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Mechanical Effects of Recycled Packaging Plastic in Bituminous Binders and Mixtures

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MECHANICAL EFFECTS OF RECYCLED PACKAGING PLASTIC IN BITUMINOUS BINDERS AND MIXTURES

PhD Thesis

PREFACE

Acknowledgments

I feel especially fulfilled to sign this PhD thesis with my family name. Not only because it represents that this is my creation and production but also because it represents what this is: a family accomplishment. And I think it is only fair that this is the first acknowledgment in this document because my whole relation of co-support with my parents was built into believing in Education as a mean for developing a person inside a society. Even though they never had the opportunity to access a university as students themselves.

And since this document closes this PhD phase, it is important to acknowledge how it started.

Thinking about the research project that led to this thesis, I thank my two Directors, my two Tutors, and their teams for starting this project and entrusting its accomplishment to me.

Also, I would like to acknowledge my two institutions – Università di Parma and ENTPE –; my friends from the lab; my loved ones - who emotionally supported me; and everyone who worked for that all tests would be performed.

And finally, I would like to acknowledge *PON Ricerca* and *La Région Auvergne-Rhône-Alpes*, for funding the costs of this research.

Towards a future of circular materials and ideas

This thesis was developed thanks to the support of a lot of people with whom I shared my affections during this journey. It would be hard to identify everyone that was fundamental to the existence of this document. Thus, with them in mind, I included this section constructed from exchanges we had during these years in an attempt to understand the journey of working with research/science.

The novel O Quinze, by Rachel de Queiroz, portrays the story of characters from the northeastern region of Brazil who had to face a seasonal drought in a year in which the entire region experienced a long period of lack of water. In this story, we find an important dialogue where the characters, strongly moved by their faith, defend that even when there is no indication that it might rain, it is important to continue sowing and hope that it will eventually rain, even if the environment suggests it is almost impossible.

Although this story comes from a different place, time, and context, I think the resilience of these characters could be used to create a parallel with the way I understand science today. Because I think that when an academic production comes into the world, a researcher is also moved by a faith that it will eventually be fruitful.

And, of course, I think it is important to consider today's global scenario, where governments each time give more space to currents of thought that deny scientific findings. In challenging times such as these, it would be useful to bring some hope to our scientific community. It is only supported by this

community that me and other researchers can materialize efforts such as a PhD thesis. In the same way, the lack of support can result in the loss of promising work that never comes to an academic production.

This notion of community also resonates with my understanding of Education as a dialogical and co-intentional act, in which knowledge is not transmitted unilaterally but constructed through reciprocity. For this reason, I would like to mention the Brazilian education system, especially the work of its patron, Paulo Freire, which provided me with all the foundations necessary to pursue and complete this task.

In fact, the research developed in this PhD is the major representation of 8 years that I dedicated to working mostly as a professional of research. Naturally, I must also acknowledge all the other positions that provided me with financial resources to take this step. Therefore, this thesis is the outcome of all work I carried out during this period, accomplished over two years and a few months spent in Italy and France – a mixed experience of two countries that now join the list of places I lived in.

Many argue that one of the greatest virtues for those who succeed is the ability to adapt to the new. In my case, this meant working simultaneously at the two universities that hosted me and acting sometimes as a bridge between them. It was in this position that I realized that such a journey is almost impossible when it is not faced collectively. And I am grateful to have met the people that made me understand that.

Of course, at this point it is also important to mention that this journey has gone through a lot of critical moments that made me wonder if it would even be possible to reach the finish line. Many of these are almost inherent to the path of someone who chose to work abroad, such as having to learn a new language; trying to find a place to live when you have just arrived; enduring months of a stressful visa process; and looking for a part-time job in parallel. And even if in my case this was doubled, I think nothing is harder than being months or years apart from our family/home country due to financial constraints or not being able to take a time off.

But most importantly, due to having faith in the outcome of this project.

On other side, one good outcome of this process was discovering that I was a person with all the tools and virtues to overcome these particular challenges. I figured out that even though my background was inaccessible, I could reflect that in all the places I went, always bringing a piece of that with me. And this reasoning was fundamental for finding a space for me and a place for the community I have created for myself.

Thinking about that, I wanted this text to be both a personal reminder and a note of gratitude to acknowledge everyone that participated in this process. Especially those who supported it indirectly, being present as they could. And those who were my safe place, knowing that there's not a star in heaven that we can't reach. *O meu muito obrigado*! I reiterate that I think it would be not possible to walk that road without support.

Building from that, the present thesis is the result of work developed with the aim of improving our relationship with the environment and promoting the use of recycled materials in road construction. I bring this work into the world with the faith that it will produce good fruits, even in the driest seasons.

ABSTRACT

The inclusion of alternative materials (AM) in road construction is one current practice that supports politics of Green Transition. The incorporation of the food packaging recycled plastic studied in this research addresses minimizing the creation of disposals and a more efficient use of this resource. However, there are still uncertainties about the mechanical performance of this material. In this context, this research aims to explore the mechanical effects of the incorporation of plastic in bituminous mixture in two scales, either in bitumen as a binder modifier or in wearing course, in replacement of a part of the aggregate content. For this purpose, an experimental plan divided in two phases was proposed aiming to investigate: (i) the mechanical changes observed in bitumens that interacted with recycled plastic; and (ii) the mechanical characterization of mixtures produced with this material through dry process. For the first phase a procedure using High Shear Mixer (HSM) and filtering at 150 °C was formulated in order to induce conditions of interaction similar to those found during the mixing process. After separated from the plastic, the obtained binder was chemically and mechanically characterized using, respectively, Fourier-Transform Infrared (FTIR) and Dynamic Shear Rheometer (DSR) techniques. The characterization of these materials allowed infer that in some mixing conditions such as time of exposure to high temperatures and rotation speed of the tank might be favourable for particles from the plastic being incorporated in the bitumen. This is particularly interesting knowing that this interaction might be experienced by modified mixtures even when the plastic is aimed to function as an aggregate. For the purpose of the second phase, five different mixtures were produced, with different plastic contents of 0, 2.5, 5 and 7 %. Cylindrical specimens were extracted from slabs of 50 × 50 cm mixed and compacted in laboratory. Thermo-mechanical tests were performed in tension-compression. The results suggested that the stiffness and the elasticity of the samples is significatively changed and influenced by the plastic content. In contrast, the plastic content seems to influence the workability and level of compaction. When 5% of the aggregates were replaced by plastic the performance of the material was improved in comparison to the reference sample without plastic. The Complex Modulus (|E*|) increased at lower frequencies and decreased in the higher, while similar results were found in 15 °C. This particular result reveals that at 5% not only the recycled plastic can be employed as a replacement for mineral aggregates but also it is possible to achieve effects of modification of bitumen using a dry process.

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LIST OF ABBREVIATIONS

$\|G^*\|$	Complex Modulus
a_T	Shift factor
DSC	Differential Scanning Calorimetry
DSR	Dynamic Shear Rheometer
EVA	Ethylene-vinyl acetate
FTIR	Fourier-Transformed Infrared
HDPE	High-Density Polyethylene
HSM	High-Shear Mixer
LDPE	Low-Density Polyethylene
PE	Polyethylene
PET	Polyethylene terephthalate
PMB	Polymer-Modified Bitumen
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
SBS	Styrene butadiene styrene
TGA	Thermogravimetric analysis
Vv	Volume of voids
WLF	Williams-Landel-Ferry equation
φ	Phase angle
G'	Storage Modulus
G''	Loss Modulus
$\|E^*\|$	Complex Modulus
E'	Storage Modulus
E''	Loss Modulus
CV	Coefficient of Variation
TTSP	Time-temperature superposition principle
PID	Proportional-integral-derivative
LVE	Linear viscoelastic
HMA	Hot Mix Asphalt
DNIT	Departamento Nacional de Infraestrutura de Transportes

LLDPE	Linear Low-Density Polyethylene
PAV	Pressure aging vessel
RTFOT	Rolling thin film oven test
WMA	Warm-mix Asphalt
MWD	Molecular weight distribution
ITS	Indirect Tensile Strength
LCCA	Life-Cycle Cost Assessment
AM	Alternative material
SWM	Solid waste materials
RAP	Reclaimed asphalt pavement
SARA	Saturates, Aromatics, Resins and Asphaltenes
G_0	Glassy modulus
G_{00}	Static modulus

SUMMARY

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CHAPTER 1
INTRODUCTION

1.1 Green Transition, Circular Economy, and Plastic disposal in Europe

The environmental costs of production and management of infrastructures reflect a tendency of development made under the assumption of unlimited resource availability and no long-term impacts. In recent years, solutions have emerged to reshape this sector that remains essential for social development. In this perspective, the recycling and reintegration are strategies that can be implemented. For example, waste post-consumption plastic residues are largely available while most of developed countries must deal with big landfills that for years were considered out of function.

In Europe, a Green Deal was signed in which agencies and governments compromise to make countries from the European Union climate-neutral by this year of 2050, proposing a transition for the industry (European Commision, 2019). In this Green Transition, as it is referred, solutions that promote resource efficiency and reduction of carbon emissions are being implemented.

Among these solutions, a Circular Economy of resources is encouraged to reshape the production and consumption in all sectors. This model of resource management aims to give a new usability for certain materials after consumption to avoid disposals. The industry of plastic is inserted in this context since their use is already part of the culture and transportation of goods. Incorporating this specific type of product in a circular economy would speed up the process of treatment of the environmental problems caused by plastic landfills in developed countries.

In Europe, the efforts for a more environmental economy of plastics have reflected in a reduction of the consumption of plastic materials in cases where it can be replaced by recycled materials and in a higher insertion of material from landfills in the industry. In accord to Plastics Europe (Plastics Europe, 2022), since 2016 , the amount of waste plastic resources incorporated in recycling has more than doubled while the amount sent to landfills has reduced in almost half.

Data from 2019 shows that the production of plastic landfills in the United States have increased at that year. In total, it is estimated that the production of plastic waste rose to 44 Mt. And, from this amount less than 20% was recycled or incinerated, resulting in around 37 Mt of plastic landfill (Milbrandt et al., 2022). Among those, the greater accounted part was residues of polyethylene or polyethylene terephthalate (PET) used in food/drink packaging.

In all scenarios observed, packaging represents a noteworthy proportion of the plastic products that are still in production. Since their service life lasts only until the transported product - such as food or drink - is consumed, ensuring the circularity of this resource is fundamental. In contrast, an estimation from the year of 2015 showed that the amount of plastic that ended up in landfills accounted globally around 60 % of the plastic ever produced (Geyer et al., 2017).

In parallel, developing countries present a different scenario in which the different sectors of the industry present growth, which brings the increase of consumption of natural resources and the use of more accessible technologies.

For example, reports from the OECD show that in the year of 2019 the consumption of plastic varied depending on the economy. The amount in kg per capita accounted 255.2 in the United States; 152.9 in EU Countries; 143.9 in Oceania; 69.0 in China, and 50.9 in Latin America (OECD, 2022). At the same time, while economies from the global north make higher use of plastic, the costs for treatment and recycling of these materials are lower in countries from the global south (Li et al., 2024). It is relevant to consider the costs of the management of these products, since from this perspective their exportation would be a possible solution.

Considering solutions that can present effective results globally, sectors of the industry that deal with movement of great amounts of material, such as Construction, could assume a position of interest in the utilization of that type of material. Other experiences already showed advances with alternative materials such as crumb rubber, steel slag and reclaimed asphalt pavement (RAP). In these experiences, alternative materials start being acknowledged as an available and economical resource. To support that discussion and indicate the best destination for plastic resources, concepts studied in the science of materials might be helpful to understand its behavior in each application.

