagation of an asphalt mixture and assured that the crack propagation phase describes the second part of failure mechanism during dynamic loading because the first phase (which is the crack initiation phase) is mainly covered by the fatigue test, the SCB was conducted at 10°C, in line with previous mechanical tests.



a) b) c)

d) e)

Figure 5-22 - SCB test procedures – a) geometrical properties of prepared specimens; b) centre crack manual manufacturing c) notch detail d) loading configuration e) crack propagation after test

5.3.6 *Resistance to permanent deformation*

The Wheel tracking test was conducted to determine the susceptibility of bituminous materials to deform under load. A total of 12 specimens were tested in water at 60 °C, as per Procedure B in EN 12697-22.

In detail, to analyze the resistance of designed asphalt materials to deformation, the wheel-tracking slope and the mean rut depth in water were considered. In detail, the wheel-tracking slope in water, in mm per 1 000 load cycles, is calculated as follows:

$$WTS_{water} = \frac{d_{10000} \cdot d_{5000}}{5} \ [mm] \tag{24}$$

Where WTS_{water} is the is the wheel-tracking slope, in millimeters per 1 000 load cycles, while d_{5000} and d_{10000} is the vertical displacement after 5 000 load cycles and 10 000 load cycles, in millimeters (mm); while the rut depth in water for the material under test at n cycles has considered as the mean rut depth of the four specimens tested for each mixtures to ± 0,1 mm.

The test was conducted using a wheel-tracking apparatus which consists of a loaded wheel that bears on a sample held on a table as shown in Figure 5-23**a.** The wheel beyond the table moves backwards and forwards while a transducer providing monitors the rate at which a rut develops to the top of the specimen.

a) b) c) d)

Figure 5-23: Resistance to permanent deformations. a) Wheel-tracking apparatus; b) specimen cut on lateral surface; c) wheel passage surface without discontinuities; d) final rut depth.

5.3.7 Pavement Structures design

As final laboratory step program, road pavements solutions (PSs) were investigated by pursuing the following target: finding a proper thickness for each of the four component layers of a flexible pavement by fixing a traditional HMA solution for the wearing and base layers, and fixing in turn each investigated solutions as the binder layer. Pavement design was performed under the assumption of an elastic multilayer, characterized by homogenous materials [57], and laid on granular subbase with a Young's elastic modulus of 116 MPa, and a subgrade with a deformation modulus of 50 MPa.

The fixed thickness for each layer defined above was equal to 4 cm for the wearing course, 5 cm for the binder layer, 20 cm for the base layer, and 20 cm for the subbase layer. The service life of each stratigraphy solution in compliance with the defined goals was identified by calculating: a) the accumulated fatigue damage (FD) that should be lower than 1 by using Miner Equation [58] and b) accumulated rut depth (R), which should be lower than 2 cm, by using Verstraeten Equation [59] (see Table 5.12 for more details).

The predictive models reported mentioned above, were joined with the experimental results of the fatigue and rutting resistance of the binder layer mixtures described in previous sections, in particular, the number of passages that leads to fatigue cracking (N_{ij}) of the binder layer and the depth of the rut accumulated in the binder layer after the number of passages predicted across the service life (R_j) were those obtained from the mentioned mechanical tests.

Table 5.12 - Predictive models for fatigue damage and rutting distresses.

Pavement distress	Formula
Fatigue damage	$FD = \sum_j \sum_i \frac{n_i}{N_{ij}}$ where • n_i is the number of passages of the Equivalent Standard Axle Load (ESAL) in the i-th period of analysis (season) • N_{ij} is the number of passages of the ESAL in the i-th period of analysis (season) that leads to the fatigue cracking of the j-th layer
Rutting damage	$R = \sum_j R_j = \sum_j \sum_i \varepsilon_{ij} \cdot h_j$ where • ε_{ij}·is the permanent deformation in the i-th period of analysis (season) that is accumulated in the j-th layer of the pavement after the predicted ESAL passing • h_j is the thickness of the j-th layer

5.4 *Environmental impact*

5.4.1 Legislation Framework

The Life Cycle Assessment (LCA) is a method that evaluates the set of interactions that a product or service has with the environment, considering its entire life cycle which includes the pre-production phases (therefore also the extraction and production of materials), production, distribution, use (therefore also reuse and maintenance), recycling and final disposal. Thanks to the impetus deriving from European policies on environment, energy, resources and waste, LCA is increasingly becoming a necessary tool for defining public policies and for the competitiveness of businesses. At the European level, LCA represents, to date, an element of qualification in all fields where an assessment of sustainability is required. It is a methodology that allows to evaluate the ecological advantages of a product, through the quantification of the environmental impacts connected to the production processes and other activities of the company. As for the information provided to the consumer, the LCA can be of support to increase the truthfulness of the message on the ecological characteristics of a product, which acquires credibility as it is accompanied by numerical data on the impacts.

The LCA procedure is internationally standardized by the EN ISO 14040 and 14044 standards. The LCA (as defined by the ISO 14040 standard) considers the environmental impacts of the case examined on human health, the quality of the ecosystem and the depletion of resources. The objectives of this methodology are to define a complete picture of the interactions with the environment of a product or service, helping to understand the environmental consequences directly or indirectly caused and therefore daring to those who have the decision-making power (who has the task to define the regulations) the information necessary to define the behaviours and environmental effects of an activity and identify opportunities for improvement in order to reach the best solutions to intervene on the reduction of the environmental impact.

The two main regulatory references that represent the main methodological standard for the execution of an LCA analysis applied in a general way, not referred to road works, will be analysed in detail below, since there is still no specific legislation in the national and European context.

5.4.2 EN ISO 14040- 14044

The increased awareness of the importance of protecting the environment and the possible impacts associated with the products/services manufactured and consumed has increased interest in the development of methods to better understand and reduce these impacts. One of these techniques under development is Life Cycle Assessment (LCA). The LCA can support:

- the identification of opportunities to improve the environmental performance of products in the different stages of their life cycle
- information to those who make decisions in industry and in governmental or non-governmental organizations (for example strategic planning, choice of priorities, design or redesign of products or processes)
- the choice of relevant environmental performance indicators with the related measurement techniques
- marketing (for example, the implementation of an ecological label system, an environmental claim or the production of an environmental product declaration).

For LCA professionals, ISO 14044 describes in detail the LCA implementation requirements. LCA deals with environmental aspects and potential environmental impacts throughout the product life cycle, understood as consecutive and interconnected phases of a product system, from the acquisition of raw materials through manufacturing and use, up to the treatment of end of life, recycling and final disposal (i.e. “from cradle to grave”).

The LCA study involves four phases, represented with the related connections in Figure 5-24

- Phase 1: the objective and scope definition
- Phase 2: the inventory analysis
- Phase 3: the impact assessment
- Phase 4: the interpretation

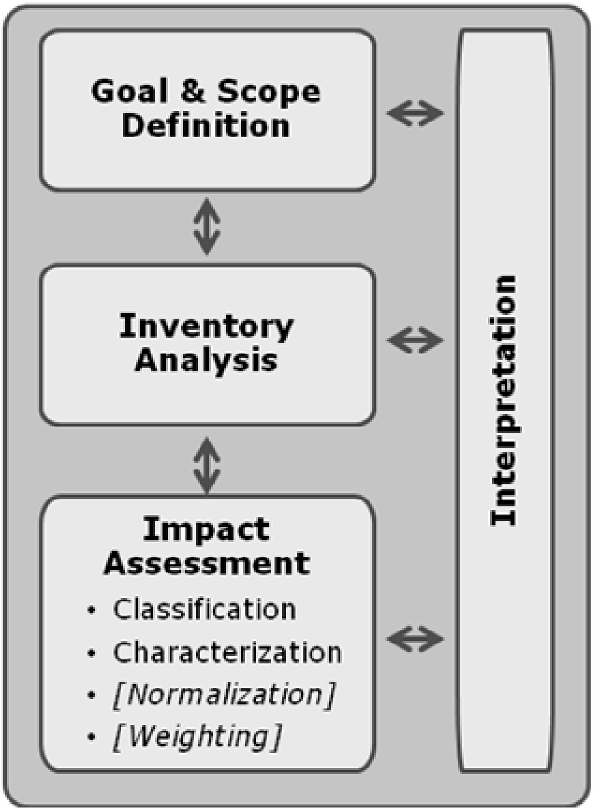


Figure 5-24 Stages of an LCA (ISO 14044)

The objective indicates the reasons for the study and the audience to whom the analysis is intended. The field of application, including the limits of the system and the level of detail of the LCA, depends on the subject and the intended use of the study. The depth and breadth of the LCA can differ considerably depending on the objective of a particular LCA. The scope includes the definitions of the product system studied, the functional unit, the system boundary, the allocation procedures, the selected impact categories, the methodologies for assessing the impacts and their interpretation, the quality requirements of the data and assumptions underlying the analysis.

The **life cycle inventory analysis** phase (LCI phase - "Life Cycle Inventory") is the second phase of the LCA. This is the inventory of incoming and outgoing data relating to the system to be studied. The LCI implies the collection of the data necessary to achieve the objectives of the defined study.

The **life cycle impact assessment** phase (LCIA phase - "Life Cycle Impacts Assessment") is the third phase of the LCA. The purpose of the LCIA is to provide additional information to help evaluate the LCI results of the product system in order to achieve a better understanding of their environmental significance.

The **Life cycle interpretation** is the final stage of the LCA procedure, in which the results of an LCI or an LCIA, or both, are summarized and discussed, according to the definition of the goal and scope, as a basis for conclusions, recommendations and decisions.

There are cases in which the objective of the LCA can be met by carrying out a single inventory analysis and interpretation. This is generally known as the LCI study. EN ISO 14040 covers two types of studies: **life cycle assessment** studies (LCA studies) and **life cycle inventory** studies (LCI studies).

In general, information obtained through an LCA or LCI study can be used as part of a much more comprehensive decision-making process. Comparing the results of different LCA or LCI studies is only possible if the hypotheses and context of each study are equivalent. Therefore, EN ISO 14040 contains several requirements and recommendations to ensure transparency on these topics.

LCA is one of several existing environmental management techniques (for example: risk assessment, environmental performance assessment, environmental audit and environmental impact assessment) and may not be the most suitable technique to be used in all situations. The LCA generally does not deal with the economic and social aspects of a product, but the life cycle approach and methodologies described in EN ISO 14040 can be applied to these other aspects.

LCA is a relative approach, structured around a functional unit. The functional unit defines what is studied. All subsequent analyses are then related to the functional unit, as all the input and output elements of the LCI and the LCIA profile are related to the functional unit.

As reported by the EN ISO 14040, the basic characteristics of the life cycle assessment methodology are listed:

- the LCA systematically examines the environmental aspects and the impacts of the product systems, from the acquisition of raw materials to final disposal, in accordance with the defined objective and field of application
- the relative nature of the LCA is due to the functional unit characteristic of the methodology
- the degree of detail and the temporal extension of the LCA are a function of the objective and field of application
- the LCA methodology is open to welcome updates on the state of the art of technology
- there is no single method for conducting LCA. Organizations have the flexibility to practically implement LCA in accordance with EN ISO 14040
- LCA is different from many other techniques (such as environmental performance assessment, environmental impact assessment and risk assessment), however it can use information collected by other techniques
- the LCA does not provide for the assessment of specific or absolute environmental impacts for the following reasons: the environmental impacts are related to a reference unit, there

is an intrinsic uncertainty in their modelling and, in most cases, they are expected impacts in future time

- the LCI and LCIA phases provide a perspective on the environmental problems and resources required of one or more product systems
- the LCIA assigns the LCI results to the impact categories. For each category, a life cycle impact category indicator is selected and the result of this indicator is calculated
- the LCIA profile provides information on environmental problems associated with the elements entering and leaving the product system
- there is no scientific basis for reducing LCA results to a single score or number, since weighting requires the choice of values
- Life cycle interpretation requires the use of a systematic process to identify, qualify, verify, evaluate and present conclusions based on the results of the LCA in order to meet the requirements described in the objective and scope of study
- the interpretation of the life cycle also provides for the identification of links between the LCA and other environmental management techniques, underlining the strengths and limitations of the LCA in relation to the definition of its objective and scope.

The object of the LCA is therefore the product system, understood as a system having one or more functions and divided into a series of unitary processes. The unit processes are connected to each other by flows of intermediate products and/or waste to be treated, they are related to other product systems by product flows and with the environment by elementary flows.

Dividing the product system into unitary component processes makes it easier to identify the elements entering and leaving the product system itself. The level of detail of the modelling that is required to meet the objective of the study determines the boundary of a unitary process. Elementary flows can include the use of resources and releases into the air, water and soil associated with the system. These data are the results of the LCI and constitute the input element for the LCIA.

The system boundary determines the unit processes that must be included in the LCA. It is necessary to establish which unitary processes to include in the study and the level of detail with which these unitary processes are to be studied.

EN ISO 14040 lists the unitary processes that must be included in the system boundary:

- acquisition of raw materials
- main process sequence
- distribution and transport
- production and use of fuels, electricity and heat
- use and maintenance of the product
- disposal of waste and process products;
- recovery of products after use (including energy recovery)
- manufacture of auxiliary materials
- manufacture, maintenance and disposal of main equipment.

The elimination of life cycle stages, processes, incoming or outgoing flows is allowed only if it does not significantly change the overall conclusions of the study and, in any case, must be appropriately justified. In particular, in the practice of LCA, various exclusion criteria are used, listed below according to the definitions of EN ISO 14044:

- mass: all the input elements that cumulatively contribute, in a way greater than a defined percentage, to the mass flow of the product system to be modelled must be included in the study

- energy: all the input elements that cumulatively contribute, in a greater than a defined percentage, to the input energy flow of the product system to be modelled must be included in the study
- environmental relevance: all input elements that contribute more than a quantity defined by the system data collected specifically for their environmental relevance must be included in the study.

The qualitative and quantitative data to be included in the inventory must be collected for each unit process included within the system boundaries. The collected data, whether measured, calculated or estimated, are used to quantify the input and output elements of a unitary process. When data is collected from those published in public sources, reference must be made to the source.

Since the data collection could cover different communication sources and published references, to achieve a uniform and consistent understanding of the product system to be modelled, measures need to be taken, including:

- drawing of non-specific process flow diagrams, which describe all the unitary processes to be included in the model, with their interrelationships
- detailed description of each unitary process with respect to the factors that influence the input and output elements
- list of flows and relevant data for the operating conditions associated with each unitary process
- development of a list specifying the units of measurement used;
- description of the data collection and calculation techniques required for all data.