1.2 Use of plastic and polymers in asphalt mixtures

The incorporation of solid waste in pavements is remarkably an alternative for decreasing the costs of production and maintenance on these infrastructures (Huang et al., 2007). As the waste disposal crisis continues worldwide, some materials find a good potential when used in road construction, offering advantage on reducing both environmental pollution and constructive costs. Among these materials, recycled plastics can be used. Similar to industrial polymers designed properly for road construction, waste plastics often present an elastic behaviour that could be incorporated into the pavements.

While incorporating waste plastics into road construction might offer a relevant cost-saving in materials, the general expenses associated with construction processes remain a major challenge to be overcome. Many regions still do not have access to resistant and durable pavements. This impact transportation, economic development and quality of life.

The conception of a new type of pavement must consider both feasibility and attending to traffic load demand. For this purpose, technical parameters must be attended. Regarding the feasibility, it is important to guarantee the workability of mixture. For example, mixtures incorporating polymer/plastic might tend to be more difficult to work and transport with due to the inherent properties of these materials. Alternatively, it is also necessary to survey the structural strength before implementing a new material. The analysis of these two factors are means to assist the proposition of best practices on the utilization of these alternative materials.

The service life is another key factor when implementing recycled materials. Frequent repairs and early degradation lead to additional costs and are not environmentally viable. Therefore, plastic-enhanced pavements must not only be an eco-friendly alternative but also provide long-term resilience to minimize maintenance needs and reduce environmental impact.

Some studies are thus necessary to ensure suitable properties for bituminous mixtures before incorporating plastic.

1.3 Problem Statement and Significance of the Research

Despite the widespread use of plastics in numerous applications, the management of their post-consumption residues remains inadequate. As mentioned before, this often results in landfills, incineration, or environmental pollution. In practical terms, it is important to consider that each residue/waste comes from a different source which also means a different source and structure of polymer.

The lack of effective strategies for reusing and integrating plastic waste into industrial processes put in evidence various consequent problems, as recycled plastics still lack a proper destination that aligns with a Circular Economy. This issue not only contributes to environmental degradation but also highlights a missed opportunity to explore the potential of this residue as a resource to be employed in construction.

Exploring innovative methods to integrate plastic waste into industrial processes, such as its use in modifying bituminous binders, is a means to mitigate environmental impacts while enhancing material performance.

The use of this resource in road construction put in perspective a solution for the major issue of plastic disposal, since a great amount of material would find reintegration in the industry. However, this also brings a list of concerns regarding the technical incorporation of these resources into pavements. These points are the focus of the research problem addressed in this research: the uncertainties of the mechanical performance of mixtures modified with food-packaging recycled plastic.

The incorporation of plastics into bituminous binders and mixtures represents a promising avenue to both improve the mechanical properties of the material and provide a viable pathway for plastic reuse. In this context, the study highlights the dual benefit of inserting into circularity an alternative material and mitigating the disposal problem.

1.4 Objectives

Based on the problem addressed in this study, the research objectives were established, comprising a general objective followed by specific objectives.

1.4.1 General Objective

The general objective is to identify the effects of interaction and incorporation of three-layer recycled food packaging plastic in the behavior of bituminous materials.

1.4.2 Specific Objectives

Two specific objectives were defined; the first specific objective was subdivided into two parts according to the structure of the experimental plan developed for this research. The specific objectives were the following:

I(A). Identify the conditions and parameters that affect the interaction between plastic waste and conventional binders;

I(B). Investigate the impacts of the interaction between plastic and bitumen in the mechanical behavior of the binder;

II. Characterize the mechanical behavior of mixtures that incorporated recycled plastic by the dry method.

1.5 Thesis organization

This thesis dissertation is structured into 7 chapters, as presented and summarized in

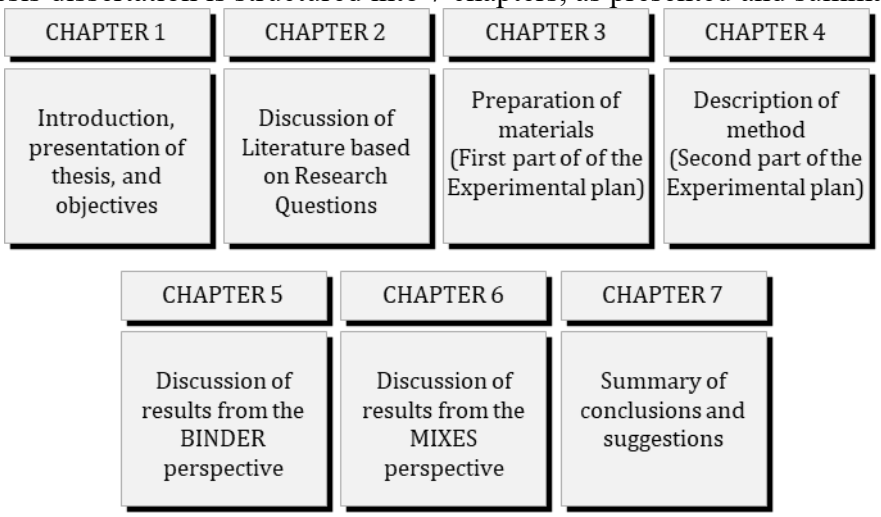


Figure 1-1.

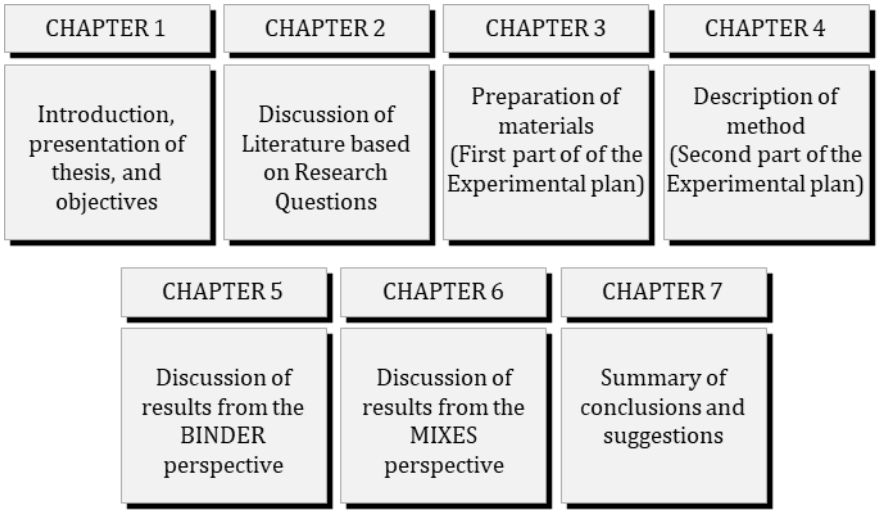


Figure 1-1 – Division of chapters in this thesis dissertation

The structure of chapters aimed to follow the linearity Literature Review, Methodology and Results, which is the basis of the structure of this document. Each chapter presents a description of their content and how it is inserted in the panorama of the experimental plan.

CHAPTER 2
LITERATURE REVIEW

This chapter explores the use of recycled plastics in bituminous mixtures and outlines the methodology adopted in this research based on existing literature. The analysis was structured into two parts: first, a review of studies on the effects of recycled materials in asphalt mixtures, and second, the formulation of research questions addressing key aspects of polymer-bitumen interaction.

2.1 Overview of Chapter

This chapter aims to discuss both the use of recycled plastics as a material for producing bituminous mixtures and the steps of the methodology adopted in this present research based on the existing literature for these subjects. Although this research was developed with a focus on these materials as alternative resources, this chapter also emphasizes their position as a legitimate construction material and seeks to investigate their properties and potential benefits with the same rigor applied to traditional materials.

The analysis involved the identification and documentation of literature addressing the effects of recycled materials and polymers in different scales and aspects of bituminous mixtures. This step covered a mapping of the scientific gaps identified in those studies, contextualized according to the time in which each study was published. In sequence, the formulation of research questions in light of the data collected was carried out to address the problematic outlined in this thesis.

Accordingly, the content of this chapter was divided into two parts. The first part comprises three sections, including the fundamentals of modified mixtures, a survey of the state-of-the-art in modified asphalt mixtures, and a discussion about modifications involving recycled plastics with a particular emphasis on the differences between the conceptual processes of modification (Dry and Wet method). The second part, presented in the final section of this chapter, outlines the research questions developed through a guided analysis of the surveyed literature, framed in light of the specific objectives established for this research.

Each research question is discussed individually in a dedicated subsection. For each question, the existing findings from the literature are examined, followed by the identification of scientific gaps that may represent potential limitations or challenges for the experimental plan proposed for this research. In view of this, the research questions formulated for this research were the following:

i. What types of polymers are more efficient for asphalt mixtures?

ii. What phenomena are involved in the blending between polymers and binders?

iii. How to identify the presence of plastic in the composition of a bitumen?

iv. Which mechanical differences are expected when mixing mineral and polymeric aggregates?

These subsections frame the theoretical basis of the present study, highlighting the unsolved key points that must be considered when developing the experimental plan for this report.

The consolidation of scientific comprehension regarding bitumen modification with plastics remains a research topic in development, which impacts the validation of updated design protocols. The absence of an established mix design methodology for plastic-modified mixtures further accentuates the importance of investigating the scientific gaps related to the incorporation of recycled/heterogeneous plastics, which constitutes the focus of this research.

2.2 Fundamental concepts: bituminous mixtures and recycled plastics

This section presents a review of the fundamental general aspects of the two categories of materials investigated in this research: bituminous mixtures and recycled plastics. Although this research is centered in the scientific limitations of understanding the effects resulting from the incorporation of highly heterogeneous and recycled plastics—often composed of various polymer types—into bituminous materials, it is essential to first establish the foundational aspects of each material.

A brief description of the composition and mechanical behavior of each material individually, as well as of the nature and origin of recycled plastics in construction applications, provides the necessary context for understanding the interaction mechanisms explored in the following sections of this chapter.

2.2.1 Bituminous mixtures – composition and mechanical performance

From a chemical perspective, a fundamental point to be considered is the basic nature of both materials exposed for interaction: polymers, and bituminous binders. Each of these materials possesses distinct molecular structures usually described by models. Variations in molecular structure are often reflected in the rheological behavior of neat materials.

Concerning binders, the composition of these materials is often chemically described as a colloidal system in which the asphaltenes and resins are dispersed in a solution of saturates and aromatics (Corbett, 1969; Lesueur, 2009). The proportions between these four categories of components (saturates, aromatics, resins, and asphaltenes) are referred in the literature as SARA fractions (Bernucci et al., 2022).

This classification provides a framework of the chemical characterization of the bitumen and will be referred in further discussions held in the following sections.

2.2.2 Recycled plastic – composition and use in the construction

Plastics are present in most social activities, including the consumption and packaging of everyday goods. Although commonly referred to under a single term, plastics used in industry are composed of one or more types of polymers - materials whose structures consist of large macromolecules, which are molecules of high relative molecular mass, formed by the repeated linkage of smaller units (IUPAC, 1996).

The specific function a plastic is designed to perform - whether structural, flexible, or protective - dictates the selection and combination of polymers used in its formulation. In the context of food and beverage packaging, a wide list of materials can be employed, each offering distinct chemical and physical properties suited to the intended application.

During the recycling process the shape and size of the plastics can be modified but their polymeric constituents remain the same. After being treated for adapting their form, these materials can be considered for construction. The application of recycled plastics as an Alternative Material (AM) to improve the performance of unmodified binders can be considered as they are a source of polymer less expensive and to enhance a circular economy.

Based on the literature surveyed, the most pertinent polymers highlighted in these studies are presented in the following list. In this subsection and further sections of this document, these materials will be referred to by its abbreviated nomenclature.

i. Polyethylene Terephthalate (PET)
ii. Polyethylene (PE)
iii. High-Density Polyethylene (HDPE)
iv. Low-Density Polyethylene (LDPE)
v. Polyvinyl Chloride (PVC)
vi. Polypropylene (PP)
vii. Polystyrene (PS)

The polymers in the list are ordered according to the frequency of mentions in the studies that investigated the use of recycled plastics in asphalt materials within the literature surveyed for this research.

This research investigated the register of use of recycled polymers in the literature including studies of review of existing database. Each of them has shown a particular degree of effectiveness either through their interaction at the binder scale or through their influence on the physical and mechanical behavior of the final mixture. The mechanisms through which these modifications occur depend on both the characteristics of the mixtures and the intrinsic properties of the polymers—topics that will be further explored in the following sections.

In practice, all modification aspects must consider an adequate contact surface between the plastic and the bituminous material in the mix. This is an important factor taking into account that most of the waste plastic is placed in disposals without a pre-treatment to be prepared for use in construction. Then, a procedure to change size and shape in a pellet or in a shredded form is a fundamental step for improving the contact between the two phases (Heydari et al., 2021). This includes an extra cost to the final cost of the pavements (Sasidharan et al., 2019).

2.3 Survey of existing review studies on plastic modification

In the course of the examination of the literature, multiple publications were identified that aimed to compile the state of the art regarding the use of recycled polymers in the production of new pavements. This type of research is highly relevant for identifying the main advances in this area and for encouraging the investigation of the many gaps that still remain in the understanding of the use of these materials.

This section summarizes the findings from the state-of-the-art reviews. From this perspective, the purpose of this discussion is not to present a new state-of-the-art, but to rather present and discuss existing research, highlight key advancements, and identify the main challenges that have been put in evidence in this area of study. For a detailed understanding, the reader is referred to the dedicated review papers.

Huang *et al.* presented a review for the use recycled solid waste materials (SWM) in different types of asphalt mixtures, which included an incoming concern with the production of residual plastic without destination (Huang et al., 2007). Among the requirements for including alternative aggregates in the construction of pavements, this study includes the fulfillment of the geometric standard for aggregates (BS EN933) and the attention to leaching of chemical subproducts (BS EN1744). From this study it was observed that the initial mechanical results observed applicability of the Low-Density Polyethylene (LDPE) in binder courses.

Also in this survey, the procedures for including the waste plastic in mixtures are divided into two different categories: a *Wet Process* and a *Dry Process.* Each procedure determines if the plastic is mixed with the bitumen before starting the mixing process or if it replaces part of the aggregates. In general, studies that approach wet processes focus on the mechanical performance on a binder scale, since this allows to observe proper evidence of chemical modification. The main differences between the two procedures are discussed in a dedicated section in this chapter.

The distinction between the techniques for incorporating the plastic into the bituminous materials into two individual processes are also mentioned in other review studies (Cardoso et al., 2023; Xu et al., 2021). Xu, Zhao, and Li reviewed different forms of waste plastic used in asphalt pavements – pellet form (a), shredded form (b), flake form (c), and powder form (d) - and its implications from the perspective of the type of polymers and the adaptation of constructive methods. An example extracted from this review is presented in Figure 2-1.



(a) (b) (c) (d)

Adapted from Xu *et al.* (2021)

Figure 2-1 – Forms of recycled plastics used for construction

Among the various effects associated with the addition of polymers to bituminous binders, improvements in high-temperature performance are generally observed. However, the extent of these effects can vary depending on the polymer type, as well as the shape and size of the polymer particles. In addition, phenomena such as storage stability and the modification mechanism were presented as important factors influencing the mechanical performance of the mixtures — a key aspect to be evaluated in this study — with strong dependence on the chemical composition of the polymer and its melting point.

Alternatively, Cardoso *et al.* conducted a systematic investigation of studies published between the years of 2018 and 2023 that analysed the phenomena of rutting and fatigue cracking in mixtures that incorporated plastic in its composition. Based on this perspective of analysis it is possible to identify the waste plastic in the group of the additives for improvement of performance in two of the main failure conditions for mixtures: rutting and fatigue cracking. The study identified forty-nine papers in different countries.

The data involved mixtures that incorporated in average 1% of plastic by weight and observed in the majority of the results an improvement of rutting performance. The effects of the incorporation of plastic on fatigue seem to be more inconclusive given the data matrix, requiring further investigation. It is important to highlight that no evidence was observed indicating influence of gradation or shape of the plastic in the mechanical performance. The research identified different types of polymers that will be discussed in the following sections.

Concerning the modification of bituminous binders by mobilization of polymeric content, another systematic review was developed by Vargas and El Hanandeh including an application of neural network modelling to develop predictive models of the effects of the plastic (Vargas & El Hanandeh, 2021). Eighty-two papers regarding the bitumen modified with plastic waste

were selected for this analysis and the period of study was placed between the years of 2009 and 2020. The parameters considered for identifying the effects of the plastic were penetration, softening point and viscosity.

In general, the neural network modelling provided models with high adherence to the experimental data ($R > 0.90$). In the most part of the cases it was observed that the incorporation of polymers resulted in reduction of penetration and in increment of the softening point and viscosity of the bitumen. The influence of the polymer showed to be relevant in the manifestation of the effects. Among all it was observed a strong predisposition of the Polyethylene (PE) in modifying the binder.

Another key point important to be noticed is that in general the binders presented an improvement of performance at high temperatures when modified with the majority of the polymers considered in this study (mainly PE, PP and PVC). However, at low temperatures, this improvement was reported only in a small percentage, in accord to the matrix investigated. This observation brings an important point of attention to the performance at high temperatures as a parameter to identify the modification of binders by polymers.

In the perspective of the National Asphalt Pavement Association based in the US, published in NAPA-IS-142 (Willis et al., 2020), the recycled plastics possess a nature that allow it to be used as an product for bituminous pavements. In a study that encompassed 110 worldwide publications from 1991 to 2020, seven different types of recycled polymers were identified and had their behaviour studied. Among those, the polyethylene presented the best suitability to the use in pavements, comparing to polymers that are already employed in this domain. At the same time, the same report investigated that around 29 % of plastic found in local solid waste disposals corresponded to low-density or high-density polyethylenes.

It is relevant to mention that in this investigation it was found around 200 research projects that moved to field using experimental section of pavements constructed with recycled plastic. The projects included different category of roads, including city streets and interstate roads. In the main findings it was possible to observe that these experimental pavement sections presented a good rutting performance, as reported from the laboratory studies. However, one of the studies reported a larger incidence of cracking when comparing to pavement sections constructed with unmodified binder or SBS modified binder.

The succeeding subsections extend the discussion focusing on the effects of the modification induced by the incorporation of polymers in mixtures in the scale of the bituminous binder and the differences observed in the literature when comparing the Wet Process and the Dry Process.

2.4 The modification in the binder scale

As mentioned in the introduction of this section, the binder modification carried by the contact with the plastic results in effects that can be observed in tests used for the technical characterization of the binders such as penetration and softening point (Imanbayev et al., 2022; Vargas & El Hanandeh, 2021; Wu & Montalvo, 2021; Zou et al., 2022). When it comes to the implications of those modifications in the mechanical performance inside modified mixtures it is relevant to understand the chemical and mechanical effects of these modifications on a microscopic scale. In practice, all modification aspects must consider an adequate contact surface between the plastic and the bituminous material in the mix.

Considering both commercial and recycled polymers, the molecular weight distribution (MWD) is a factor that requires attention. This parameter can interfere in the proper blending of polymers that were not specifically developed to be applied as binder modifier, since wider MWD present the best suitability (Ho et al., 2006).

Taking into perspective the binder scale in the mixture, the size, and the shape of the particles of polymer and waste plastic perform a fundamental role in determining their interaction with the bituminous phase. For example, particles that do not reach the melting point and present the same size as the particles of aggregate are unlikely to interact with the binder, behaving in theory as inert components within the mixture. On the other hand, the observation of smaller particles brings attention to a discussion of whether there is a molecular-level interaction or if they rest in suspension inside the bituminous phase without significant effect.

This discussion highlights the need to explore parameters such as form, granulometry and melting point of plastics before moving to the analysis of interaction. Then, considering a scenario of perfect blending, an important point of attention is determining whether the effects are driven by chemical or physical phenomena.

As previously mentioned, asphalt binders are composed of SARA (saturates, aromatics, resins and asphaltenes) fractions. In general, unmodified and aged binders with a higher concentration of asphaltenes present a stronger structure which reflects in a higher stiffness and viscosity (Hofko et al., 2016). The SARA fractions can also be a first parameter to explain its mechanical performance. The rheological properties may vary depending on the presence and disposition of each component in the system (Mangiafico et al., 2016; Wang et al., 2019). For example, the concentration of the solid phase (asphaltenes) influences in the viscosity of the binders (Mangiafico et al., 2016).

The microstructure is commonly referred to when making a technical decision about a binder to be employed in projects. Binders that do not present a sufficient proportion of asphaltene and solution in the SARA fractions might present a decreased viscosity which can reflect in their applicability in terms of attending to the requirements of the project. When pavements are expected to perform at specific conditions of climate and traffic and suitable materials are unavailable, a modification of the composition or the chemistry of the binders can be considered (Bahia et al., 2001). Alternatives for carrying that out could be: (i) the implementation of a chemical process that results in the rearrangement of the proportions or (ii) the blending of the binder with an agent modifier, such as polymers.

For the first solution, oxidative aging can be considered since it is a process that has as a consequence the modification of the SARA fractions. In general, one expected consequence of the aging processes is the increase on the proportion of asphaltenes and the decrease on the proportion of aromatics, decreasing the proportion of solvent and resulting in more stiffer binders (Takahashi et al., 2019; Werkovits et al., 2023). During the aging process, the molecules in all four fractions pass through an ensemble of phenomena, commonly referred as aging, that includes evaporation, oxidation, molecular rearrangements, condensation, degradation, and production of subproducts (such as carboxylic acids and alcohols) (Werkovits et al., 2023).

Some fractions, such as the aromatics, which have higher polarity, might rearrange and lose mass due to oxidation. As the different fractions exhibit distinct reactivities to this process, the result is often a reduction in naphthene aromatics and, in some cases, polar aromatics, leading to a relative increase in the asphaltene fraction (Petersen, 2009).

A second approach for modifying a binder that is less viscous that what it is expected would be altering their chemical composition by adding an agent capable of improving the mechanical behavior, such as a polymer. As an example, polymer modified bitumens (PMB) are widely employed in pavement construction. When it comes to PMBs, the oxidation must as well take into consideration the effects of the oxidation in the molecules of plastic dispersed in the binder.

One of the polymers with large industrial use for modification of bitumens is the Styrene Butadiene Styrene (SBS). During modification, their molecules can associate with the light fractions of an unmodified bitumen improving the elastic phase of the binder (Airey, 2004). Technically, it is known that it is possible to increase the stiffness and improve temperature susceptibility with SBS and Ethylene Vinyl Acetate (EVA) modified PMBs. Figure 2-2 presents

examples adapted from Sengoz & Isikyakar (Sengoz & Isikyakar, 2008) of fluorescent images of PMBs modified with SBS and EVA showing the different phases.