The macro categories into which data can be classified include:

- incoming energy elements, incoming raw materials, auxiliary materials or other incoming physical entities
- products, co-products and waste
- releases into the air, water and soil
- other environmental aspects.

All calculation procedures must be explicitly documented, and assumptions must be clearly indicated and justified. The same calculation procedures should be consistently applied throughout the study. The incoming and outgoing elements related to combustible materials, for example oil, gas or coal, can be transformed into incoming and outgoing energy streams by multiplying them by the related heat of combustion. In this case it must be recorded whether the highest or lowest calorific value has been used.

The inputs and outputs must be allocated to the different products according to clearly defined procedures, which must be documented and justified together with the allocation procedure. The sum of the elements allocated in input and output of a unit process must be equal to the elements in input and output before the allocation of the unit process.

The allocation process is performed according to the following procedure:

Step 1: Wherever possible, allocation should be avoided by splitting the unit process to be allocated into two or more subprocesses and linking the inbound and outbound data related to those subprocesses, or by expanding the product system to include additional functions relating to co-products.

Step 2: Where the allocation cannot be avoided, the input and output elements of the system should be divided among its different products or functions so that they reflect the underlying physical relationships between them.

Step 3: Where physical relationships alone cannot be established or used as a basis for allocation, the inputs should be allocated between products and functions in a way that reflects the other relationships between them (e.g. in proportion to the economic value of the products).

The allocation procedures must be applied uniformly to the similar input and output elements of the considered system.

For reuse and recycling, additional processing is required for the following reasons:

- reuse and recycling may imply that the incoming and outgoing elements associated with the unitary processes for the extraction and treatment of raw materials and the final disposal of products are shared by more than one system of products
- reuse and recycling can change the properties inherent to the materials
- specific attention should be paid to the recovery processes when defining the system boundary.

Product systems that provide for recycling and reuse operations can be closed-loop, i.e. the material is recycled within the same product system, or open-loop, i.e. the material is intended to be reused in another recycling system products.

Different allocation processes are applicable to reuse and recycling, in particular:

- a closed-loop allocation process is applied to closed-loop product systems. It also applies to open-cycle product systems where there are no changes in the properties inherent to the recycled material. In such cases, the use of secondary material replaces the use of virgin materials
- for open-loop product systems, where the material is recycled into other product systems and the material undergoes a change in its properties, an open-loop allocation process is applied.

Such allocation procedures for divided unit processes should use as a basis for the allocation, if possible, in order: the physical properties, the economic value or the number of subsequent uses of the recycled material.

The LCA phase must be carefully planned to comply with the objective and scope of the LCA study. The LCIA phase must take into account the following sources of uncertainty:

- quality of LCI data as a function of the objective and field of application
- system boundary and data excluded, as the results of the LCI must be sufficient to calculate the results of the indicators for the LCIA
- environmental relevance of the LCIA results, which can be reduced due to the functional unit and the aggregation and allocation procedures.

The LCIA phase therefore includes the collection of the results of the indicators for the different impact categories, which together represent the LCIA profile for the product system.

The LCIA is made up of mandatory and optional elements. The mandatory elements are the following:

- selection of impact categories, category indicators and characterization models
- assignment of LCI results to the selected impact categories (classification)
- calculation of category indicator results (characterization).

When selecting impact categories, category indicators and characterization models in the LCA, reference must be made to the information and related sources. This also applies to the definition of new impact categories, category indicators and characterization models. The selection of impact categories must reflect a complete set of environmental problems related to the product system studied, taking into account the objective and field of application. In addition, for each category indicator, the environmental mechanism and the characterization model that relate it to the results of the LCI must be described.

For each defined impact category, the mandatory elements of the LCIA are:

- the identification of the purpose of the category, or on which environmental aspect the impact category affects
- the definition of the category indicator, understood as a quantifiable chemical phenomenon that causes an environmental impact
- the identification of the appropriate LCI results that can be assigned to the impact category, taking into account the category indicator and the identified purposes;
- the identification of the model and characterization factors.

Furthermore, the purposes of the categories and their environmental relevance must be defined. In addition to these mandatory elements, EN ISO 14044 also includes a series of recommendations, such as the international recognition of the impact categories, category indicators and characterization models used and their technical and scientific validity.

The LCIA classification phase involves the assignment of the LCI results to the impact categories and should consider the following aspects:

- the direct assignment of the LCI results relating to a single impact category
- identification of the results

After the characterization and before the other optional elements of the LCIA, the elements entering and leaving the product system must be represented by:

- the compilation of the results of the category indicators for the different impact categories, known as the LCIA profile
- inventory results that have not been assigned to impact categories, for example due to low environmental relevance
- data that are not elementary inventory flows.

Some of the optional elements of the LCIA reported by the EN ISO 14044 are the normalization of the category indicators with respect to a reference value, the classification by grouping of the impact categories, the weighting (assignment of weights to the different impact categories and aggregation of the results of the weighted indicators) and the analysis of data quality.

The applications of LCA in the field of environmental management tools include, among others:

- environmental management systems and the assessment of environmental performance such as the identification of the significant environmental aspects of a product
- environmental labels and declarations (ISO 14020, ISO 14021 and ISO 14025)
- the integration of environmental aspects in the design and development of a product (ISO/TR 14062)
- the inclusion of environmental aspects in product standards (ISO Guide 64)
- environmental communication (ISO 14063)

5.4.3 Life Cycle Assessment of designed asphalt solutions

LCA principles (EN 14040) were used for investigated four functional units, namely the designed PSs) made up of a wearing course, binder layer that differs by four asphalt mixtures here studied (HMA_{NB}, HMA_{PMB}, HMA_{PC} and HMA_{GRPC}), base and subbase layers; the road segment length was fixed at 1-km section and width equal to 10.5 m.

The main processes included in the "from cradle to gate" system boundary were combined for simplicity into 5 macro-processes, as follows:

- production and supply of materials: natural aggregates, bituminous binders (NB and PMB) and pellets used for making polymeric compounds (PC and GRPC) were produced into specific industrial facilities, placed respectively at 60 km, 240 Mn and 100 km from the asphalt manufacturing plant.

  In particular, while the NB derived from the heaviest fraction obtained from the distillation process of crude oil, PMB required an additional high shear milling phase than NB by adding SBS polymers.

  Instead, the conversion of virgin or waste plastic into pellets (either for making PC and/or GRPC compounds) involves the plastic collection, sorting, shredding, and palletisation (in which plastic shreds are heated up to 190 °C and then extruded to become pellets). After production, the amount of raw materials shown in the Table 2 was hauled to the asphalt plant.

- production and supply of the asphalt mixtures: the hot asphalt mixtures were manufactured at a high temperature (160 °C for HMA_{NB}, HMA_{PC} and HMA_{GRPC} and 180 °C for HMA_{PMB}) in a batch plant. The average annual natural gas and electricity consumption per tonne of asphalt mixture were made available by a local asphalt plant.
- construction of a road pavement section: the traditional construction technique involves a paver and a roller machine that work in series to lay the asphalt mixture on the surface and compact it. No differences exist in terms of equipment and productivity between traditional and modified asphalt mixtures.
- regular maintenance phase: ordinary activity carried out for all road pavements configuration and consequently not taken into account for the comparative analyses.
- end of life of the pavement: at the end of the predicted service life, the pavement is entirely milled, loaded in trucks, hauled to the nearest disposal site (45 km from the road under analysis) and dumped into the landfill.

The inventory data sources for the mixture production, construction, and disposal of the asphalt pavement were gathered drawing from several database sources [60][61][62].

A comparative analysis [63], was carried out involving four PSs made with layers with constant thicknesses that return different global service lives since different asphalt mixtures are used for making each binder layer. Thus, the inventory flows and the consequent environmental impact indicators of the life cycle of each PS configuration should be spread over the whole service life and only those referring to the same analysis period, which has been set equal to that of the reference PS with HMA_{NB} as the binder layer, should be considered.

This process is also known as allocation, namely the partition of the flows between the system under study and other systems that lay outside of the system boundary (EN 14040). In the present case, the environmental impact indicators have been calculated through the following equation

$$E_{ij} = E_{ij,N} \cdot \frac{N_{HMA_{NB}}}{N_j} \tag{25}$$

where

- E_{ij} is the value of the i-th environmental indicator (in the range from 1 to 18) of the j-th PS configuration (in the range from 1 to 4) referred to the service life of HMA_{NB};
- $E_{ij,N}$ is the value of the i-th environmental indicator (in the range from 1 to 18) of the j-th PS configuration (in the range from 1 to 4) referred to an analysis period equal to the service life N of the solution;
- $N_{AC_{NB}}$ is the service life of the reference PS configuration which provides HMA_{NB} as the binder layer, equal to 20 years;
- N_j is the service life of the j-th PS configuration (in the range from 1 to 4).

ReCiPe impact assessment method [64] was selected for assessing 18 environmental impact categories: climate change (GWP, kg CO_2 eq), stratospheric ozone depletion (ODP, kg CFC11 eq), ionizing radiation (IR, kBq Co-60 eq), damage of ozone formation on terrestrial ecosystems (OFT, kg NO_x eq) and human health (OFH, kg NO_x eq), fine particulate matter formation (PM, kg PM2.5 eq), terrestrial acidification (A, kg SO_2 eq), freshwater eutrophication (FE, kg P eq), marine eutrophication (ME, kg N eq), terrestrial, freshwater and marine ecotoxicity (T-ECO, F-ECO and M-ECO, kg 1,4-DCB eq), human carcinogenic (CT, kg 1,4-DCB eq) and non-carcinogenic toxicity (NCT, kg 1,4-DCB eq), land use (LU, m^2 crop eq), mineral resource scarcity (MR, kg Cu eq), fossil resource scarcity (FR, kg oil eq), and water consumption (W, m^3).

5.5 *Main results and discussions*

One of the main objectives of this study was to address the major issues regarding the design of high-performance recycled polymer modified asphalt mixtures based on the dry process. In this regard, three hot asphalt mixtures for road pavement binder layers were designed and compared. The reference mixture (HMA_{NB}) was produced using neat 50/70 bitumen and limestone aggregates from a local quarry. The other mixtures were prepared to highlight some key similarities and differences between such mixtures and the HMA_{NB}:1) HMA_{PMB} had the same OBC and volumetric properties as HMA_{NB}, but the neat binder was replaced with PMB containing SBS; 2) HMA_{PC} was also identical to HMA_{NB} in terms of the aforementioned parameters, but a polymer compound made from recycled plastics was added directly into the mixing machine during the dry process;) HMA_{GRPC} that had the same volumetric properties of HMA_{NB} but a graphene enhanced modifier made from recycled plastics was added directly into the mixing machine during the dry process.

5.5.1 Indirect tensile test and Moisture damage

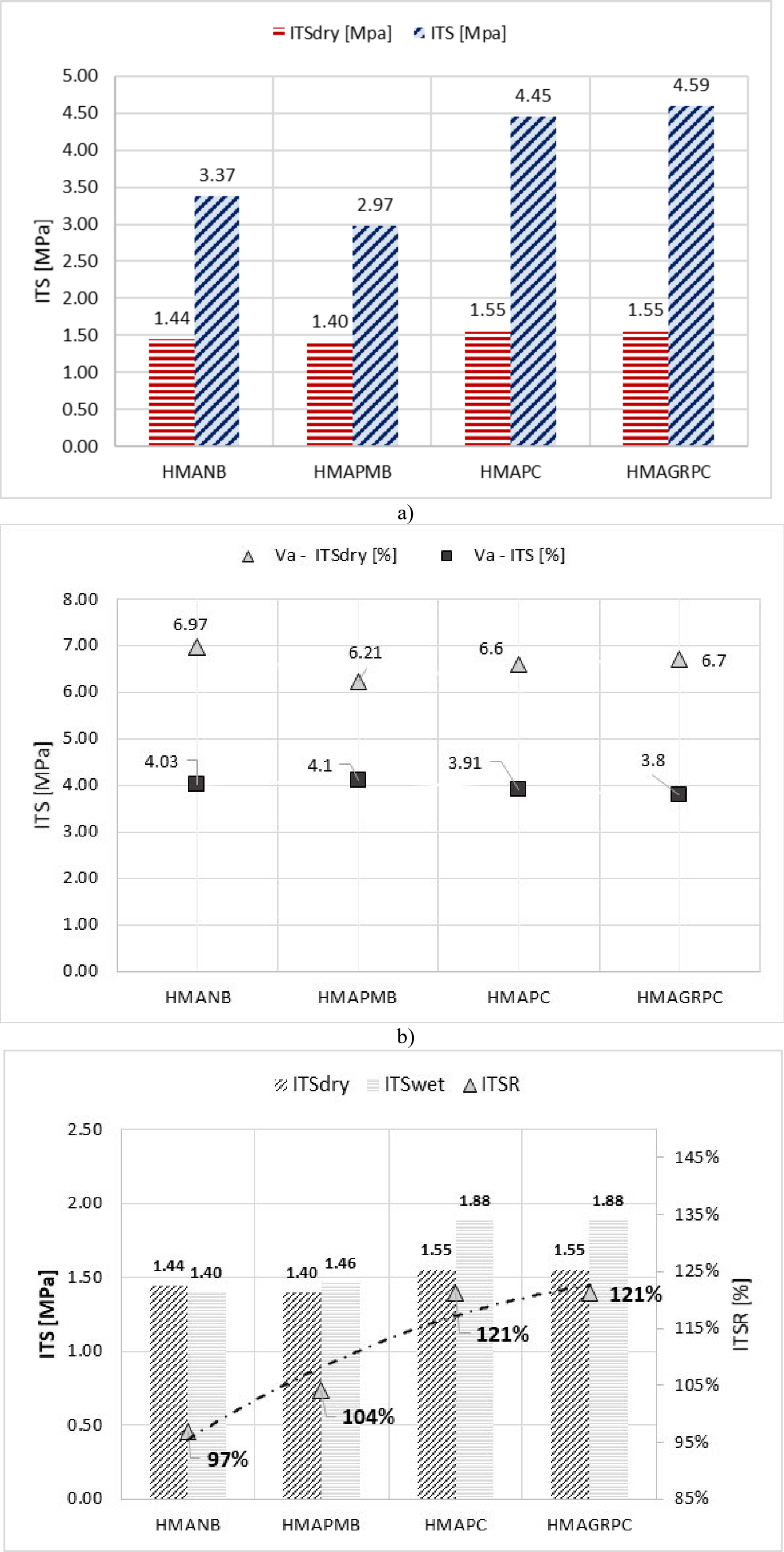
Figure 5-25 shows the results related to the moisture damage resistance evaluated by indirect tensile strength load configuration tests as described above. In detail it is possible to observe how:

a) In terms of ITS determined at 10°C on specimens compacted at N_{max} gyration number according to the proposed procedure (see Table 5.9), Figure 5-25**a** displays that the asphalt solutions containing the recycled polymer compound introduced by dry way, exhibit the highest ITS value equal to 4.45MPa and 4.59 MPa for HMA_{PC} and HMA_{GRPC} respectively, with an increment of 32% than traditional solution and of 50% than the asphalt mixture packaged using PMB for the HMA_{PC}. However, the asphalt solution modified using PMB shows the poorest ITS value (2.97 MPa) with a reduction of 13% than the traditional mixture assumed as reference. It is necessary to observe how the introduction of the graphene enhanced modifier leads to an increment of ITS resistance that estimated in a +36% than traditional mixture made with neat bitumen and a +54% referring to the PMB solution.