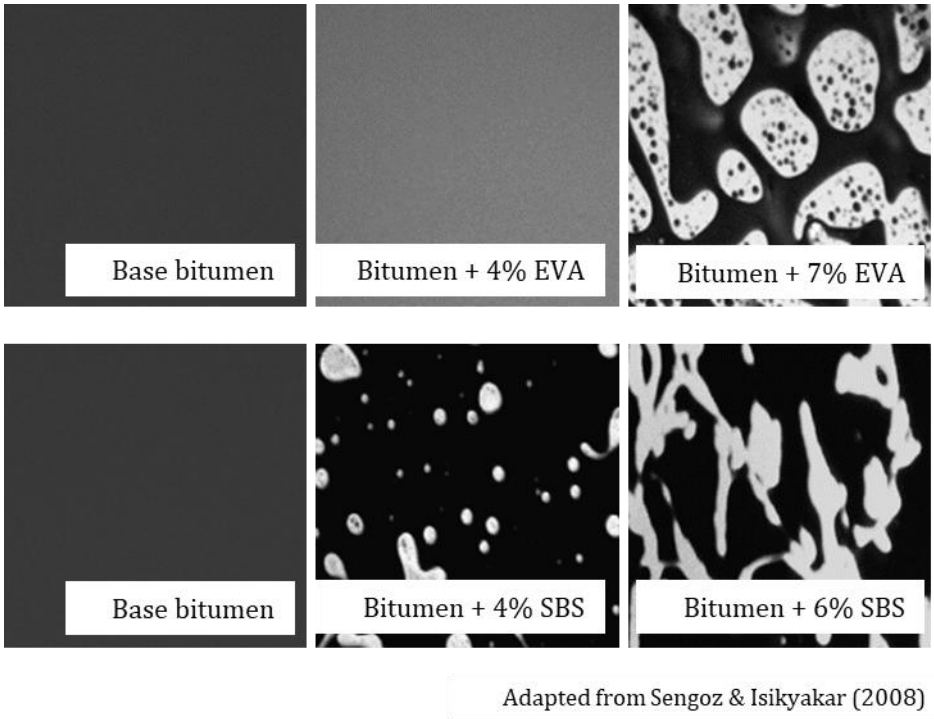


Figure 2-2 – Fluorescent images of SBS and EVA PMBs with 100x magnification (adapted from Sengoz & Isikyakar)

A technical parameter to be considered for all binders modified with the addition of polymers is the storage stability. This parameter measures the ability of the binder to maintain a uniform distribution of polymer over time. If phase separation occurs easily, with the polymer and bitumen forming distinct layers, the material is not practical for long-term storage without agitation before application. The application of SBS requires attention to this parameter because particles of this polymer can easily pass through a coalescence process in modified binders. Liang *et al*. observed that PMBs mixed with a content of 0-5% SBS at 170 °C and rotation speed of 4000 RPM presented phase separation after 48 hours (Liang et al., 2015). The phase separation was observed by means of detection of morphology with microscopy and evaluation of mechanical properties. The use of *sulfur* was related by Wen et al. as a way to control the stability of binders modified with SBS, allowing a better distribution of this product (Wen et al., 2002).

In parallel, the use of a thermoplastic polymer such as EVA can also be considered for improvement of performance parameters such as stiffness and viscosity (Panda & Mazumdar,

1999; Sengoz & Isikyakar, 2008). In the tests performed by Panda & Mazumdar it was observed that the EVA provided a good storage stability even without additional product (Panda & Mazumdar, 1999).

Investigating in a molecular scale, the interaction between the composition of a unmodified asphalt binder, represented by the SARA fractions, and the structure of the polymer can be described by a property referred as Compatibility (Dony, 2019; Lesueur, 2009; Polacco et al., 2015). The compatibility is a qualitative property that indicates whether the polymeric matrix in suspension inside a binder is successful in alter the molecular structure of the binder and maintain stable, which would mean in other words, compatible. Thus, it is fundamental comprehend that inside compatible PMBs the mechanism of modification comes rather from the association of the polymers to the oil-phase of the binder than from solubilization.

Lesueur studied the microscale of bituminous binders, including PMBs, proposing a chemical comprehension of the interaction phenomena found in these binders (Lesueur, 2009). This study observes that at micron scale all PMBs are heterogeneous. When in contact with the SARA fractions of the bitumen, the polymers tend to be swollen by the light aromatic components present in the dispersed phase of the SARA structure, forming a Polymer-rich phase also dispersed in the binder.

Figure 2-3 shows an example of microscopy of a same binder modified with EVA in different proportions, with different Polymer-rich phases represented by the areas in yellow.

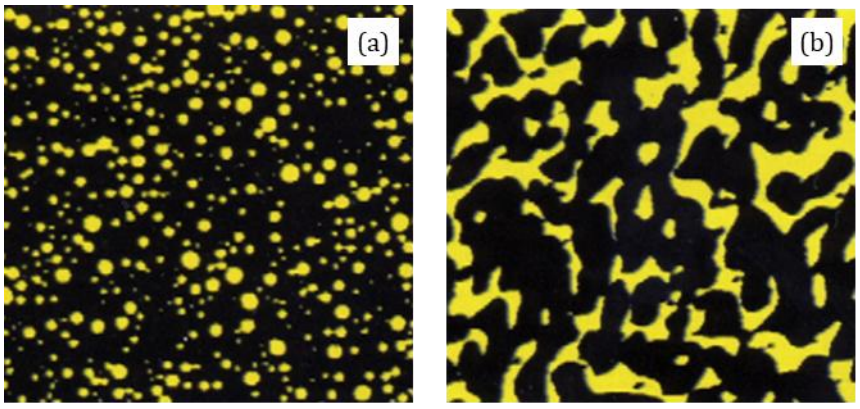


Figure 2-3 – Microscopy of PMBs modified with EVA (a) PMB with 3% EVA; (b) PMB with 7% EVA. Adapted from Lesueur

A material that is completely miscible in the bitumen is not desired in the perspective of compatibility since it cannot properly create this different phase induced by the particles of polymer. Alternatively, a material that would be partially miscible and could present droplets in a sufficient size to associate to other components of the binder not showing indications of heterogeneity in a macro scale would represent a material with a good compatibility for application as modifiers in PMBs.

Continuing in the perspective of the SARA components, other points highlighted by the study were that high asphaltene content reduces polymer/bitumen compatibility, while the aromaticity of maltenes must fall within a specific range to achieve good compatibility (Lesueur, 2009).

Another study proposed that the system defined by a PMB could be placed in one of three zones divided by three different levels of compatibility (Dony, 2019). In accordance with that, those would be:

i. Total miscibility: this occurs when the polymer is completely dissolved and cannot improve the mechanical behaviour of the binder with the cohesion of the network created by association with molecules of the binder. This is associated with highly aromatic bitumen blends.

ii. Compatibility / improvement of behaviour: this describes a system binder-plastic that was interacted in the exact proportions for achieving an improvement of performance.

iii. Incompatibility: in this system the particles of polymers are coarsely dispersed and can be observed without the use of a microscope. In this case the mechanical improvement of the bituminous binder is no longer possible since the network of support for the polymeric structure was broken or not achieved.

The delimitation of the three zones is important when the nature of the polymer is known, and the level of the interaction can be controlled. Considering the SBS, for example, the limits between the zones were defined based on the influence of the aromaticity of the SARA fractions rich in maltene and the asphaltene proportion.

A state-of-the-art study about the internal structure and morphology of modified binders was developed by Polacco et al. (Polacco et al., 2015). In this study, it was observed that the effectiveness of polymer modification depends on achieving phase inversion, an arrangement where the polymer phase becomes continuous and significantly enhances asphalt properties.

However, if the swelling of the polymer is excessive, it can lead to complete dissolution, causing the polymer to lose its structural integrity and rendering its benefits ineffective.

Improper swelling can result in macroscopic phase separation during storage, making the material unusable due to the loss of homogeneity and excessive viscosity in the polymer-rich phase. Figure 2-4 presents a graph adapted from Polacco et al. (Polacco et al., 2015) which shows the relation between the level of swelling in a figurative bitumen compared to the evolution of the mechanical properties.

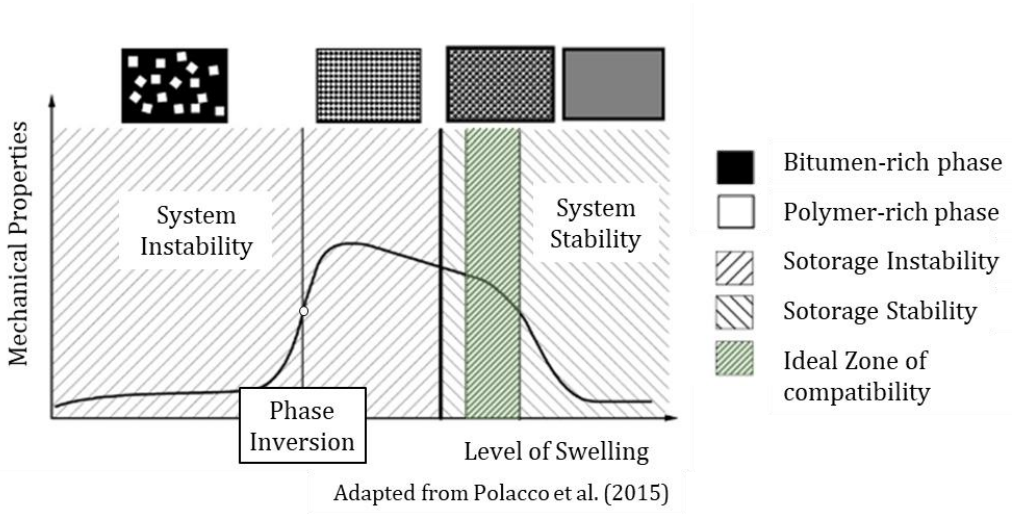


Figure 2-4 – Representation of phase inversion and zone of ideal compatibility based on level of swelling (adapted from Polacco et al., 2015)

Based on these findings, compatibility in polymer-modified asphalts (PMAs) is more closely related to the ability of the binder to maintain its heterogeneous nature while ensuring a stable dispersion of the polymeric phase within the asphalt matrix. This means that rather than achieving a fully homogeneous mixture, the key to compatibility lies in preventing phase separation over time, particularly under storage and application conditions.

Since bitumen is inherently a complex and variable material, its interaction with polymers depends on multiple factors, including molecular weight, polarity, and chemical composition. A compatible system ensures that the polymer remains finely and uniformly dispersed throughout the asphalt, preventing macroscopic phase segregation.

Achieving and maintaining this stable dispersion requires an optimal balance of aromatic content, asphaltene concentration, polymer characteristics (such as styrene-to-butadiene ratio in SBS copolymers), and the presence of potential compatibilizers. In practical terms, compatibility translates to a binder that remains stable during storage, transport, and

application, minimizing separation and ensuring consistent performance across different environmental and loading conditions.

It is also important to remark that when dealing with a material composed of two or more different types of polymers, it is complex to hypothesize a 100 % compatibility between all the polymers and the binder. In this context it is important to consider the fact that each polymer requires a different exposure time and SARA ratio to reach an optimal swelling zone.

2.5 Differences between Dry Process and Wet Process

This section discusses the methods found in the literature for implementing polymers in the conception of asphalt mixtures. It also examines the mechanical effects obtained. In general, these procedures could be divided into two main groups:

i. Wet processes: in these procedures the plastics/polymers are used for changing the mechanical behaviour of the bituminous binders. Thus, the base polymer and the virgin binder are blended into a Polymer-modified Bitumen prior to its mixing with the other components of the mixture.

ii. Dry processes: in these procedures the plastics/polymers are understood in the mixture as an aggregate integrating the structure of the mixture. In these cases, there is no requirement of previous mixture.

Figure 2-5 shows a schematic difference between the two categories of processes.

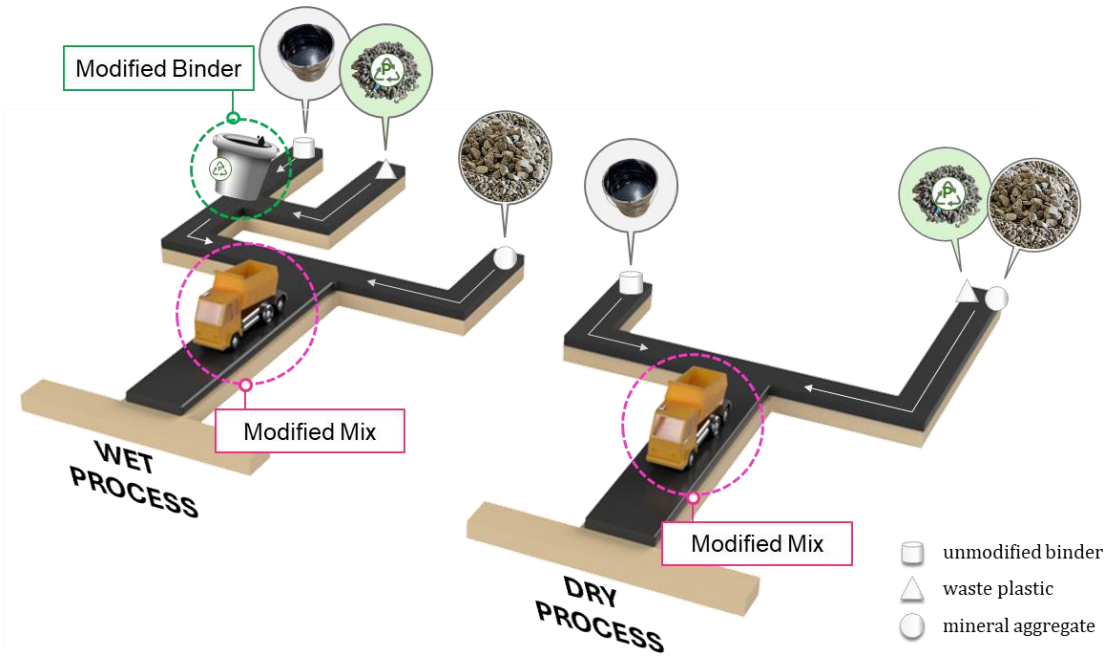


Figure 2-5 – Schematic differences between the Wet Process and the Dry Process

Each procedure is described with its own particularities. For example, the procedure for pre-mixing might diver, in the scope of the Wet Process. In the same way, the method for inserting the plastic in the Dry Process vary depending on the procedure adopted for each mixture.

However, it is possible to anticipate similar advantages and disadvantages for each category, despite the specificities of the procedures. In an economic perspective, it is known that the Wet Process is expected to be more expensive due to the costs with modification of bitumen . (Xu et al., 2021). Table 2-1 summarizes the advantages and the drawbacks of each method.

Table 2-1 – Advantages and drawbacks of different processes adapted from Xu et al.

Method	Advantages	Disadvantages
Wet Method	▪ Higher viscosity (mixture) ▪ Engineering experience	▪ Expensive ▪ Poor storage stability ▪ Requires specialized mixing ▪ Requires specialized storage
Dry Method	▪ Cheaper ▪ Easier to implement ▪ Simple production process	▪ Lack of normative ▪ No guarantee of higher viscosity

Adapted from Xu et al. (2021)

When using recycled materials, it is also important to consider material consumption among the advantages. The more recycled material that can be incorporated into the mixture design, the greater the environmental and economic benefits. In general terms, the Dry process tends to be more advantageous since the waste plastic is employed replacing the aggregates on the mixture, which represents in quantity the majority of materials in the mixture. In the next paragraphs, that treats the Dry and the Wet process individually, this will be further discussed.

The chemical interaction of these materials in the binder will depend mostly on the melting point of each polymer and its surface area (Wu & Montalvo, 2021; Xu et al., 2021). While chemical interactions plastic-binder are expected to improve the performance at high performances, it is important to evaluate the low temperature effects and eventually consider a pre-treatment to avoid poor performance (Wu & Montalvo, 2021; Xu et al., 2021).

2.5.1 Wet Process

Taking into perspective the Wet Process, the benefits of the procedure rely on the gains in the mechanical perspective. With respect to that, the main expected effect is the increase of the storage modulus and decrease of phase angle at high temperatures (Isacsson & Lu, 1999). Based on what was discussed in the previous section, a Wet procedure depends on reaching a good compatibility among the binder and the polymer, achieved when the polymer-rich phase can

act as an elastic filler while the binder change the behaviour (Lesueur, 2009; Wieser et al., 2021; Yang et al., 2020).

Considering that in the Wet Process the polymer is applied as a modifier of the binder, the content of alternative material that is considered in the project depends on the amount of binder projected to the mixture. Thus, the projects need to specify the polymer content as a percentual of the binder. In order to achieve a desirable viscosity and storage stability the content of plastic should be around 5% of weight of binder (Duarte & Faxina, 2021). Other studies consider that the optimal percentage may vary depending on the kind of polymer found in the source, fluctuating around 4.5%. Specifically, the ideal concentration starts at approximately 3.57% for PET and can reach up to 6.25% for PVC (Vargas & El Hanandeh, 2021).

However, when dealing with materials composed of multiple polymers, these specific percentages no longer apply, as each polymer reaches compatibility at different concentrations. A key point in treating these materials is the different interaction mechanisms between each polymer and the binder, making it difficult to establish a uniform proportion that ensures proper compatibility and storage. This complexity is particularly important to be concerned when dealing with recycled materials that did not pass through a previous industrial treatment.

Besides the improvement in mechanical performance, other factors should also be considered when evaluating the effectiveness of PMBs used in the Wet Process. The polymeric structure brings effects not only to the mechanical behavior but also to properties such as impermeability, adhesion, and cohesion. These characteristics directly influence the mixture's resistance to moisture damage and overall durability. As an example, binders modified with recycled PET that presented an improvement of viscosity also presented a decrease of the moisture susceptibility (Agha et al., 2023).

In other type of mixtures effects are also observed. Regarding porous bituminous mixtures, that also require good adherence and low moisture susceptibility, binders modified with recycled LDPE has presented a good performance in laboratory tests, with low tendency of leaching of pollutant agents (Hao et al., 2024). Modified asphalt emulsions used for Chip Seals also presented higher tendency to present adhesive failures in its interface when conditioned with immersion in water (Mesquita et al., 2024).

Also, in a practical point of view, a key point to verify the cost benefits of the Wet Process is still to verify the energy required for compaction and the effects of the polymer in the ageing susceptibility of the binders. Considering also as an effort to include the mixtures with

alternative PMBs in the industry, a Life-Cycle Cost Assessment (LCCA) including all the effective costs of the mixture would be recommended.

The production of PMBs is an important phase for the implementation of the Wet Process and probably the one with the biggest associated costs. During this process, a structure for heating the binder and mix it with the polymers need to be disponible. Key factors influencing the quality of polymer-modified binder include temperature, mixing duration, and shear rate. These factors must be carefully controlled to ensure both compatibility and reproducibility of the compound. For laboratory tests, the PMBs can be produced with the association of a High Shear Mixer (HSM) and a thermal chamber.

The production temperature required for producing PMBs usually depends on the polymer's melting temperature and glass transition temperature. Typically, once this temperature is exceeded, the base binder reaches a viscosity suitable for blending. When considering industrial SBS, for example, this temperature is reached around 170 and 185 ° C (Costa et al., 2019; Larsen et al., 2009; Liang et al., 2015). For alternative polymers a thermal analysis can be carried out in order to determine the phase transition and the ideal temperature (Majewsky et al., 2016).

Mixing duration also significantly impacts the uniformity of polymer dispersion within the binder. Insufficient mixing time can lead to inadequate compatibility, while prolonged mixing may cause surpass the interval of adequate compatibility and stability. Different blending process parameters, including mixing time, have a substantial effect on the properties of polymer-modified asphalt (Larsen et al., 2009). Another important factor is the shear rate, which affects the alignment and distribution of polymer structure within the binder. High shear rates can enhance polymer dispersion and improve the mechanical behavior of the modified asphalt (Kalantar et al., 2012). However, excessive shear may break down the polymer structure.

In this context, the process of incorporating polymers into bituminous binders is complex and requires precise control over temperature, mixing duration, and shear rate. Balancing these factors ensures proper dispersion of the polymeric phase, maintains the desired rheological properties, and prevents degradation of both the binder and the polymer additive, ultimately leading to a good pavement performance.

2.5.2 Dry process

In a different perspective, the alternative materials (recycled and/or polymeric) can be inserted into mixtures as a replacement of part of the aggregate content, in the methods referred to as Dry process. In these methods, a fundamental parameter to be controlled in the plastic is the size of the particles and the gradation curve. The perception of the polymer as an aggregate also brings attention to secondary parameters that are fundamental to the dosage of mixtures, such as size, shape and density.

A key point for achieving the targeted structure of the mixture is knowing the melting point and the glassy transition of the polymer used as an aggregate. In contrast to the Wet Process, the Dry Process requires ensuring that the polymers do not melt. It is important to note that partial modification of the binder can still occur in the Dry Process, given the complexity of the polymeric structure. Thus, the structure of the aggregates in mixture will depend on the thermal susceptibility of the polymers in relation to the mixing temperature in the plant.

A study of literature review developed by Heydari et al. focusing on the effects of the incorporation of plastics in Marshall Stability showed that there are some key points to be addressed when it comes to methods of production that involves the Dry Process (Heydari et al., 2021). Among those, the sequence of construction was found to impact the final mixture, especially when working with plastics that have a low melting point.

When the plastic content is inserted into the mixture along with the hot aggregates, it might melt and spread in the air voids of the mixture. In contrast, if the plastic content is added to the final mix, it is harder to observe this effect. Since the air void is related to the flow number and the rutting resistance, it is fundamental to consider that in the design of the mixtures.

In a parallel study that focused on mixtures produced by the Dry Process between 2003 and 2023, Bueno and Teixeira observed that there is still no consensus on the method for incorporating the waste plastic in the mixture (Bueno & Teixeira, 2024). Regarding the size and shape, a good performance was achieved when using a particle below 2.36 mm and the plastics in a flake-form were not recommended. However, it is important to remark that the results vary for each type of polymer present in the waste plastic. For example, while the Polyethylene terephthalate (PET) behaved well in Dry mixtures due to the high melting point, polyethylenes (PEs) presented a good suitability to both dry and wet mixtures, behaving also as a coat to the aggregates when incorporated in the mixture with heated aggregates.

Following studies that focused in such materials, it is possible to observe that polymers with low melting point such as LDPE could enhance the creep performance of HMA if added in plant during mixture (Mazouz & Merbouh, 2019). The particularity of this material on melting in temperatures used for heating aggregates is likewise highlighted as they can partially melt when heated with the aggregates (180 °C) and work as a coat for the coarse aggregates, impacting positively the adherence to the binder (Miranda et al., 2023; Radeef et al., 2021).