b) In terms of ITS_{dry} (red bars in Figure 5-25**a**) there are no substantially differences between the designed asphalt solutions since it moves from 1.4 MPa of traditional mixture and PMB solution to 1.55 MPa of both asphalt mixtures modified using dry process.

c) The ITS values determined at 10°C on specimens compacted at N_{max} gyration number (blue bars in Figure 5-25a) are roughly twice of ITS_{dry} values determined at 15°C on specimens compacted at 50 gyration number (red bars in Figure 5-25a); in detail, referring to the results shown by the HMA_{PC} and HMA_{GRPC}. the values of ITS are almost three times highly than the ITS_{dry} parameters. In detail, moving from ITS to ITS_{dry} analysis it is possible to find an increment of 75% for traditional asphalt mixture solution, and of 51% and 69% for the mixtures prepared using PMB and recycled polymers compound respectively. This results are surely due to the different air voids values deriving from the less compaction effort applied for ITS_{dry} specimens as shown by the grey triangle (ITS_{dry} air voids) and black squares (ITS air voids). in Figure 5-25b;

d) In terms of moisture damage, Figure 5-25c clarify that all investigated solutions have a good water resistance since all the mixtures exhibit an ITSR over 90% which indicate that not many differences occur between the ITS evaluated in wet and dry conditions. Also in this case, the graphene enhanced asphalt solution exhibits the highest moisture damage.



a)

b)

c)

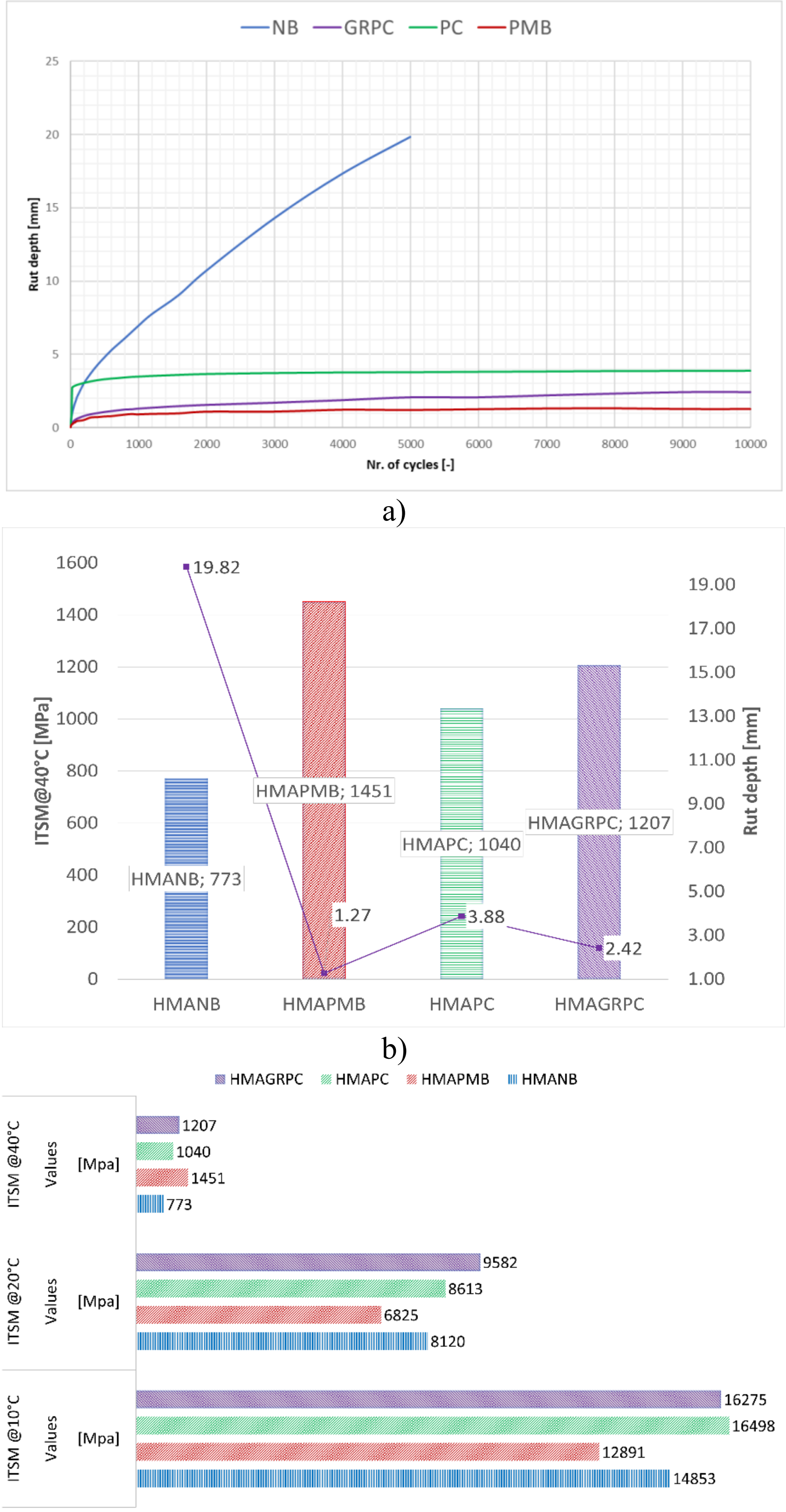
Figure 5-25: ITS analysis. a) ITS$_{10°C}$ *vs V*$_a$*, and ITS*$_{dry15°C}$*, b) ITSR vs ITS*

5.5.2 Rutting resistance

Figure 5-26 shows the results related to the rutting phenomenon, which was investigated in terms of the resistance of the HMA to the vertical compressive stress by ITSM evaluation (Figure 5-26**b**) and the susceptibility of the HMA to deformation (Figure 5-26**a**). In detail, Figure 5-26**c** represents the mean *ITSM* for each of the three asphalt mixtures at 10, 20, and 40 °C. In detail, it is possible to observe that:

a) Not all modified asphalt mixtures display an increment of stiffness modulus than traditional solution at all investigated temperatures. In detail, the PMB solution shows an reduction of 13% at 10°C and of 16% than HMA_{NB} solution and an increment of 88% at 40°C; otherwise, the asphalt solution prepared with recycled polymer compound HMA_{PC} displays a stiffness modulus an improvement of stiffness modulus equal to: 11% ,6% and 34% at 10,20 and 40°C respectively if compared to the traditional HMA prepared using neat bitumen. At the same time, it is necessary to remark how the asphalt solution modified using the graphene enhanced modifier exhibits the highest stiffness values at 10(+10% vs HMA_{NB} and +26% vs HMA_{PMB}) and 20°C (+18% vs HMA_{NB} and +40% vs HMA_{PMB}), while at 40°C it substantially improves the mechanical response of the stiffness in comparison with HMA_{NB} and HMA_{PC} solutions (+56% and +16% respectively), but the ITSM value is lightly lower than the PMB solution (1451 MPa for PMB vs 1207MPa of GRPC solution).;
b) The traditional asphalt solution exhibits the poorest resistance to permanent deformations, since it reaches a rut depth of 20.00mm at 5325 cycles; otherwise, all modified asphalt solutions display lower rut depth (1.27 mm for PMB solution, 3.88 mm for the asphalt mixture containing the recycled polymer and 2.42 for the GRPC solution) in correspondence of a higher numbers of cycles (10.000).

Moreover, asphalt solutions made up using PMA technology follow the same trend as the other two HMAs, regardless of the nature of applied load and the temperature. (Figure 5-26**c**).



a)

b)

c)

Figure 5-26: High-temperature mechanical properties. a) rutting resistance; b) ITSM at 40 °C vs rut depth c) ITSM test results at 10,20 and 40°C

To better understand the mechanical response, in terms of stiffness modulus, of HMA_{NB} and HMA_{PMB} solutions a comparison between ITSM values (see Figure 5-26c) with the rheological properties of the bitumen used in the mixtures (see Figure 5-5), it can be observed that at 20°C and 40°C the HMA_{NB} and HMA_{PMB} mixtures are consistent with the G* and δ trends (Figure 5-27a). At 40 °C, PMB is stiffer than the neat bitumen and more elastic, as reflected by the lower phase angle (see the green section in Figure 5-27a). Looking at the HMA_{PMB} mixture as a whole, it can be observed that at 40 °C, it has a mean ITSM value 88% higher on average than that observed for HMA_{NB} and that it reflects the rheological behavior of PMB, which exhibits a mean G* value higher than the neat bitumen. This can be attributed to the SBS polymer in the PMB, which maximizes the performance of the mixture at high temperatures, resulting in more elastic behavior under repeated load cycles. At 20 °C, the HMA_{PMB} mixture exhibits a mean ITSM 16% lower than HMA_{NB}, which is consistent with the complex shear modulus of the binder used in the mixture (see the red section in Figure 5-27), the mean value of which does not differ significantly between the PMB and the neat bitumen in this area. Similarly, within a region around the 10°C test temperature (orange section in Figure 5-27) it is possible to observe how a) the neat bitumen exhibits lower phase angle values than the PMB bitumen, and b) the shear modulus of PMB is 14% lower than that of neat bitumen. The same percentage reduction was observed for the HMA_{PMB} mixture when compared at 10°C with the HMA_{NB} mixture in terms of stiffness modulus.

These results, help to ascertain that while the behavior of HMA_{NB} and HMA_{PMB} depend on the rheological properties of the binders used, the mechanical improvement in asphalt mixtures modified using dry process (HMA_{PC} and HMA_{GRPC}) is substantially due to the addition of the polymeric compounds and it is also possible to ascertain that the use of different compounds leads to different mechanical performances.

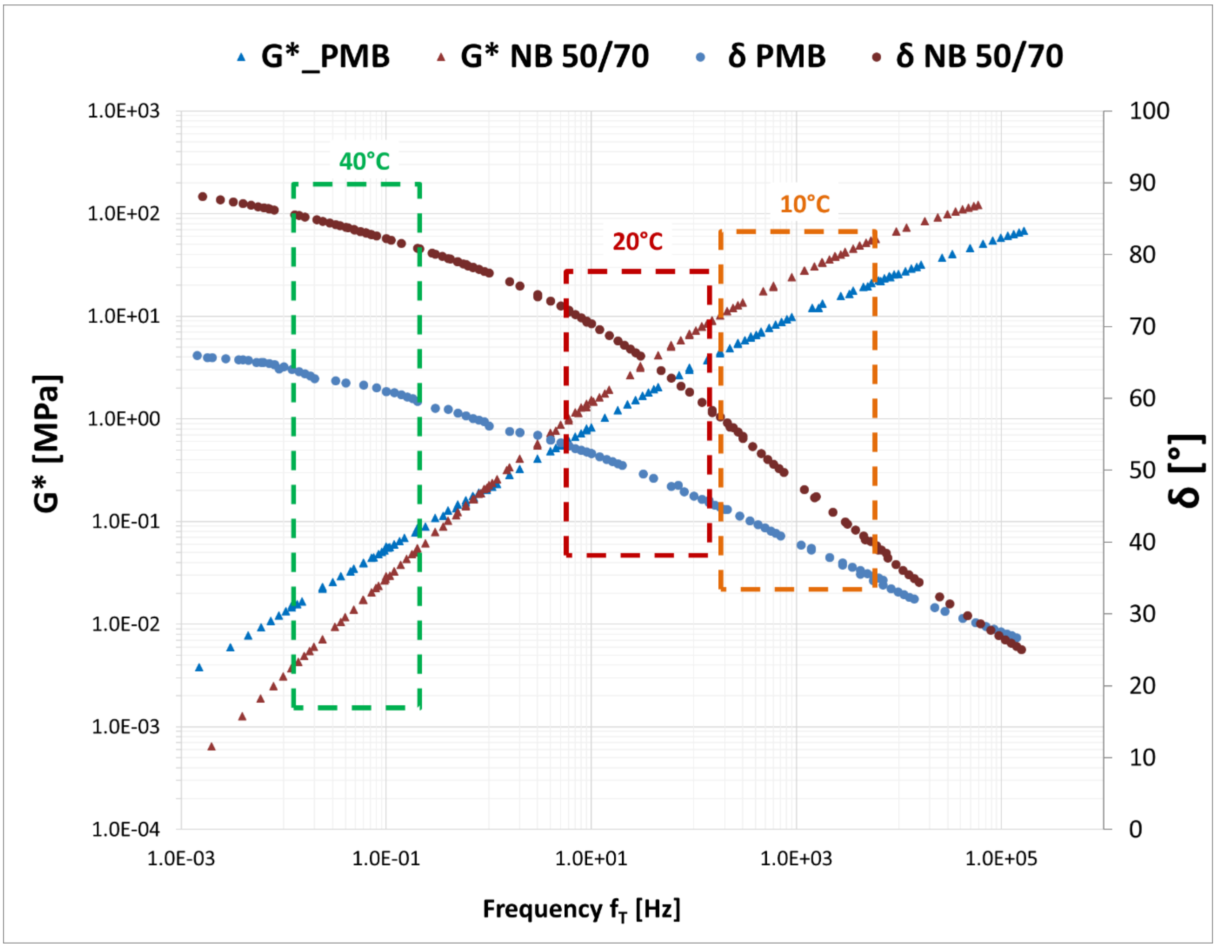


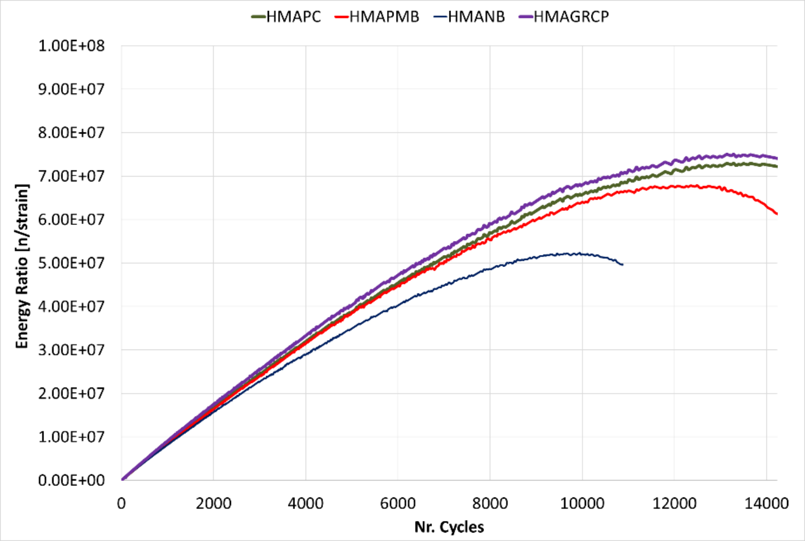
Figure 5-27: Comparison of mixtures: a) ITS vs ITSM at 10°C, b) G and δ for neat bitumen and PMB, c) ITSM at 20 °C and 40 °C*