Polymers with higher melting point, such as PET and PP, behave differently under these conditions due to their capacity on keeping their structure and shape under the mixing conditions. In dry mixtures, these materials can have an elastic behavior inside mixtures (A. Singh & Gupta, 2024). Recycled PP and PS have shown good adaptability to the dry process in terms of performance. However, it is relevant to consider that the workability of the mixture might change in the mixture and compaction (Lastra-González et al., 2016). In fact, the PS has shown to attend the reference performance when replacing 1% of the bitumen content of project in the mixture (Vila-Cortavitarte et al., 2018).

Considering the production and storage of recycled plastics, it is also relevant to understand that these materials are usually composed of different types of polymers and can eventually be mixed with plastics from other sources in their treatment. Recycled carton packaging composed by a mix of polymers has shown suitability to be used in the dry method as a material for asphalt mixtures (Monticelli et al., 2023; Roberto et al., 2023).

The mobilization of content in the binder-polymer interface is a phenomenon hard to be isolated, even when the plastic/polymer is incorporated in the mixture as an aggregate and it is not considered a binder modifier. Polymers with low melting point might coat the aggregates instead of performing as a replacement. In these cases, it is important to understand if the partial mobilization can reflect negatively in the aggregate structure, or if the performance of the mixtures will be affected by a partial change of the gradation curve of project.

2.6 Insights from the literature: a question-based review

In the previous sections it was presented that the residue of plastic can be applied directly in the mixtures, with the aggregates through the Dry Process (Huang et al., 2007). On other perspective, the practice of modifying the binder with the plastic directly is also referred as Wet Process. For these binders, the compatibility and the storage stability are parameters to be focused.

As discussed, the concepts related to the production of polymer- and recycled plastic-modified mixtures, as well as the state of the art regarding the performance of these materials, were presented. This section provides insights into the production of these samples, with a focus on the current research and the gaps identified from the review based on the formulated questions.

2.6.1 What types of polymers are more efficient for asphalt mixtures?

As previously mentioned, recycled plastics are composed of various types of polymers, several of which have been investigated for potential application in pavement construction. The use of semi-crystalline polymers, such as PET, PE and PP are mentioned more frequently in most of the literature surveys. These materials can be incorporated in flakes, shredded or in pellet shape. Figure 2-6 shows three examples of materials that will be discussed in this subsection.



Adapted from Agha et al. (2023), Pasetto et al. (2022), and Miranda et al. (2023)

Figure 2-6 – Examples of recycled materials registered in the literature

A key point to optimize if a polymer is more suitable for a dry or a wet process is understanding the interval of temperatures where it melts and reaches its glassy transition. These intervals of temperature vary from each polymer depending on the structure of and the organization of the molecules. By means of a differential scanning of calorimetry (DSC) it is possible to identify intervals of temperature where there is a change of phase in the polymeric structure. Figure 2-7

presents a summary of the DSC of four types of polymers (PE, PP, PET and PVC) (Majewsky et al., 2016). The lowest point in the curves refers to the referring melting point.

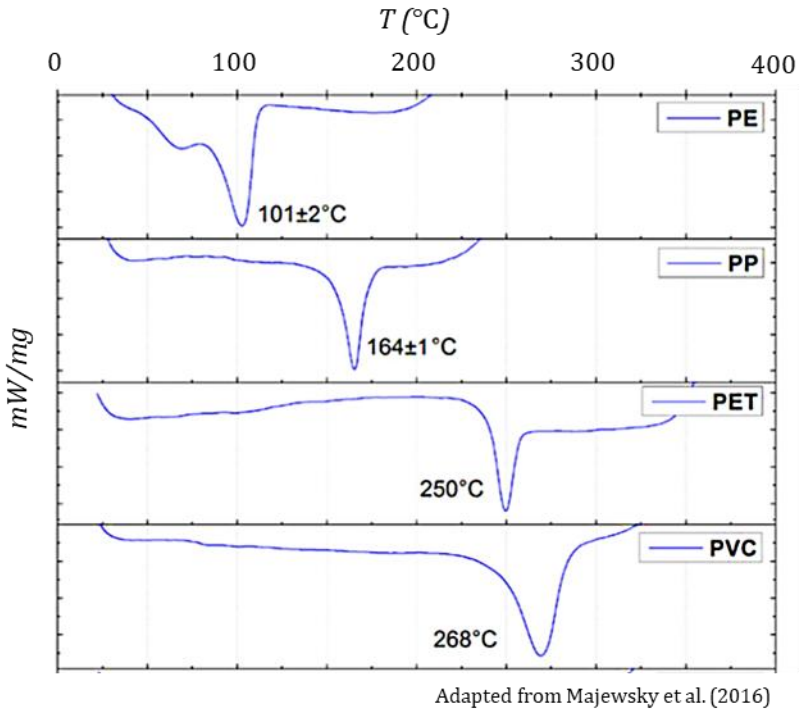


Figure 2-7 – DSC of PE, PP, PET, and PVC

Compounds containing PET are referred to in most of the studies as the leading recycled plastic to be incorporated in modified mixtures. These groups have a high melting point, around 250 °C (Majewsky et al., 2016; Willis et al., 2020), which makes them suitable for incorporation through dry processes. Besides the environmental advantage, studies reported that using this method for producing mixtures with recycled PET could result also in an increase on rutting resistance (Cardoso et al., 2023).

Moghaddam et al. investigated the rutting behavior of mixtures modified by the substitution of 0.1 to 1% of the total weight with crushed PET (Moghaddam et al., 2014). The mixtures were produced at 160 °C following a dry process. In this study, mixtures with higher PET content presented a decrease in the Indirect Tensile Strength (ITS). Alternatively, the results suggested that under dynamic loading conditions, there was an indication of improvement in the rutting behavior.

In a study that compared modified mixtures, Modarres and Hamedi observed that for certain temperatures a similar effect of the modification by SBS could be achieved when using the

same proportion of recycled PET (Modarres & Hamedi, 2014). The study compared the resilient modulus at 20 and 5 °C, observing similar amplitude of modulus at 20 °C. In contrast, at 5 °C a higher modulus was obtained with the mixtures modified with SBS, indicating a divergence of behavior in low temperatures. In both cases, this study considered contents from 4 to 6% polymer by weight of the mixture.

Ferreira et al. analysed the effects on HMA performance and structure after replacing part of the sand content (8% by volume) with recycled micro PET (Ferreira et al., 2022). Chemical and Thermogravimetric characterization were carried to estimate the level of interaction between sand and polymer and in order to verify that there was no change of phase in the range of temperatures applied to the aggregates in the production of the samples (around 150 °C). The results showed that the replacement improved the resistance to moisture damage of the unmodified asphalt mixture with TSR from 92.6% to 101.5%.

In a comparative analysis of the two types of process focused on the fatigue life, it was observed that the dry process reflected an improvement of resistance against fatigue cracking. On the other hand, the wet process also presented improvements regarding the resistance against moisture damage (Agha et al., 2023). Regarding the cracking resistance, Azarhoosh et al. has shown that the use of PET from recycled bottles as a coat for recycled aggregates could improve the adhesion to the binder (Azarhoosh et al., 2021). For this purpose, 5% of the aggregate was replaced by recycled PET. This material was incorporated into the aggregate structure in shredded form varying the particle size from 3 to 4 mm and pre-heated in a temperature of 250-260 °C prior to the mixture to the asphalt binder.

PE compounds usually present a lower interval of melting temperature compared to PET, which might vary from 100 to 130 °C (Majewsky et al., 2016; Willis et al., 2020; Xu et al., 2021). This polymer corresponds to a significant proportion of the industry production, accounting for more than 30% of European Market (Plastics Europe, 2021). Usually, these materials are available in the industry as HDPE, LDPE, and LLDPE (Low Linear Density Polyethylene). These categories change in terms of specific gravity due to the multimolecular chain.

Considering that bituminous mixture production can be held at temperatures in the range of the melting point of PE compounds, this material could be incorporated following a Wet Process or a Dry Process, depending on the mixing time.

González et al. investigated the interaction between a conventional bitumen 60/70 and different compounds of PE (González et al., 2002). This study produced modified asphalts by mixing

polymers and polymer blends with the bituminous binder at 160 °C for 6 hours at a rotation speed of 1200 RPM in a proportion of 5% by weight of base bitumen. The results indicated that even though LDPE was expected to present better solubility due to lower melting point, the blends with HDPE and compounds with HDPE presented better increment of performance. This result indicates that the interaction bitumen-polymer depends on the final structure composed by the polymer inside the modified binder, which changes based on the conditions of blending.

One parallel register of use found for this polymer was as modifier of binders in Stone Matrix Asphalt (SMA). Al-Hadidy and Yi-qiu used a grinded LDPE replacing from 2 to 8% of the bitumen proportion by weight (Al-Hadidy & Yi-qiu, 2009). The modified binders were produced in a rotation mix, at 160 °C and rotation speed of 1750 RPM. In contrast, this study applied only 5 minutes as time for blending the bitumen and the polymer. The use of grinded content in this case reflects in an easier blending of the two materials. As result, this study showed that adding LDPE to the bitumen increases shear resistance and reduces temperature susceptibility. Concerning the modified mixtures, the samples exhibited higher tensile strength and increased stiffness, suggesting better durability and crack resistance at -10 °C, the temperature chosen to investigate low-temperature performance.

Ho et al. have shown that recycled LDPEs can be applied into bitumen modification (Ho et al., 2006), which allows the application of these materials in wet processes. Taking into perspective the molecular weight distribution (MWD), this study has observed that LDPEs with wider MWD would be more suitable to application through this type of method. The modifications were observed particularly regarding low-temperature performance.

Also, regarding wet processes, Haider et al. evaluated the performance of modified mixtures. The study was held with modified binders designed with 3 to 12% LDPE by weight which were used in the production of modified mixtures. The performance tests focused on moisture damage (Haider et al., 2020). This study concluded that the use of LDPE reflected in mixtures with lower rutting depth. However, under these conditions, LDPE was more sensitive to moisture damage.

Regarding incorporation through dry processes, evidence found in the literature indicates the use of higher polymer contents. In these cases, the polymers are incorporated as part of the aggregate content, which allows the use of a higher content of recycled materials, making the dry processes more interesting from the environmental point of view. However, considering that HDPE and LDPE have their melting points and glass transition in temperatures close to

those used to produce mixtures, it is important to take in consideration eventual mobility of content of polymer from the aggregate structure to the binder phase of the mixture.

Pasetto et al. investigated the behaviour of mixtures modified with HDPE following one methodology of dry process where the shredded plastic were pre-mixed with the heated aggregates before, and then submitted to mixture with a neat 60/70 pen grade unmodified bitumen at 160 °C (Pasetto et al., 2022). In this study two proportions of plastic were tested, 0.25 and 1.5%. This study showed that even when the recycled plastic was incorporated via a dry method, where it was not directly targeted a change the mechanical behaviour of the mixtures, an improvement on the stiffness of the mixtures designed with 1.5% of polymer was observed, especially at intermediate and higher temperatures. This mixture also led to about 60% and 90% lower creep rate with respect to the mixture with 0.25% plastic and the reference mixture without plastic.

Considering the melting point of the HDPE, it would be possible to attribute the change of mechanical behaviour to the mixing temperature set to HMAs. The importance of the mixing temperature brings the attention to mixtures produced at lower temperatures.

A study comparing HMA and Warm-mix Asphalt (WMA) produced with recycled LDPE was carried out by Almeida et al (Almeida et al., 2021). In this study, the procedure of fabrication and parameters of performance were obtained comparing mixtures with neat bitumens and mixtures produced with 6% of a LDPE-based component incorporated by dry process. In relation to the production, it was possible to observe that while the HMA-modified sample presented a decrease in the air voids, the WMA-modified sample presented an increase of this parameter, resulting in a higher air void volume than the one targeted in the design of the mixture.