5.5.3 *Cracking resistance*

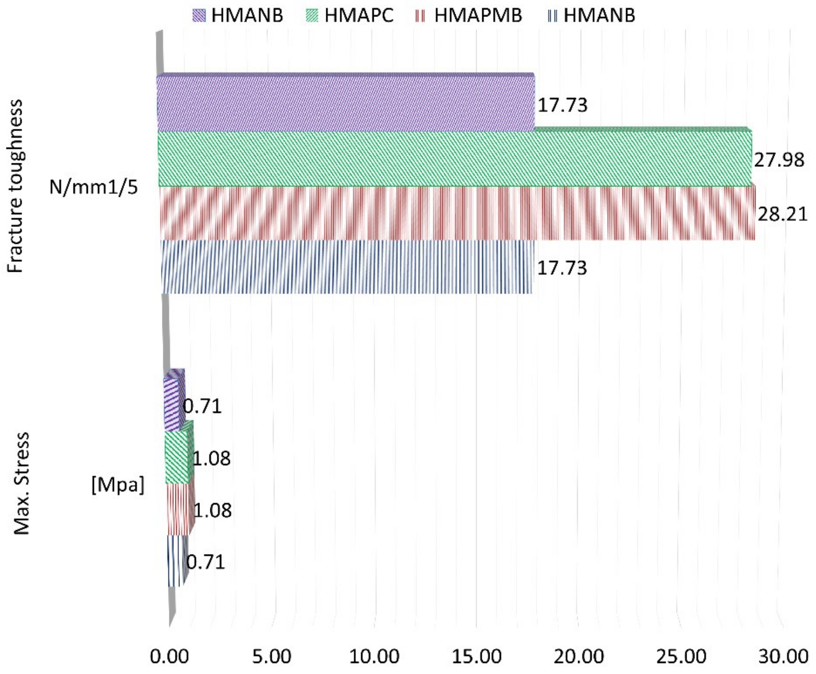
Referring to the failure mechanism during dynamic loading, the fatigue test results (Figure 5-28**a**) reflect the resistance of the asphalt mixtures to the first phase of failure, namely, the crack-initiation process. These results were compared with those of the SCB test (Figure 5-28b), which was conducted to investigate the resistance of the HMAs to crack propagation, which was the second part of the failure.

Figure 5-28**c** shows that HMA$_{GRCP}$ exhibited the greatest fatigue line (+45%) value and a superior resistance to crack than traditional asphalt solution, displayed with an increment of 50% in terms of maximum fracture stress and of 54% in terms of fracture toughness. Moreover, it is interesting to observe how the asphalt solution made up with recycled polymer compound

(HMA_{PC}) exhibits a very good resistance to crack initiation (high fatigue line value) that did not link with the greatest resistance to crack-propagation, because the SCB test result are almost the same of the asphalt mixture modified using PMB. This result can be surely related to the type of modification technology adopted and to the type of polymer/polymer compound added to the asphalt mixture. In particular it is possible to observe how the asphalt solution modified with the graphene enhanced modifier exhibits the best cracking resistance both in terms of cracking initiation phase and cracking propagation.



a)



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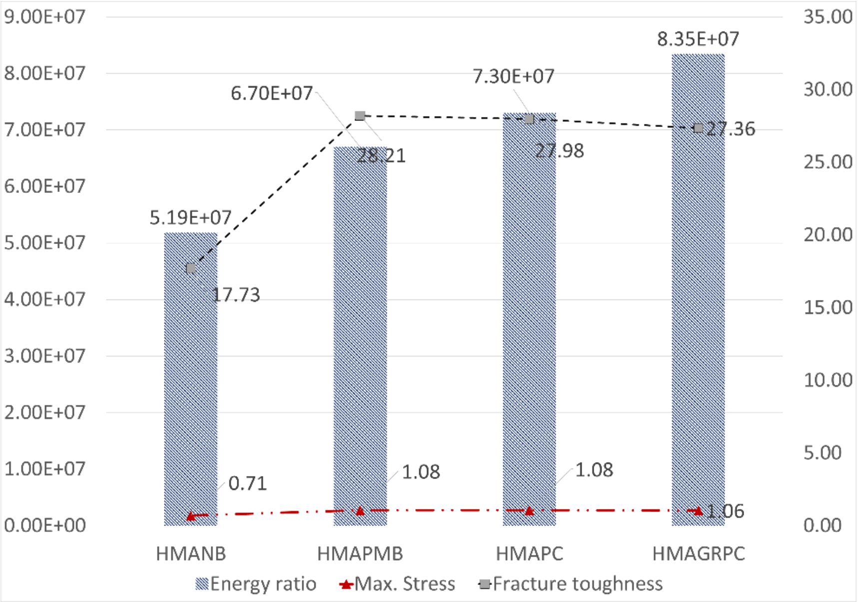


c)

Figure 5-28: Resistance to cracking. a) fatigue test results, b) SCB test, maximum stress and fracture toughness, c) relation between fatigue and SCB tests

5.5.4 Environmental impact

The Environmental impact has been evaluated considering the four pavement solutions (PS), which was designed using the four mixtures as the binder layer described before (HMA_{NB}, HMA_{PMB}, HMA_{PC} and HMA_{GRPC}), taking the linear elastic multilayer of the Boussinesq theory as the structural model of the pavement to calculate the stress-strain state and thus predict service life according to the fatigue damage and rutting resistance of the solutions as described on previous sections.

Starting from the analysis of the flows that stream trough the macro processes of the system (namely materials, fossil fuels, waste and pollutant emissions to air and water), 18 environmental impact indicators were calculated for each Pavement Structure involving HMA_{NB}, HMA_{PMB}, HMA_{PC} and HMA_{GRPC}.

Firstly, Table 5.13 shows some selected impact indicators (which showed the greatest variation between the solutions under analysis) for each macro-phase of the life cycle of the functional units, each one referring to its own design service life. As noticeable, all the indicators referring to the pavement construction and end of life phases do not show any variation since all the functional unit refer to the same pavement surface and thickness of the asphalt layers. Similarly, the asphalt mixture production and supply phase entails both the same impacts for PS1 (HMA_{NB}), PS3 (HMA_{PC}) and PS4 (HMA_{GRPC}), which are manufactured at the same temperature as discussed before. On the other hand, HMA_{PMB} demands around 10% more natural gas (required for drying the aggregates in the drum dryer) and electricity (that powers the high-temperature storage and feeding system of bitumen and the mixing of aggregates, filler, and bitumen for the production of the hot asphalt mixture) to produce 1 ton of asphalt mixture compared to HMA_{NB}, HMA_{PC} and HMA_{GRPC}; therefore, the selected impact indicators of PS2 are on average 8% higher than those of PS1, PS3 and PS4.

Looking at the aggregates production and supply phases, the slight differences in the mass composition of HMA_{NB} and HMA_{PMB} versus HMA_{PC} and HMA_{GRPC} reflect on the final impact indicators. Regarding bitumen production and supply, the production of PMB instead of NB entails additional environmental impacts; in particular, PMB emits additional 1.02 kg of hydrocarbons and 0.85 kg of SO_2 in air and 0.81 kg of sulphur compounds in water compared to NB for each kg of produced binder, which affects the GWP, FE and TECO.

Lastly, the PS3 and PS4 involve the production of PC and GRPC in a dedicated facility, which on average entail only 1% of the total emissions of the life cycle, being the least environmentally relevant process also due to the low amount in the mixture, up to 3% for the NCT indicator, which mainly depends on the CH_4 emissions to air during the palletisation process.

Therefore, without considering the different service life of the solutions, the wet (HMA_{PMB}) and dry (HMA_{PC} and HMA_{GRPC}) modification of asphalt mixtures entails additional environmental burdens compared to the HMA_{NB}. In addition, the PSs using recycled plastic pellets in the binder layer do not show a significant improvement of the impact category indicators compared to those with the HMA_{PMB} (on average −0.3%), above all due to high environmental burdens of the plastic palletisation process and long transportation distance. Moreover, the avoided amount of plastic waste going to landfill is not included in the analysed system boundary, therefore some of the positive benefits of using recycled plastic pellets for asphalt dry modification instead of bitumen modification are not accounted for in the present analysis.

Table 5.13 - Global warming potential, freshwater eutrophication, terrestrial ecotoxicity, human non carcinogenic toxicity and fossil resource scarcity for each phase of the life cycle referring to the four analyzed functional units.

Functional units	**Aggregates production and supply**	**Bitumen production and supply**	**Polymer pellets production and supply**	**Production of hot asphalt mixture**	**Pavement construction**	**End of life**
	GWP (kg CO_2 eq)					
PS1	1.54E+05	6.99E+04	0.00E+00	5.35E+04	3.38E+03	2.04E+05
PS2	1.54E+05	7.98E+04	0.00E+00	5.76E+04	3.38E+03	2.04E+05
PS3	1.53E+05	6.99E+04	3.55E+03	5.35E+04	3.38E+03	2.04E+05
PS4	1.53E+05	6.99E+04	3.00E+03	5.35E+04	3.38E+03	2.04E+05
	FE (kg P eq)					
PS1	4.26E+01	1.21E-01	0.00E+00	7.09E+00	1.32E-01	1.76E+01
PS2	4.26E+01	1.40E-01	0.00E+00	7.62E+00	1.32E-01	1.76E+01
PS3	4.25E+01	1.21E-01	9.68E-01	7.09E+00	1.32E-01	1.76E+01
PS4	4.25E+01	1.21E-01	8.40E-01	7.09E+00	1.32E-01	1.76E+01
	TECO (kg 1,4-DCB eq)					
PS1	1.70E+06	2.21E+04	0.00E+00	5.03E+05	4.54E+03	1.34E+06
PS2	1.70E+06	2.49E+04	0.00E+00	5.41E+05	4.54E+03	1.34E+06
PS3	1.69E+06	2.21E+04	2.43E+04	5.03E+05	4.54E+03	1.34E+06
PS4	1.69E+06	2.21E+04	2.08E+04	5.03E+05	4.54E+03	1.34E+06
	NCT (kg 1,4-DCB eq)					
PS1	1.45E+05	9.83E+02	0.00E+00	3.10E+04	5.11E+02	1.33E+05
PS2	1.45E+05	9.97E+02	0.00E+00	3.33E+04	5.11E+02	1.33E+05
PS3	1.45E+05	9.83E+02	8.13E+03	3.10E+04	5.11E+02	1.33E+05
PS4	1.45E+05	9.83E+02	6.87E+03	3.10E+04	5.11E+02	1.33E+05
	FR (kg oil eq)					
PS1	4.61E+04	3.35E+05	0.00E+00	1.65E+04	1.50E+03	6.63E+04
PS2	4.61E+04	3.35E+05	0.00E+00	1.78E+04	1.50E+03	6.63E+04
PS3	4.60E+04	3.35E+05	8.24E+02	1.65E+04	1.50E+03	6.63E+04
PS4	4.60E+04	3.35E+05	7.19E+02	1.65E+04	1.50E+03	6.63E+04

As mentioned before, functional units should be compared through the same time frame or analysis period. Therefore, Table 5.15 shows the total value of the impact category indicators of the functional units under analysis, assuming 20 years as the analysis period.

It can be noted that all the PSs involving the wet and dry-modified mixtures have an overall lower environmental impact of the life cycle compared to that of the PS1 with HMA_{NB} as binder layer, averaging 25% lower environmental impact indicators; in particular, PS4, PS2 and PS3 show each one an average reduction compared to PS1 equal to 37, 22 and 16%, respectively.

In addition, using the HMA_{PMB} entails the greatest reduction in correspondence of ME indicator (-23.5%), which is concentrated for 99% in the end-of-life phase and caused by run-off of phosphorus compounds from waste treatment industry and landfilling of asphalt waste.

Looking at the environmental performance of the dry-modified solutions, PS3 shows on average 8% higher indicators than those of HMA_{PMB}; this is due to two main reasons: a) the energy expenditure (350 kg of crude oil) and relative emissions to air of CO_2 (3.1 t), CH_4 (21 kg) and particulate matter (8 kg) during the synthesis of the polymer, palletisation process of the PC and transport to the asphalt plant, that cause an increase of GWP (+6%), A (+5%) and FR (+8%); b) the lower service life of PS3 compared to PS2 (see Table 5.14).

Table 5.14 - Pavement design parameters: Poisson ratio, thickness of the asphalt layers, accumulated fatigue damage, rut depth and predicted service life of the four designed pavement solutions.