In relation to the performance, it was observed that the incorporation of plastic improved the rutting resistance of both types of mixture. Despite slightly lower moisture resistance, the WMA with plastic achieved an ITSR close to 80% and maintained good workability. The addition of plastic improved stiffness at 20 °C but resulted in lower values compared to Hot Mix Asphalt (HMA). Fatigue resistance was reduced due to increased stiffness, though performance aligned with HMA under higher strain levels.

Taking into perspective the experiences developed with Dry processes it is possible to conclude that a certain level of improvements is expected from mixtures even if the melting temperature

is not reached. However, it is important to note that the workability of plastic in these conditions is expected to be lower. This might result in higher air voids and higher moisture susceptibility.

Samples produced with higher contents of polymer were studied by Ullah et al. (Ullah et al., 2021). In this study, mixtures composed of 5, 15 and 25% LDPE and HDPE were individually analyzed. As expected from the previous discussions, this study showed that a higher content of polymer results in a lower rutting depth. Among those, it is possible to highlight that for 5% and 15% of polymer incorporation, this decrease was more evident in the mixtures designed with HDPE. Similarly, the incorporation of HDPE resulted overall in a higher resilient modulus than the LDPE. In the two cases the peak was reached in the sample produced with 15% of polymer.

Alongside PE, PP is also frequently cited in studies on recycled polymers. This component is a semi-crystalline polymer that has a melting point that varies from 160 to 165 °C (Majewsky et al., 2016; Thirtha et al., 2005; Willis et al., 2020), which is still a temperature relatively close to what is applied to aggregates in asphalt mixture productions. Based only in this feature it would be possible to place PP as a viable material for both Dry and Wet processes.

The effects documented for the incorporation of PP present some similarities to those observed from PE, LDPE and HDPE. Usually, the modification of the bitumen with this polymer should result in decrease of penetration and increase of both the softening point and viscosity. Another similarity was observed in the optimum proportion of polymer for achieve best performance of binders (Vargas & El Hanandeh, 2021). This average proportion found for LDPE and HDPE were respectively 4.37 % and 4.43 %, while for PP, 4.38 %. However, reported data suggests that binders modified with PP showed lower variations, when comparing the effects of these two groups of polymer (Brasileiro et al., 2019).

Miranda et al. investigated the effects of five different plastics (compounds of LDPE, HDPE and PP) in the characterization parameters of bituminous binders and mixtures (Miranda et al., 2023). In this study, two different procedures for implementing the dry process were considered: (i) pre-heating the plastic with aggregates, for polymers fit in the dry procedure; and (ii) adding the plastics in the last 5 minutes of mixture, for polymers that would accept both a dry and a wet procedure.

The results suggested that those materials could perform similarly to those designed with PMBs and that LDPE, HDPE and PP could work in modified mixtures separately or as polymeric blends. However, it was highlighted that one sample produced with a blend (that included PP)

exhibited increased stiffness and a propensity for brittle behaviour at low temperatures. One similar observation was made by Ahmedzade et al. when investigating the effects of the PP in bituminous binders (Ahmedzade et al., 2015). In this study, the incorporation of PP reflected in an increase of the stiffness in low temperatures, which is less desirable, particularly when taking into consideration regions that perform at cold weather during most part of the year.

Diverging from PET, PE and PP - that usually have semi-crystalline structure - PS and PVC can be considered amorphous polymers. These materials present a completely disordered molecular structure, with no crystalline regions. Regarding the melting behaviour, these materials tend to soften gradually without a sharp melting point, observed in semi-crystalline structures. Similarly to other polymers, studies have indicated that modification with PS and PVC can also display effect on the penetration parameter (Brasileiro et al., 2019).

Although presenting a higher melting point, PS present a glass transition around 100 °C (Willis et al., 2020). Studies on the incorporation of PS in asphalt mixtures through a Dry Process could result in a reduction in the bitumen consumption without loss of performance (Vila-Cortavitarte et al., 2018). When achieving 1 % binder replacement, the mixtures improved mechanical properties and rutting was reduced by 50%. However, when the PS content was 2 % the mixture presented lower workability and cohesion.

Comparing to the other polymers, waste PS reflect in a lower elastic behaviour in the modified asphalt mixture. In parallel to PP, this polymer tend to increase strongly the rigidity of mixtures, which might result in poor performance in colder regions and increase cracking failure (Xu et al., 2021). However, considering the environmental performance, it is relevant to take into consideration potentially harmful substances that might result from the heating of this material.

Incorporating PVC to bituminous mixtures by wet processes can also be used to improve their performance (Cardoso et al., 2023; Fakhri et al., 2022). Benefits can be observed in both rutting and fatigue. Recycled PVC also improves moisture resistance and helps prevent cracks in cold temperatures. At high temperatures, PVC-modified asphalt performs better, but it may slightly reduce skid resistance. However, the use of this product must be followed of an environmental survey since it was observed some subproducts created in the incineration (Sun et al., 2003).

In the perspective of this discussion, Table 2-2 presents a summary of the main categories of polymers found in recycled materials. For each material, it is presented features that are linked to the construction of modified mixtures and benefits on performance when designed through these methods.

Table 2-2 – Summary of polymers found in recycled plastics

	PET	**LDPE**	**HDPE**	**PP**	**PS / PVC**
Structure	Semi-crystalline	Semi-crystalline	Semi-crystalline	Semi-crystalline	Amorphous
Glassy temperature	-	-	-	-	100 to 260
Melting temperature	~ 250	~ 110	~ 130	~ 160	-
Recommended procedure	Dry	Wet / Dry	mostly Dry	Wet / Dry	Wet
Optimum proportion *	3.57 %	4.37 %	4.43 %	4.38 %	6.25% (PVC)
Stiffness	↑	↑	↑	↑	
Main Benefits	Aggregate coating	Increase rutting resistance	Increase rutting resistance	Higher stiffness	-
Drawbacks	Lower workability	Moisture damage Lower fatigue resistance	Moisture damage	Lower Marshall stability	Leaching
Availability **	5 %	13.4 %	8.7 %	15.4 %	14.5 %

Values obtained from (Vargas & El Hanandeh, 2021) *
Values estimated from (Plastics Europe, 2024) **

2.6.2 What parameter could be used to rate the blending between polymers and binders?

The concept of compatibility has already been introduced and discussed in previous sections of this chapter, being presented as a fundamental parameter to achieve an optimized polymer-bitumen interaction. However, it is important to recognize that each kind of polymer achieves compatibility under specific proportions and blending conditions. These conditions are going to be fundamental to determine the performance of the mixture.

When working with polymers that reach the melting point in temperatures below 170 °C, such as LDPE, HDPE and PP (Majewsky et al., 2016), this question is even more complex because it is not possible to identify the proportion of the plastic that might melt during production of the modified mixture/bitumen and if this content is enough to assembly a polymeric phase inside the binder molecular structure. On the other hand, other polymers, like PET, PVC and PS, are more unlikely to blend and present consequently a great possibility of not presenting a good compatibility to the binder (Xu et al., 2021).

Different from other binder properties, compatibility is not represented by a single numerical parameter that can be measured to indicate whether the interaction was reached. Instead, the most effective approach to assess the blending would be by analyzing the experimental evidence led by the compatibility of each polymer, individually. For example, the literature shows that the presence of polymers in the binder structure could result in modification of conventional characterization parameters, such as penetration, softening point and viscosity. Another evidence of blending is observed by an increase on the elastic behavior of the binder in high temperatures, characteristic of polymers.

When investigating the behavior of polymers present in recycled plastics when these materials are incorporated in mixtures through a dry process, three possibilities were observed, as illustrated in the scheme presented in Figure 2-8. The first possibility is that the plastic will work as a superficial coat to the aggregates, helping in adhesivity to the binder. The second possibility is that the plastic will remain solid, integrating the aggregate skeleton. However, the third possibility is that these particles could melt completely and integrate the binder phase, resulting in a wet process effect in a dry procedure. It is relevant to consider the possibility of the three movements occur at the same time, when using polymers that can perform both the wet and dry process, such as PE, LDPE, and HDPE.

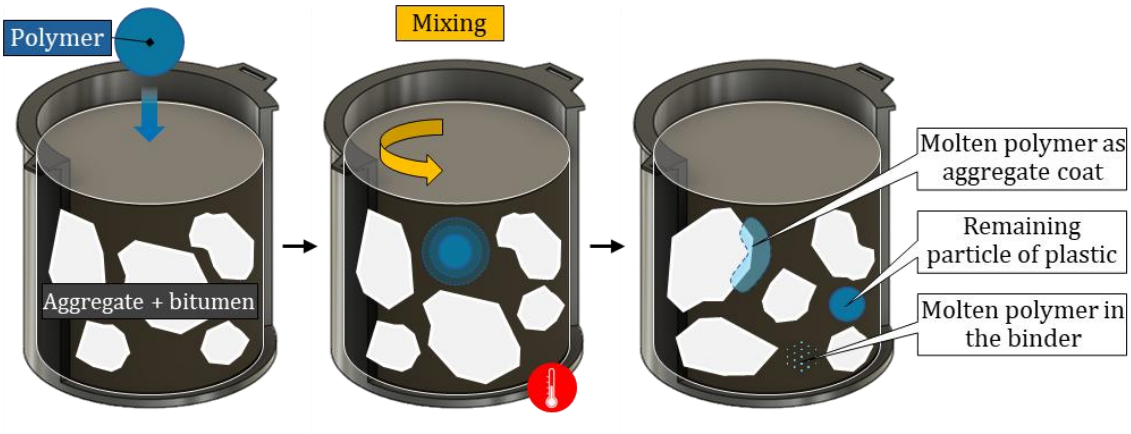


Figure 2-8 – Example of mixture designed with polymer by the dry method (scheme)

In this case, two of these possibilities of movement bring key points that must be observed. Considering the plastic remains partially solid in the mixture it is important to take these new particles into account and how the granulometry is impacted. Another point is the amount of plastic that is partially melted into the binder. Focusing on the compatibility discussion, it is important to consider the amount of plastic that can achieve this effect otherwise the result will be only melted plastic without mechanical improvements.

One similarity observed from the most part of the studies that investigated this interaction was the consideration of a control material in the experimental matrix. Independently of the type of parameter, the insertion of this input in the analysis allows a comparative evaluation of the binders and the identification of potential interaction. However, one research gap identified in this literature evaluation was the lack of an empirical parameter that could measure and compare different levels of compatibility from different modified binders.

2.6.3 How to identify the presence of plastic in the composition of a modified bitumen?

The previous sections explained the mechanism of modification of a binder by means of the creation of a polymeric-rich phase that associates to the molecular structure of the binder. This modification can eventually affect the viscosity and the mechanical properties of the binder. On the other hand, a polymer may eventually dissolve into the binder, but its content might be insufficient to create a molecular structure. Alternatively, the mixing process could lead to a micro-abrasion of the polymer, dispersing small particles throughout the binder. In both cases,

there would be a possibility of not identifying differences in mechanical behavior that confirmed whether that the plastic dissolved.

In this perspective, studies that aim describe the modification by incorporation of plastics also count on alternative tests to provide more precise conclusions. Tests that characterize the chemistry of the materials are a frequent alternative in that matter. Grounded in the composition basis of the binder in SARA components some techniques such as chromatography supported by other laboratory process can be used to characterize neat binders (Corbett, 1969). However, the manipulation of materials becomes more complex when the level of molecular interaction between the polymer and bitumen components is unknown.