Parameter	Units	PS1 (HMA_{NB})	PS2 (HMA_{PMB})	PS3 (HMA_{PC})	PS4 (HMA_{GRPC})
Poisson ratio	-	0.35			
Wearing course thickness	cm	4			
Binder layer thickness		5			
Base layer thickness		20			
FD	-	0.994	0.944	0.946	0.938
R	cm	0.360	0.346	0.352	0.349
Predicted service life	y	20	26	24	32

Instead, the PS4 with HMA_{GRPC} compensates the efforts of the GRPC production by prolonging the service life of the pavement up to 32 years; in particular, the greatest reduction of environmental indicators is reached for MECO (-58%, -22% and -34% compared to PS1, PS2 and PS3, respectively), due to lower NO_x emissions (-3 kg) for the supply of raw materials, and NCT (-56%, -20% and -30%, compared to PS1, PS2 and PS3, respectively), due to lower emissions of nitrogen and phosphorus compound entailed by the industrial manufacturing of aggregates and waste treatment.

Table 5.15 Midpoint impact category indicators for the pavement solutions under analysis referred to an analysis period of 20 years.

Indicators	**Units**	**PS1 (HMA_{NB})**	**PS2 (HMA_{PMB})**	**PS3 (HMA_{PC})**	**PS4 (HMA_{GRPC})**
GWP	kg CO_2 eq	484396.5	383340.9	406362.0	304432.5
ODP	kg CFC11 eq	0.2	0.2	0.2	0.1
IR	kBq Co-60 eq	21691.1	16838.2	18187.2	13624.0
OFH	kg NO_x eq	2571.4	2025.1	2149.1	1611.1
PM	kg PM2.5 eq	3921.6	3032.5	3272.5	2453.8
OFT	kg NO_x eq	2803.5	2213.1	2342.7	1756.3
A	kg SO_2 eq	1823.6	1453.5	1528.5	1145.3
FE	kg P eq	67.5	52.4	57.0	42.7
ME	kg N eq	626.7	482.1	522.7	392.0
TECO	kg 1,4-DCB eq	3571067.9	2778528.4	2993336.8	2242767.4
FECO	kg 1,4-DCB eq	18334.8	14176.0	15589.0	11660.3
MECO	kg 1,4-DCB eq	26175.0	20243.4	22225.0	16621.8
CT	kg 1,4-DCB eq	13908.1	10789.3	11722.3	8777.9
NCT	kg 1,4-DCB eq	310523.3	240686.1	265301.6	198188.7
LU	m^2a crop eq	44754.5	34522.7	37368.4	28016.2
MR	kg Cu eq	1691.8	1310.9	1419.4	1063.2
FR	kg oil eq	465124.5	358767.0	388213.7	291094.4
W	m^3	8096.3	6560.1	6754.9	5064.3

5.5.5 Summary of results

The principal findings of this study are summarized in Table 5.16**.** The data in this table were generated considering the following question: "What are the primary differences between the modified asphalt mixtures and a traditional hot asphalt mixture which comprises of limestone aggregates and 50/70 penetration-grade bitumen, in view of their mechanical properties?" The arrows are graphical representations of the results; so, their directions are correlated to the discussion just made in this paper and they should be read in combination with the corresponding section as defined in the table.

Table 5.16 - Trends of mechanical and environmental properties of the investigated asphalt mixtures

Mechanical related properties			**Mixture type**			
			HMA$_{NB}$	**HMA$_{PMB}$**	**HMA$_{PC}$**	**HMA$_{GRPC}$**
Conventional properties		ITS @10 °C	=	⬇	⬈	⬆
Moisture Damage		ITSR @15 °C	=	⬈	⬈	⬆
Rutting Resistance	Structural behavior (Stiffness)	ITSM @10 °C	=	⬇	⬈	⬆
		ITSM @20 °C	=	⬈	⬈	⬆
		ITSM @40 °C	=	⬆	⬈	⬈
	Susceptibility to deformation	Wheel tracker	=	⬆	⬈	⬈
Cracking resistance	Crack initiation	Fatigue test @10 °C	=	⬈	⬈	⬆
	Crack propagation	SCB test @10 °C	=	⬈	⬈	⬆
Environmental Impact	LCA	Life Cycle Assessment	=	⬈	⬈	⬆
Legend						
⬆ **Improvement**	⬈ **Slight improvement**		⬇ **Degradation**		= **Reference value**	

Table 5.16 underlines the differences between the asphalt mixtures and also highlights the following points:

- HMA_{GRPC} exhibited both- the lowest water susceptibility and the highest *ITS*.
- HMA_{PMB} exhibited the poorest response in terms of the conventional properties (*ITS*) and ITSM at .10°C
- A strong correlation was observed between the stiffness modulus values at 40 °C and the rutting resistance of the asphalt mixtures. This was because the lowest stiffness modulus (HMA_{NB}) corresponded to the highest rut depth and, the lowest permanent deformation (HMA_{PMB}) corresponded to the highest stiffness modulus.
- HMA_{GRPC} exhibited the best resistance to cracking during the crack-initiation phase; however, HMA_{PMB} achieved a better resistance to the cracking phenomenon during the crack-propagation phase.
- The HMA_{GRPC} shows the best mechanical response and the lowest environmental impact considering the entire service life of asphalt pavement.

5.6 ***Test track on real scale***

In the last phase, a test track was built to evaluate the response of the innovative polymer compound introduced in a real scale application. To ascertain this Pre- and post-production laboratory tests were conducted in addition to the periodical monitoring operations made on site. Since the binder layer was tested in laboratory scale, the wearing and base course were tested in the real scale.

In detail, two bituminous binders were used in this work: a PmB 45/80-65 (with high-content of SBS) and a 50/70 neat bitumen. It is worth mentioning that the mixtures were first optimized for the mixture containing the SBS PmB and then the same hot asphalt mixture compositions were used for producing the same asphalt mixture but containing a Graphene and Waste-hard-Plastic (GWP) asphalt modifier and 50/70 neat bitumen. Accordingly, the Optimum Bitumen Contents (OBC) following Marshall method, were 4.3% and 5.39% (for the Base/binder and surface course respectively).

The test track of this case study was conducted consisting of 4 sections: 1) 40-50 mm surface course containing SBS PmB; 2) 40-50 mm surface course containing the graphene and waste-hard-plastic asphalt modifier; 3) 40-50 mm surface course containing on an 80-100 mm base/binder course both containing the graphene and waste-hard-plastic asphalt modifier; and 4) 40-50 mm surface course containing on an 80-100 mm base/binder course both containing SBS PmB. Obviously, for this reason the existing pavement was milled up to 150mm, cleaned, and covered with a tack coat bitumen emulsion before installing the new layers.

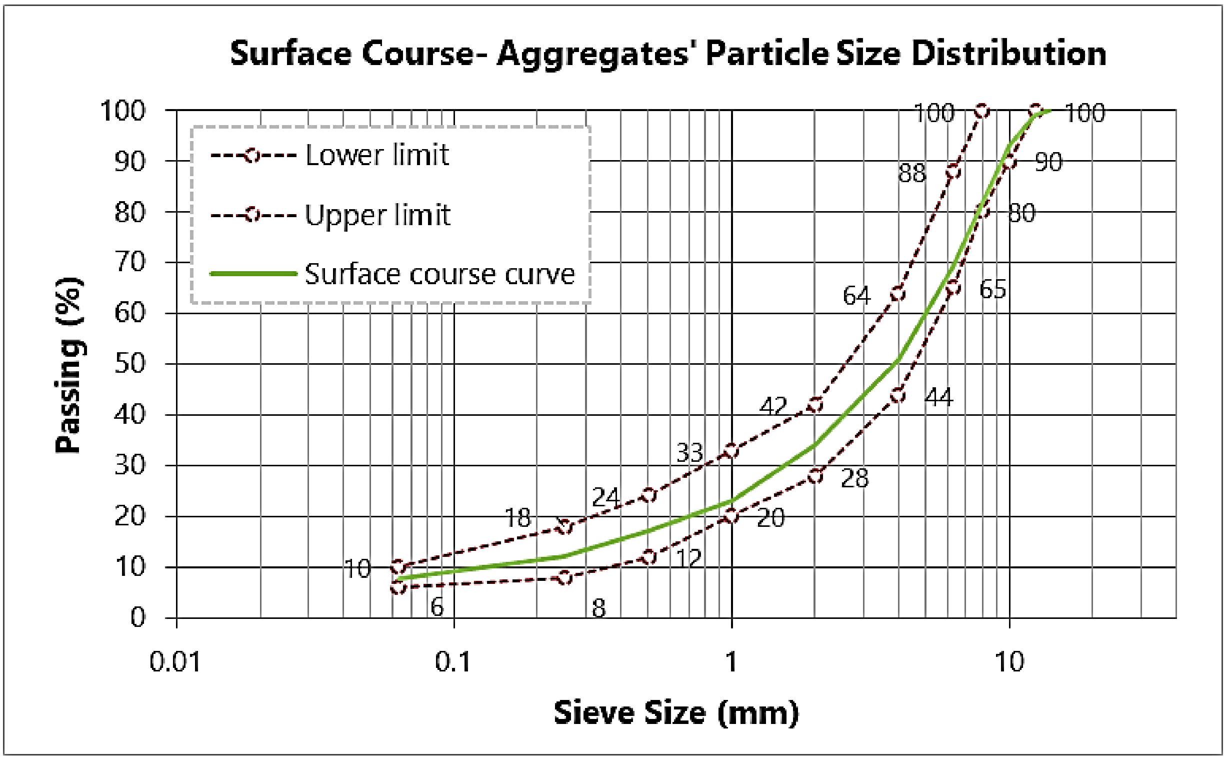
5.6.1 Designed HMA for test track

Considering the objectives of this work, the asphalt mixtures were modified by applying two different methods for the different asphalt modifiers of this study:

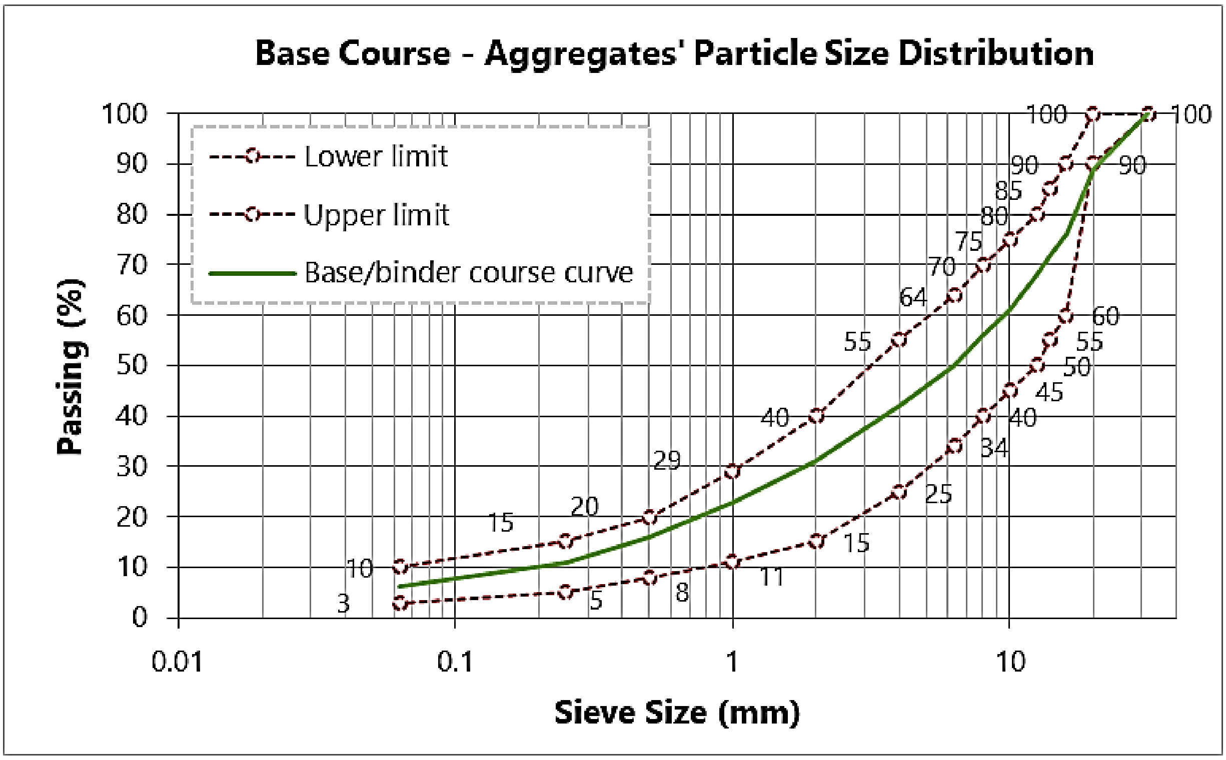
I. Dry method; a Graphene and Waste-hard-Plastic (GWP) asphalt modifier was added directly to the hot aggregates before adding the bitumen and filler. The dosage was determined during the mix design procedure and it was 6% on mass of the bitumen.

II. Wet method; the bitumen was previously modified with SBS and used to produce the asphalt mixture.

The aggregate distribution curves shown in Figure 5-29 were set according to local specifications containing 10% and 20% of Reclaimed Asphalt (RA) by mass of the aggregates for the surface (wearing) course and the base/binder course, respectively. Naturally, these OBCs also include the aged binder of the reclaimed asphalt in the mix design. As it can be seen both the surface and the base/binder course were of dense-graded asphalt mixtures.



a)



b)

Figure 5-29: The grading bands and aggregates' particle distribution.

5.6.2 Pre and Post production tests

Bearing in mind the targets of this applied study, the testing and quality control programme was divided into two main sections of lab-scale experimental works (pre- and post-production) and in-situ inspections and monitoring.

As mentioned earlier, during the pre-qualification lab tests, the mixes were produced following the dry method procedure. Accordingly, the graphene and waste-hard-plastic asphalt modifier was added to the hot aggregates at 180±5°C. Then the mix was maintained in the oven for some minutes (approx. 45 minutes) to let the additive become soft before adding the hot bitumen at 160°C. On the contrary, as a wet method, to produce the SBS PmB mix the PmB was heated and added directly to the hot aggregates. Anyway, both mixtures were produced and compacted at the same temperature. However, it is worth mentioning that as for the post-production phase, both collected asphalt samples from the job site were re-heated at 160°C and compacted at 155±2°C. It is noteworthy that except for the permanent deformation test, all the pre-and post-production test specimens were manufactured applying N_3 (N_{max}) gyration number according to the Italian specifications. In this sense, while the gyratory-compacted specimens contained plus 2% air voids, the slabs to be tested for resistance to rutting were compacted at 4% air voids content. The manufactured specimens were subjected to the following tests all according to the European standard testing methods:

- Indirect Tensile Strength (ITS) 12697-23 at 25°C EN;
- Indirect Tensile Stiffness Modulus (ITSM) EN 12697-26 IT-CY at 5, 20, 40°C;
- resistance to permanent deformation, Wheel Tracking Device (WTD) EN 12697-22 at 60°C;
- and resistance to Fatigue, Indirect Tensile Fatigue Tests (ITFT) EN 12697-22 at 20°C.

Finally, the monitoring of the test track was carried out with precise inspections of three pavement experts. For this target, the presence of visible cracking, edge deteriorations, and rutting were controlled for two executive years exactly after the first and the second year of the pavement installation. Further details are explained in the following related section.

5.6.3 Test track results and analysis

Figure 5-30 and Figure 5-31 show the ITS test's results for the surface course and base/binder course, respectively. Accordingly, the following highlights can be drawn by analysing the obtained results.

- The same trend was observed for both pre-qualification tests' results and post-production control results for both the mixtures. For both mixtures, during the pre-qualification phase, the mixture made of SBS PmB showed lower ITS vales compared to the mixture containing recycled-plastic modifier. This from one hand could show the validity of the obtained results and from another hand shows the accuracy of the mixture produced in the plant.

- For both surface and base/binder course, the asphalt mixture containing recycled-plastic modifier displays showed eighter equal or higher values compared to the mixture made of PmB.

- No large difference was obtained between the values of the surface course and the base/binder course. This could be eighter due to the very similar void content or proportion of the binder content.

In both pre-qualification tests' results and post-production control tests' results, very similar results were obtained for the asphalt mixture containing recycled plastic modifier. This, on one hand, assures the homogeneity of the mixture produced via the dry method and from another hand shows the conformity of the procedure followed in the laboratory to what was followed during the production in the asphalt plant.

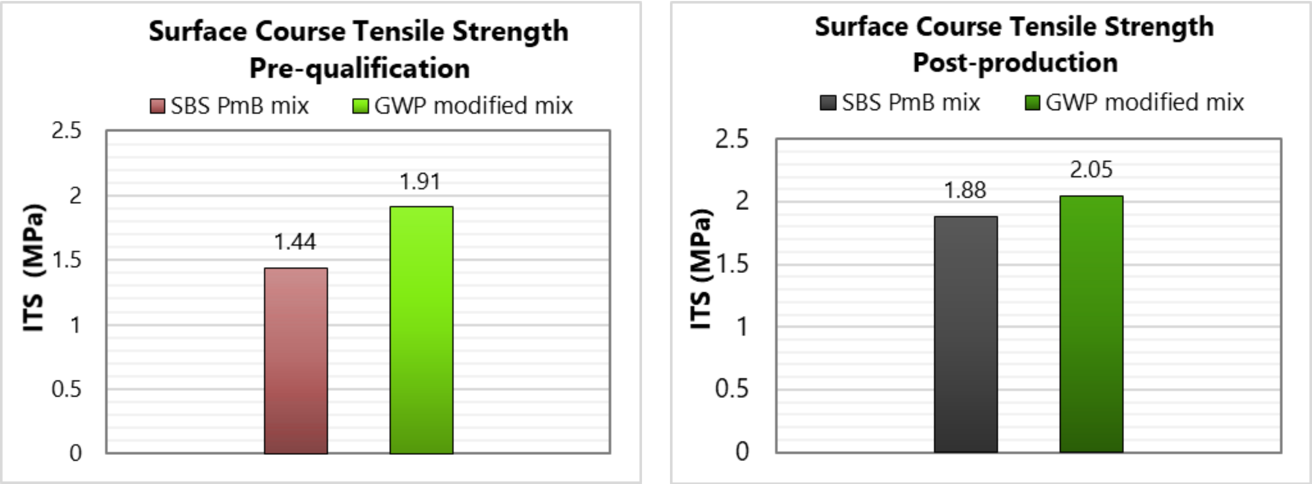


Figure 5-30: Pre-and post-production Indirect Tensile Strength (ITS) of the surface course

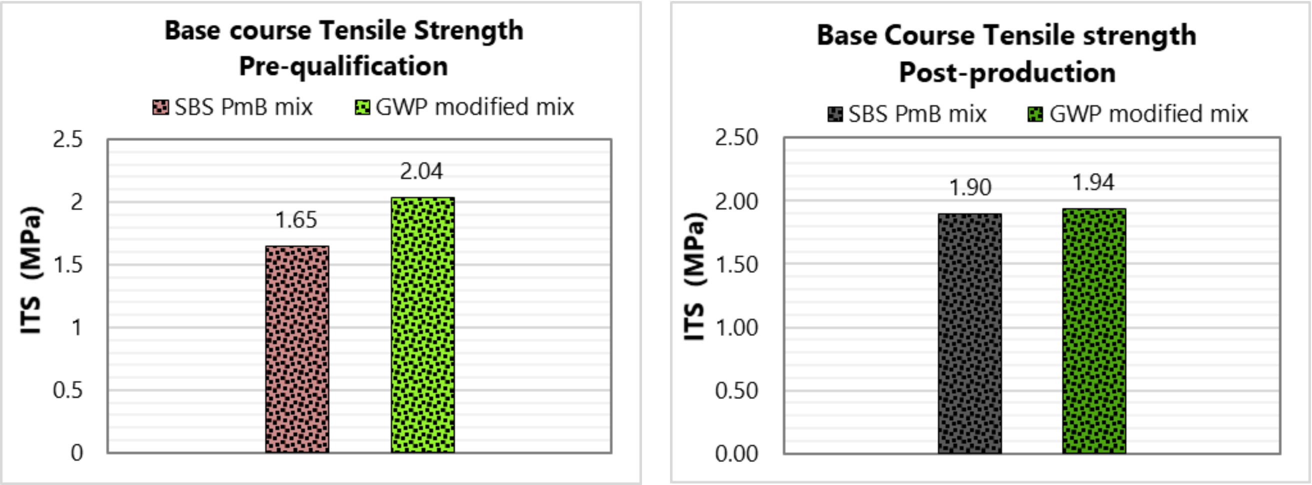


Figure 5-31: Pre-and post-production Indirect Tensile Strength (ITS) of the base/binder course

According to the results shown in Figure 5-32and Figure 5-33, for both of surface and base/binder course the asphalt mixture manufactured using the recycled-plastic asphalt modifier showed a higher stiffness modulus compared with the control mixture made of SBS PmB.. However, considering the type of road and its location in a warm climate zone, the pavement's properties at medium to high temperatures are more impactful on the service life of the pavement. In addition, considering that the stiffness of bituminous mixtures is a key parameter for the analysis and rational structural design of flexible pavements, starts from the results provided above, higher service life is expected and an improvement of resistant to permanent deformation can be observed.

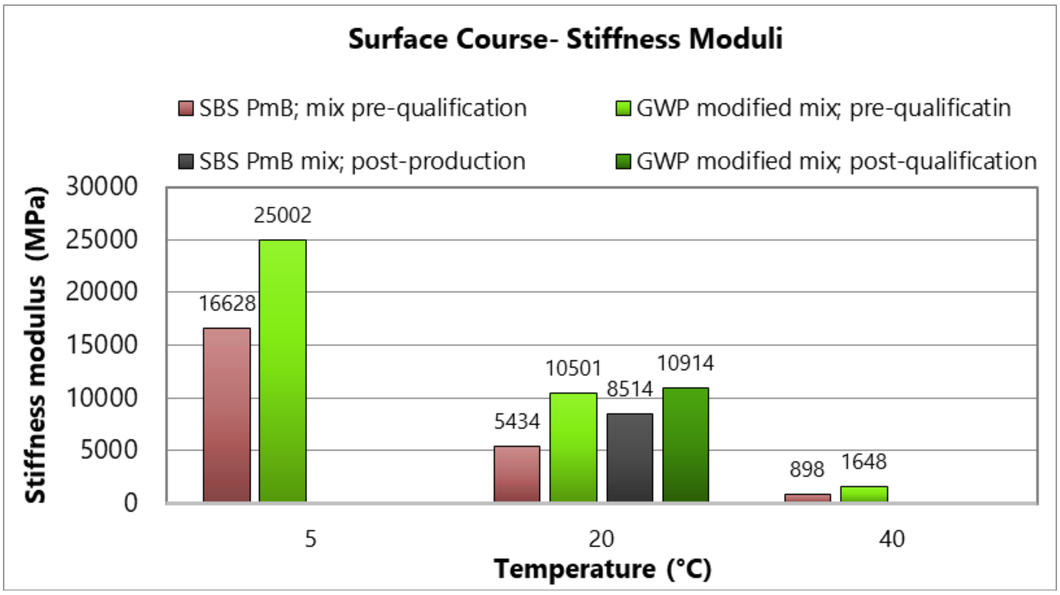


Figure 5-32: Pre-and post-production Indirect Tensile Stiffness Moduli (ITSM) of the surface course

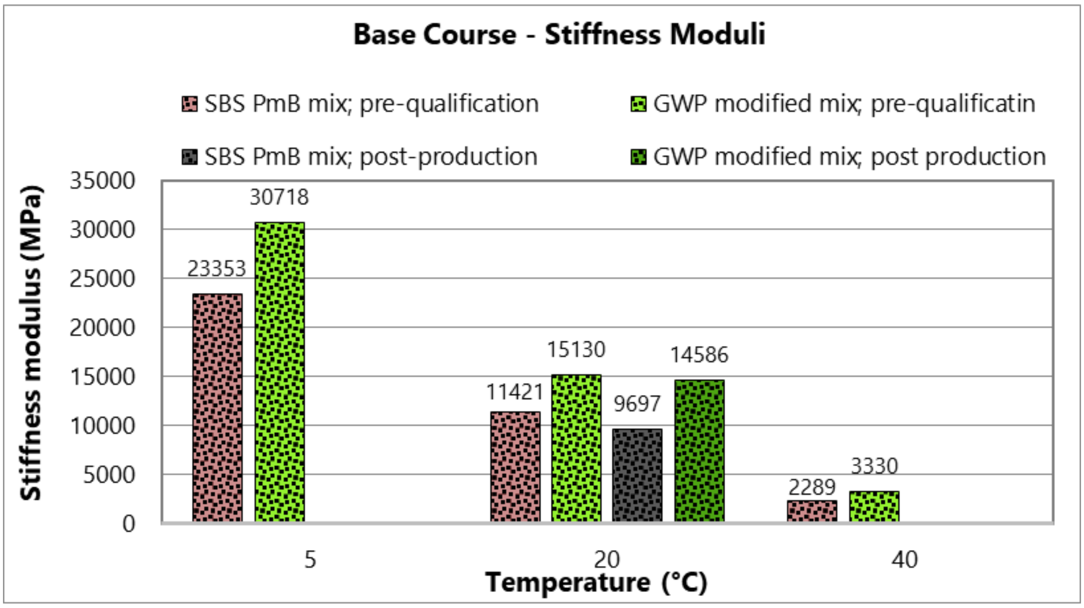


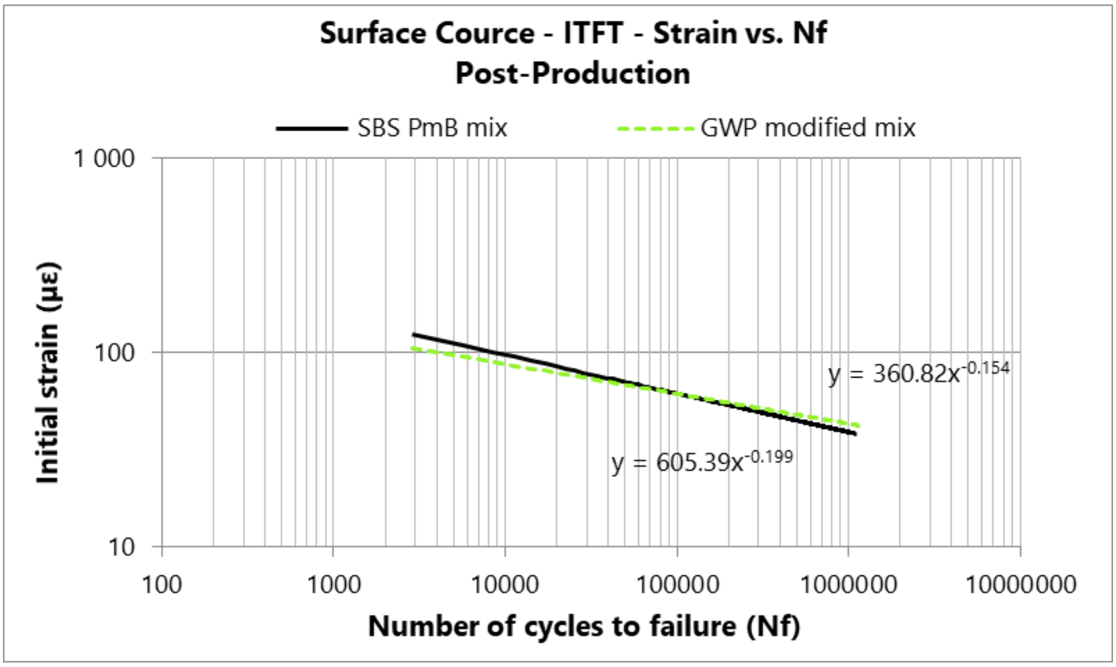
Figure 5-33: Pre-and post-production Indirect Tensile Stiffness Moduli (ITSM) of the base/binder course.

As it can be seen in Table 5.17 the resistance to permanent deformation of the mixtures is almost the same for the tested mixtures. This shows the viability of asphalt modification via dry method for heavy-duty asphalt pavements. In fact, both mixtures complied with the threshold values of the local technical specifications, which are Wheel-Tracking Slope $WTS_{air0.1}$ and $WTS_{air1.0}$ for the surface course and binder course, respectively.

Table 5.17: Wheel tracking resistance to rutting test results.

Mix	Surface course			Base/binder course		
	Rut depth (mm)	**Proportional rut depth (%)**	**Wheel-tracking slope (mm/10^3)**	**Rut depth (mm)**	**Proportional rut depth (%)**	**Wheel-tracking slope (mm/10^3)**
SBS PmB mix	1.92	3.87	0.07	2.60	2.89	0.09
GWP modified mix	1.91	3.82	0.07	2.50	2.87	0.09

Referring to the fatigue resistance, Figure 5-34and Figure 5-35 show the fatigue plots of the tested mixtures obtained during the post-production tests and analysis. As it can be seen almost the same trend was obtained for both surface and base/binder course. According to the strain vs. Number of cycles (N_f) fatigue plots, both mixtures showed relatively similar fatigue behaviour, where for the surface and base/binder course a very similar initial strain related to 1 million cycles (ε_6) was recorded. It is noteworthy that the low ε_6 values obtained in this study, was due to the characteristics (volumetrics) of the test specimens given as was mentioned in the section methods, the test specimens were compacted at N_3(max) to comply with the local specification. Naturally, low-air void compacted specimens resulted in high moduli and lower strains.



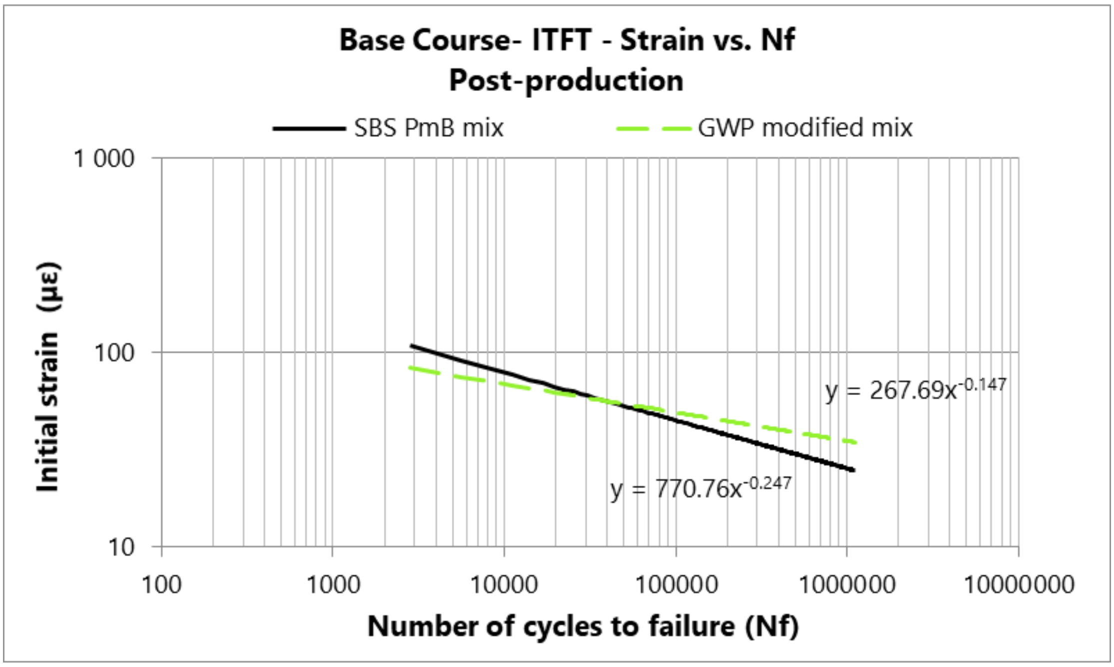
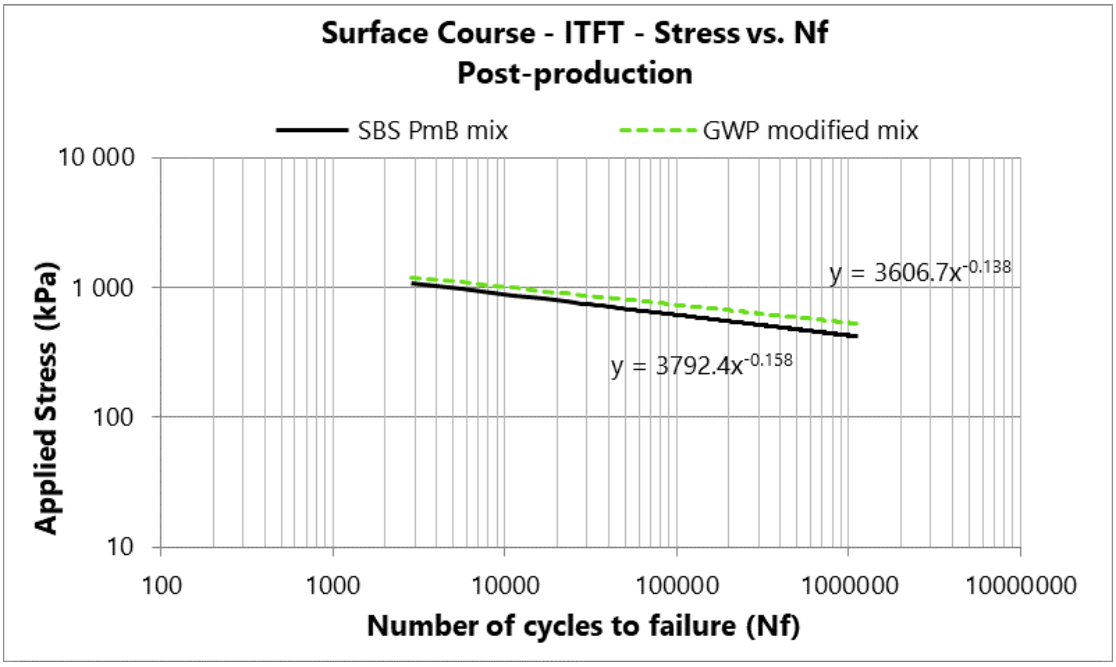


Figure 5-34: Strain vs. Number of cycles to failure (Nf) fatigue life plots of the test mixtures



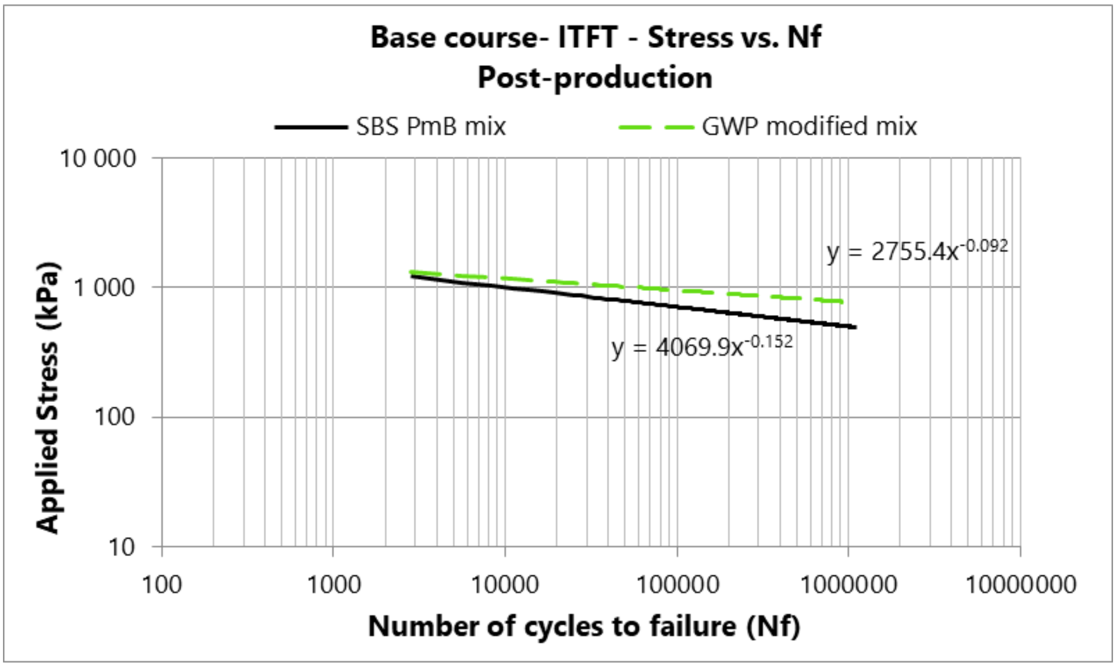


Figure 5-35: Stress vs. Number of cycles to failure (Nf) fatigue life plots of the test mixtures.

Considering that ITFT test is carried out under stress control mode, the stress vs Number of cycles to failure (N_f) fatigue plots were also elaborated, analysing the fatigue performance from a different perspective. According to the obtained fatigue plots, the same trend of strain vs. the number of cycles to failure was observed, which was also in line with other recorded characteristics of the mixtures. This has been obtained in several previous similar research studies.

5.6.4 Trial section monitoring

The periodical pavement inspection and monitoring were carried out to evaluate the pavement surface condition and to identify the presence of early-stage pavement damage. The pavement experts' inspection was carried out after the first and second year of pavement’s installation and this will continue to provide a real picture of the test section under service. According to the precise controls, no pavement distress was observed on the test track.

6 Conclusions

Engineering superior asphalt mixtures via recycling plastic and nano platelets of graphene compounds through the dry process into asphalt mixture is possible. The presented research study aims to compare a traditional asphalt mixture (HMA_{NB}) with asphalt mixtures modified with the wet process (HMA_{PMB}) and two other eco-friendly asphalt modifiers, applying the dry process (HMA_{PC} and HMA_{GRPC}). For this purpose, an SBS polymer modified bitumen was used to prepare the HMA_{PMB} mixture and two different polymeric compounds, including a plastomeric and a graphene-enhanced were studied added to the aggregates and the 50/70 penetration grade neat bitumen to prepare the asphalt mixtures in PMA technology. The mix design process was conducted for HMA_{NB} mixture following Superpave method, and the same bitumen amount was used for all investigated mixtures. Different procedures were adopted during the mixing and compaction (gyratory compactor was used) phases for every mixture, in order to reach the same volumetric properties for all investigated mixtures at N_{des} and N_{max}. Mechanical characterization of the asphalt mixtures was then conducted, to evaluate the performance of the PMA additives compared to reference mixtures of SBS PmB and 50/70 penetration grade neat bitumen.

Considering the obtained test results and conducted investigations, it is possible to conclude that the PMA modification process was found a promising solution for the purpose of increasing the mechanical properties of asphalt mixtures. This allows reducing the shortcomings related to the PmB modified asphalt. It is possible to see how the choice of a correct polymeric compound as modifiers for PMA process would result in a high-performance asphalt mixture and a correct choice for sites with extreme conditions temperature ranges and loads. The investigated properties in this research evidently showed this potential. From the analysis of results the HMA_{NB} solution showed adequate mechanical properties according to the technical specifications to be used for low traffic roads that are located in medium temperature areas; however, the investigated PmB containing asphalt mixture could be a better alternative for the roads located in high temperature climates given it showed enhanced properties at 40°C but not at 10°C and 20°C. Instead, the PMA mixtures can be adopted in a larger temperatures range condition. From the analysis of the results some highlights are concluded as follows:

- In line with the existing literature on the waste-plastic modified asphalts, the asphalt containing the graphene and waste-hard-plastic (GWP) asphalt modifier showed increased stiffness and strength. This has been achieved both investing the asphalt mixtures in laboratory and real scale making pre- and post-production tests.
- As it could be expected by considering especially the post-production stiffness and strength values, both tested mixtures exhibited very similar resistance to permanent deformation. This has also been recorded in many previous researches on the waste-plastic modified asphalts, discussed earlier in the section literature review of this paper.
- According to the test results of this study, the fatigue life of the asphalt containing recycled-plastic asphalt modifier was greater or comparable compared to the same mixture made of SBS PmB. However, the authors believe that the type of waste plastics, selected for the production of the asphalt modifier, plays a key role.
- During the production of the modified asphalt by applying dry method, neither logistic issue nor compaction difficulties were observed. In fact, the post-production tests' results were in line with those of the pre-qualification phase showing the dry-method as a more sustainable eco-friendly technology, which requires less energy.
- This study provide evidence that also via adapting laboratory-scale mixing procedure to ensure complete dispersion of the polymeric compound in the asphalt matrix, allows to design recycled PMA with comparable properties to modified asphalt mixtures with PMB.

- The graphene-enhanced pellet modifier allows to extend the service life of the asphalt pavements compared to traditional asphalt mixtures and other asphalt modification technologies which have been used so far (using polymer modified bitumen or plastomeric polymer pellets), also encouraging the road industry sector to recycle waste hard plastics, that are usually destined to waste-to-energy plants.
- Moreover, the LCA (from cradle to grave) highlighted the specific environmental fields on which the benefits of using a graphene-based modification strategy have been detected. In particular, an asphalt pavement made up of a 5 cm-thick binder layer modified with graphene-enhanced recycled polymer pellets leads to a 58% reduction of marine ecotoxicity indicator compared to that of a traditional asphalt pavement, assuming 20 years as the analysis period through which the flows of the system have been analysed.
- HMA_{GRPC} compensates the efforts of the GRPC production by prolonging the service life of the pavement; in particular, the greatest reduction of environmental indicators is reached for MECO (-58%, -22% and -34% compared to PS1, PS2 and PS3, respectively), due to lower NOx emissions (-3 kg) for the supply of raw materials, and NCT (-56%, -20% and -30%, compared to PS1, PS2 and PS3, respectively), due to lower emissions of nitrogen and phosphorus compound entailed by the industrial manufacturing of aggregates and waste treatment.
- Two years of monitoring by means of experts' visual inspection showed no distress. This could prove the viability of recycled-waste plastics as a sustainable asphalt modifier that allows both environmental reservation and circular economy.

References

[1] Asphalt Institute. (1996). Superpave Series No. 2 (SP-02). Asphalt Institute. Lexington, KY, USA.

[2] Di Maio, F., Rem, P. C., Baldé, K., & Polder, M. (2017). Measuring resource efficiency and circular economy: A market value approach. Resources, Conservation and Recycling, 122, 163-171.

[3] Kjaer, L. L., Pigosso, D. C., Niero, M., Bech, N. M., & McAloone, T. C. (2019). Product/service-systems for a circular economy: The route to decoupling economic growth from resource consumption. Journal of Industrial Ecology, 23(1), 22-35.

[4] Bocken, N. M., De Pauw, I., Bakker, C., & Van Der Grinten, B. (2016). Product design and business model strategies for a circular economy. Journal of industrial and production engineering, 33(5), 308-320.

[5] COM, E. (2014). 398 final "Towards a circular economy: A zero waste programme for Europe". Brussels, 2, 2014.

[6] https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52008DC0400

[7] Roberts, F. L., Kandhal, P. S., Brown, E. R., Lee, D. Y., & Kennedy, T. W. (1991). Hot mix asphalt materials, mixture design and construction.

[8] Munera, J. C., & Ossa, E. A. (2014). Polymer modified bitumen: Optimization and selection. Materials & Design (1980-2015), 62, 91–97. https://doi.org/10.1016/j.matdes.2014.05.009

[9] Jaskula, P., Szydlowski, C., & Stienss, M. (2018, May). Influence of bitumen type on cracking resistance of asphalt mixtures used in pavement overlays. In IOP Conference Series: Materials Science and Engineering (Vol. 356, No. 1, p. 012010). IOP Publishing.

[10] http://rahabitumen.com

[11] Amin, I., et al. Evaluation of Polymer Modified Asphalt Mixtures in Pavement Construction;

[12] Becker, Y., Mendez, M. P., & Rodriguez, Y. (2001). Polymer modified asphalt. In Vision tecnologica.

[13] Kalantar, Z. N., Karim, M. R., & Mahrez, A. (2012). A review of using waste and virgin polymer in pavement. Construction and Building Materials, 33, 55-62.

[14] Grzybowski, Kenneth F. Recycled oil-and rubber-modified asphalt and method of use. U.S. Patent No 9,944,796, 2018.

[15] Zhu, J., Birgisson, B., & Kringos, N. (2014). Polymer modification of bitumen: Advances and challenges. European Polymer Journal, 54, 18-38.

[16] S. Pyshyev et al. Polymer Modified Bitumen: Review. Chemistry & chemical technology, 2016,Vol.10, No 4(s) 631-636.

[17] Ali, n., et al. A mechanistic evaluation of modified asphalt paving mixtures. Canadian Journal of Civil Engineering, 1994, 21.6: 954-965.

[18] Yildirim, Y. (2007). Polymer modified asphalt binders. Construction and Building Materials, 21(1), 66–72. https://doi.org/10.1016/j.conbuildmat.2005.07.007

[19] Veropalumbo, R., Russo, F., Viscione, N., Biancardo, S.A., Oreto, C., 2020. Investigating the rheological properties of hot bituminous mastics made up using plastic waste materials as filler, Construction and Building Materials, 121394

[20] McNally, T. (2011). Introduction to polymer modified bitumen (PmB). Polymer Modified Bitumen, 1–21. https://doi.org/10.1016/B978-0-85709-048-5.50001-8

[21] Gama, D. A., Yan, Y., Rodrigues, J. K. G., & Roque, R. (2018). Optimizing the use of reactive terpolymer, polyphosphoric acid and high-density polyethylene to achieve asphalt binders with superior performance. Construction and Building Materials, 169, 522–529. https://doi.org/10.1016/j.conbuildmat.2018.02.206

[22] Ahmed, K., Irfan, M., Ahmed, S., Ahmed, A., & Khattak, A. (2014). Experimental investigation of strength and stiffness characteristics of hot mix asphalt (HMA). Procedia Engineering, 77, 15–5160. https://doi.org/10.1016/j.proeng.2014.07.026

[23] Khodaii, A., & Mehrara, A. (2009). Evaluation of permanent deformation of unmodified and SBS modified asphalt mixtures using dynamic creep test. Construction and Building Materials, 23(7), 2586–2592. https://doi.org/10.1016/J.CONBUILDMAT.2009.02.015

[24] Gorkem, C., & Sengoz, B. (2009). Predicting stripping and moisture induced damage of asphalt concrete prepared with polymer modified bitumen and hydrated lime. Construction and Building Materials, 23(6), 2227–2236. https://doi.org/10.1016/j.conbuildmat.2008.12.001

[25] Camargo, F. F., Vasconcelos, K., & Bernucci, L. L. (2019). Laboratory Comparison of Permanent Deformation and Fatigue Behavior of Neat, Polymer, and Rubber-Asphalt Binders. Transportation Research Record, 2673(4), 524-532. https://doi.org/10.1177/0361198119836769

[26] Tsantilis, L., Dalmazzo, D., Baglieri, O., & Santagata, E. (2019). Effect of SBS molecular structure on the rheological properties of ternary nanomodified bituminous binders. Construction and Building Materials, 222, 183–192. https://doi.org/10.1016/J.CONBUILDMAT.2019.06.095

[27] Weigel, S., & Stephan, D. (2018). Relationships between the chemistry and the physical properties of bitumen. Road Materials and Pavement Design, 19(7), 1636–1650. https://doi.org/10.1080/14680629.2017.1338189

[28] Roja, K. L., Rehman, A., Ouederni, M., Krishnamoorthy, S. K., Abdala, A., & Masad, E. (2021). Influence of polymer structure and amount on microstructure and properties of polyethylene-modified asphalt binders. Materials and Structures, 54(2), 1-17.

[29] Giavarini, C., De Filippis, P., Santarelli, M. L., & Scarsella, M. (1996). Production of stable polypropylene-modified bitumens. Fuel, 75(6), 681–686. https://doi.org/10.1016/0016-2361(95)00312-6

[30] Behnood, A., & Modiri Gharehveran, M. (2019). Morphology, rheology, and physical properties of polymer-modified asphalt binders. European Polymer Journal, 112, 766–791. https://doi.org/10.1016/J.EURPOLYMJ.2018.10.049

[31] Zani, L., Giustozzi, F., & Harvey, J. (2017). Effect of storage stability on chemical and rheological properties of polymer-modified asphalt binders for road pavement construction. Construction and Building Materials, 145, 326-335. https://doi.org/10.1016/j.conbuildmat.2017.04.01

[32] Montanelli, E. F., & Itercimica srl, I. (2013). Fiber/Polymeric Compound for High Modulus Polymer Modified Asphalt (PMA). Procedia - Social and Behavioral Sciences, 104, 39–48. https://doi.org/10.1016/j.sbspro.2013.11.096

[33] Ranieri, M., & Celauro, C. (2018). Improvement of high modulus asphalt mixtures with average quality aggregate and bitumen by application of polymeric additives. Construction and Building Materials, 178, 183–194. https://doi.org/10.1016/J.CONBUILDMAT.2018.05.126

[34] Eskandarsefat, S., Dondi, G., & Sangiorgi, C. (2019). Recycled and rubberized SMA modified mixtures: A comparison between polymer modified bitumen and modified fibres. Construction and Building Materials, 202, 681–691. https://doi.org/10.1016/J.CONBUILDMAT.2019.01.045

[35] Martin-Alfonso, J. E., Cuadri, A. A., Torres, J., Hidalgo, M. E., & Partal, P. (2019). Use of plastic wastes from greenhouse in asphalt mixes manufactured by dry process. Road Materials and Pavement Design, 20(sup1), S265–S281. https://doi.org/10.1080/14680629.2019.1588776

[36] Prahara, E., Aswita, F., & Shinta, E. N. P. (2020, July). The effect of High-Density Polyethylene (HDPE) and Low-Density Polyethylene (LDPE) on characteristics of asphalt concrete with dry and wet mixing process. In IOP Conference Series: Materials Science and Engineering (Vol. 852, No. 1, p. 012056). IOP Publishing.

[37] Riekstins, A., Baumanis, J., & Barbars, J. (2021). Laboratory investigation of crumb rubber in dense graded asphalt by wet and dry processes. Construction and Building Materials, 292, 123459.

[38] Movilla-Quesada, D., Raposeiras, A. C., Silva-Klein, L. T., Lastra-González, P., & Castro-Fresno, D. (2019). Use of plastic scrap in asphalt mixtures added by dry method as a partial substitute for bitumen. Waste Management, 87, 751–760. https://doi.org/10.1016/J.WASMAN.2019.03.018

[39] Tahami, S. A., Mirhosseini, A. F., Dessouky, S., Mork, H., & Kavussi, A. (2019). The use of high content of fine crumb rubber in asphalt mixes using dry process. Construction and Building Materials, 222, 643–653. https://doi.org/10.1016/J.CONBUILDMAT.2019.06.180

[40] Vasileios Papadimitropoulos, C., Karatzas, S., Athanasios, Chassiakos, P., (2018). Applications of Nanomaterials in Pavement Engineering: A Review, .2018, The Tenth International Conference on Construction in the 21st Century (CITC-10)

[41] Yanga, J., Tighe, S., (2013). A review of advances of Nanotechnology in asphalt mixtures. Procedia - Social and Behavioral Sciences 96, 1269- 1276.

[42] J. Le, M. Marasteanu, R. Hendrickson, A Mechanistic Design Approach for Graphite Nanoplatelet (GNP) Reinforced Asphalt Mixtures for Low Temperature Applications, Research Project, Final Report 2018-02, Minnesota Department of Transportation Research Services & Library, 2018.

[43] Amin I., El-Badawy, S. M., Breakah, T., Ibrahim, M. H. Z., (2016). Effect of functionalization and mixing process on the rheological properties of asphalt modified with

carbon nanotubes. American Journal of Civil Engineering and Architecture,4(3), 90-97. doi:10.12691/ajcea-4-3-4

[44] Marasteanu, M. O., Le, J. L., Turos, M. I., (2016). Graphene Nano-Platelet (GNP) reinforced asphalt binders and mixtures. Proceedings of E&E Congress 2016, 6th Eurasphalt & Eurobitume Congress, Prague, Czech Republic.

[45] Oreto, C., Veropalumbo, R., Viscione, N., Biancardo, S. A., & Russo, F. (2021). Investigating the environmental impacts and engineering performance of road asphalt pavement mixtures made up of jet grouting waste and reclaimed asphalt pavement. Environmental Research, 198, 111277

[46] Sarang, G., Lekha, B.M., Krishna, G., & Ravi Shankar, A.U. (2015). Comparison of stone matrix asphalt mixtures with polymer-modified bitumen and shredded waste plastics. Road Materials and Pavement Design, https://doi.org/10.1080/14680629.2015.1124799

[47] Almeida, A., Capitão, S., Bandeira, R., Fonseca, M., & Picado-Santos, L. (2020). Performance of AC mixtures containing flakes of LDPE plastic film collected from urban waste considering ageing. Construction and Building Materials, 232, 117253. https://doi.org/10.1016/J.CONBUILDMAT.2019.117253

[48] Moghaddam, T. B., Karim, M. R., & Syammaun, T. (2012). Dynamic properties of stone mastic asphalt mixtures containing waste plastic bottles. Construction and Building Materials, 34, 236-242.

[49] Veropalumbo, R., Viscione, N., Russo, F., 2019. Indirect Tensile Strength Method For Defining A Proper Practice of Asphalt Mixtures Design. WIT Transactions on Engineering Sciences, 124, 255-265. 9th International Conference on Computational Methods and Experiments in Material and Contact Characterisation, Lisbona (Portugal).

[50] Huijbregts, M.A., Steinmann, Z.J., Elshout, P.M., Stam, G., Verones, F., Vieira, M., Zijp, M., Hollander, A., van Zelm, R. ReCiPe2016: A harmonised life cycle impact assessment method

at midpoint and endpoint level. Int. J. Life Cycle Assess. 2017, 22, 138–147. https://doi.org/10.1007/s11367-016-1246-y.

[51] Fuller, W.B., and Thompson, S.E. (1907). The Laws of Proportioning Concrete. 67–143.

[52] Tapkin, S., & Keskin, M. (2019). Design gyration number determination of 100-mm-diameter asphalt mixtures. International Journal of Civil Engineering. 1–14. 10.1007/s40999-019-00399-1.

[53] Cai, X., Wu, K., & Huang, W. (2020). Study on the optimal compaction effort of asphalt mixture based on the distribution of contact points of coarse aggregates. Road Materials and Pavement Design, 1–22. https://doi.org/10.1080/14680629.2019.1710238

[54] Thyagarajan, S., Tashman, L., Masad, E., & Bayomy, F. (2010). The heterogeneity and mechanical response of hot mix asphalt laboratory specimens. International Journal of Pavement Engineering, 11(2), 107–121. https://doi.org/10.1080/10298430902730521

[55] Leandro, R. P., Vasconcelos, K. L., & Bernucci, L. L. B. (2017). Evaluation of the laboratory compaction method on the air voids and the mechanical behavior of hot mix asphalt. Construction and Building Materials, 156, 424-434.

[56] Lo Presti, D., Hassan, N. A., Airey, G., & Collop, A. (2013). Fundamental characterisation of reclaimed asphalts: the importance of testing homogeneous specimens. Road materials and pavement design, 14(sup1), 120-131.

[57] Hafeez, I., Shan, A., Ali, A., Ahmed, I., 2017. Flexible pavement design evaluation using mechanistic-empirical approaches. Technical Journal, University of Engineering and Technology, 22(2), 27-33.

[58] Asphalt Institute. Thickness Design Manual; Research Report 82-2; Asphalt Institute: Lexington, KY, USA, 1982.

[59] Kaloush, K.E., Witczak, M.W. Development of a permanent to elastic strain ratio model for asphalt mixtures. In Development of the 2002 Guide for the Design of New and Rehabilitated Pavement Structures; NCHRP: Washington, DC, USA, 2000; pp. 1–37.

[60] Blomberg, T., Barnes, J., Bernard, F., Dewez, P., Le Clerc, S., Pfitzmann, M., Taylor, R., 2011. Life Cycle Inventory: Bitumen; European Bitumen Association: Brussels, Belgium,

[61] Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., Weidema, B, 2016. The ecoinvent database version 3 (part I): Overview and methodology. Int. J. Life Cycle Assess. 21, 1218–1230, doi:10.1007/s11367-016-1087-8.

[62] Santos, J.; Pham, A.; Stasinopoulos, P.; Giustozzi, F. Recycling waste plastics in roads: A life-cycle assessment study using primary data. Sci. Total Environ. 2021, 751, 141842, doi:10.1016/j.scitotenv.2020.141842.

[63] Guinée, J. B., Lindeijer, E. (Eds.), 2002. Handbook on life cycle assessment: operational guide to the ISO standards (Vol. 7). Springer Science & Business Media.

[64] Huijbregts, M.A., Steinmann, Z.J., Elshout, P.M., Stam, G., Verones, F., Vieira, M., Zijp, M., Hollander, A., van Zelm, R. ReCiPe2016: A harmonised life cycle impact assessment method at midpoint and endpoint level. Int. J. Life Cycle Assess. 2017, 22, 138–147. https://doi.org/10.1007/s11367-016-1246-y.