The Fourier-transform infrared (FTIR) spectroscopy that can be used to identify functional groups and chemical bonds found in molecules of a sample (Abramowitz & Bauman, 1963; Duxbury, 1978). Considering, for example, that two different materials A and B could be mixed without generating a reaction. By means of this test it would be possible to identify the chemical bonds found or only in A or only in B and those found in the blend between the two. Based on that, the test is another alternative for identifying modifications in bituminous binders and their origin.

When subjected to the FTIR, each polymer generates a characteristic spectrum (Peltzer & Simoneau, 2013). The blending with other polymers or the incorporation into a modified bituminous binder are presumably mechanical processes that do not alter the base molecular composition of these materials. Based on that, the FTIR can be a technique used to investigate the presence of polymeric compounds. Figure 2-9 presents an illustration of an adapted spectrum obtained from a sample of LDPE. The image provides a representation of obtaining and reading of the spectrum.

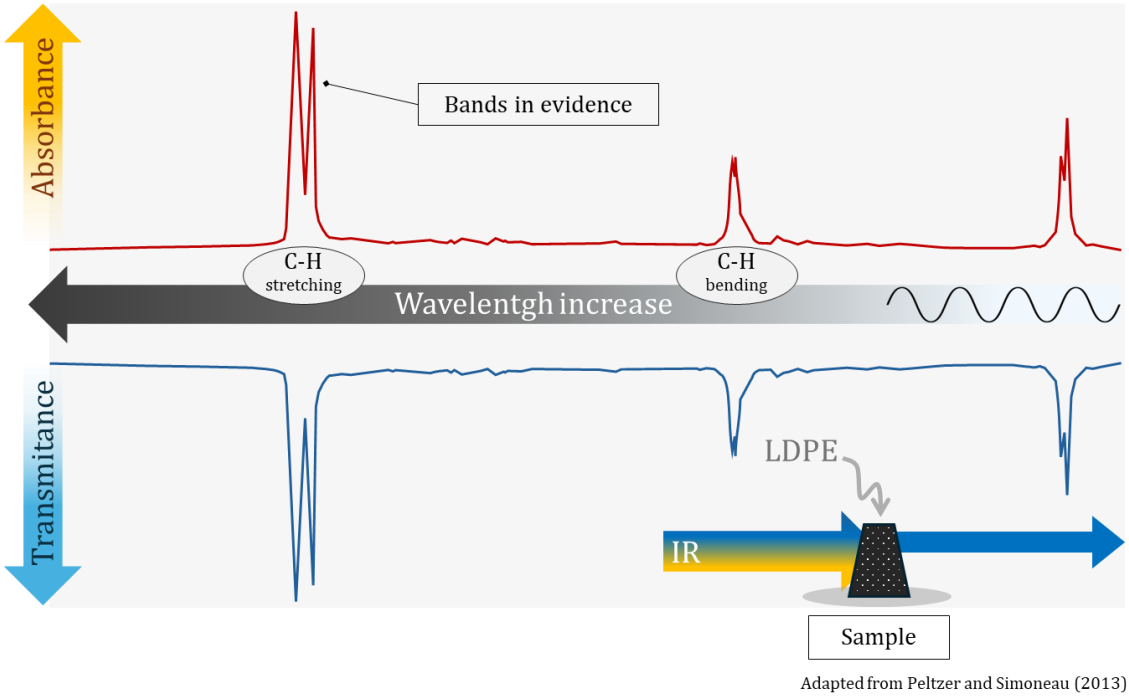


Figure 2-9 – Example of FTIR Spectrum from a LDPE adapted from Peltzer and Simoneau (2013)

The unique molecular structure and chemical composition of different polymers result in distinct spectral patterns. These patterns can be referred, for example, for identifying the type of polymers found in a polymeric blend. In another perspective, the same analysis can also be carried out to investigate the migration of components from the polymers into the base binders.

Although different observations can be made from each analysis, the FTIR technique was already found to be reproductible when analysing bituminous binders (Porot et al., 2023). In a study conducted in the scope of RILEM TC 272, unmodified binders and PMBs were tested in different laboratories. The analysis observed that although slight differences could be found in the intensity, the bands would be located approximately in the same wavenumber, with variation of less than 2 cm^{-1}. After an 8-point adjustment, all the spectra were also visually comparable.

This observation is a key point for using the FTIR test also to categorize similarities in the composition of two modified binders and also create a fingerprint for each material. The FTIR technique can also be used to characterize the SARA fractions after separation in laboratory

(Wang et al., 2019). When there is knowledge of the spectrum of the base binder it would be possible to identify by means of the original spectra an evolution of each fraction.

In fact, an important factor in this analysis is that the incorporation of recycled plastics in bituminous binders and mixtures usually requires a heating process to achieve the glassy transition of the base polymer. As mentioned previously, this results simultaneously in a partial oxidation of the binder. Feng et al. studied the ageing process of fractions from a same unmodified bitumen isolated using FTIR (Feng et al., 2016). The study observed that this technique can be used to identify oxidation in all fractions, reflecting in a way to measure the ageing degree of the bitumen.

Comparing the unmodified binders and SBS and EVA modified binders from the same source, it is possible that the association to the polymers slows down the aging process in PMBs. In this case, the polymer would perform as an aging retardant (B. Singh & Kumar, 2019). Also collaborating to this analysis, Yuan et al. investigated the laboratory ageing of PMBs modified with PE (Yuan et al., 2017). Two techniques were used for this matter: the rolling thin film oven test (RTFOT), for investigating short-term ageing and the pressure aging vessel (PAV), for investigating long-term ageing. It was observed that the presence of PE in the samples decreased the intensity of the bands of sulphoxide (S = O) and carbonyl (C = O).

Based on that, it is possible to conclude that the FTIR is a recommended technique for investigating the changes in the composition of a base binder. However, it is important to consider that the ageing exposure of the material can also create new chemical bonds. The identification of the corresponding bands must be done in order to isolate the effects of eventual additives, such as recycled polymers.

2.6.4 Which mechanical differences are expected when mixing mineral and polymeric aggregates?

This chapter explored various application experiences of polymers and recycled plastics as alternative material for production of modified mixtures. Most of the studies surveyed in the literature claim that mixtures that achieve the conditions of compatibility tend to become stiffer. This improvement in stiffness is described as a feature that results in improvement or loss of performance regarding rutting, cracking, or both phenomena in different conditions.

These are among the main failure phenomena affecting mixture. Thus, it is relevant to further investigate, from the mechanical characterization of these materials, parameters that change after incorporation of plastic. Such parameters are helpful to explain the performance of the pavements under different conditions of temperature and load.

As mentioned before, the modification with polymers such as the SBS affect the mechanical behavior of bituminous binders, especially when performing at high temperatures. Figure 2-10 presents data adapted from Airey. In the graph it is presented the master curves and the black diagram of samples produced with 3, 5 and 7% SBS in their constitution compared with the reference binder used for the modification. By this study, at lower frequencies, which in the graph correspond to the performance at higher temperatures, the bitumen was notably stiffer. Also, in the black diagram it was observed a change of phase illustrated by a decrease of phase angle.

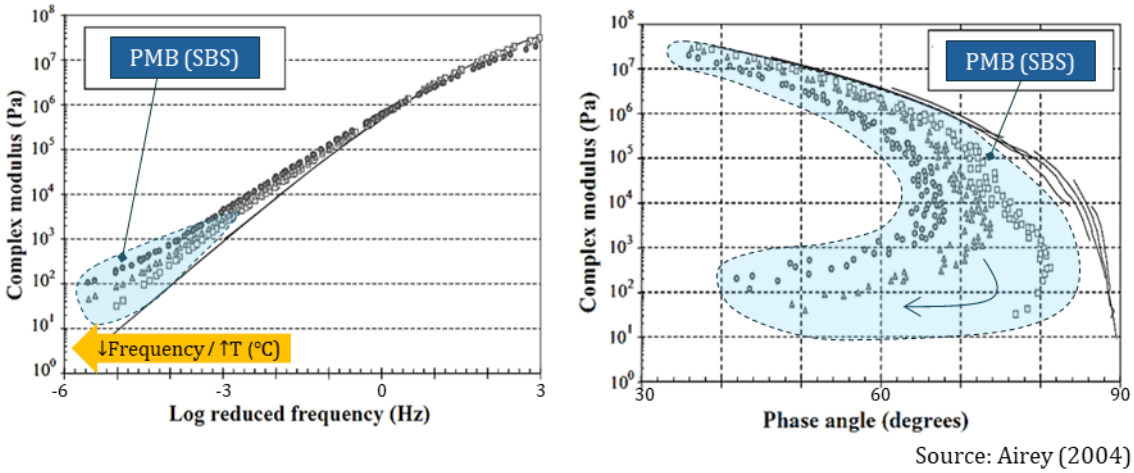
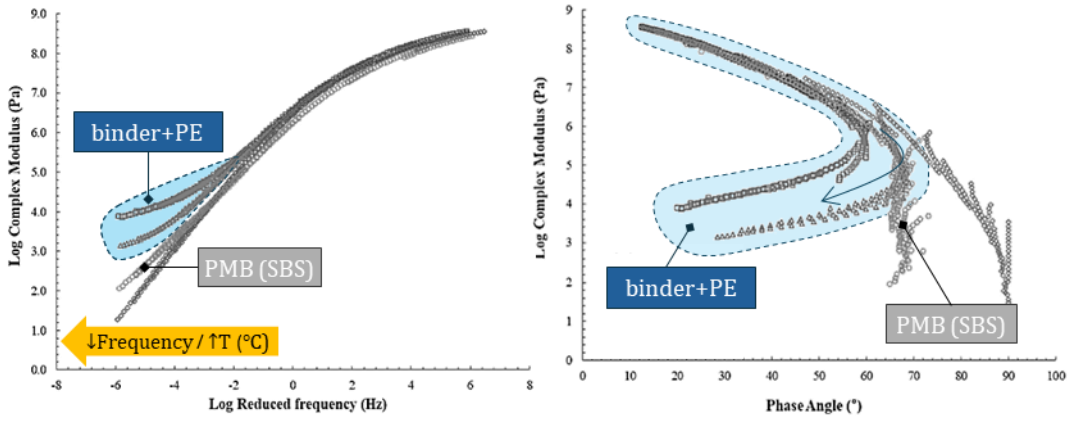


Figure 2-10 – Example of behavior of PMB with SBS adapted from Airey (2004)

Notably, the use of semi-crystalline polymers could result in similar behavior. An adaptation of data documented by Kakar et al. (2021). Comparing the effects of SBS and PE it was observed that PE could lead the binder to a higher stiffness when submitted to performance at high temperatures. The change of phase was also observed. Based on the shape of the curve it would be possible to infer that at high temperatures the binder tends to present a very elastic behavior.



Source: Kakar et al. (2021)

Figure 2-11 – Example of comparison between PMB and binder modified with PE adapted from Kakar et al.

When producing mixtures with PMBs and mineral aggregates it is already expected that the mechanical improvements obtained in the modification of the binder will also be observed in the mixture behavior. However, when designing pavements through a dry process, it is more complex to indicate how the elasticity of the polymers will impact in the mechanics of the mixture, when placed with other aggregates.

In addition, when working with materials such as LDPE, HDPE and PP that can partially melt during the mixing process, it is important to consider an alteration on both binder and aggregates. Pasetto et al. (2022) observed that mixtures produced with aggregates coated with pre-heated PE would achieve the change of behavior characteristic similar to PMBs, with change of phase and increment of stiffness at low frequencies. This result was achieved because the polymer was previously melted and mixed with aggregates.

Recycled polymers can also be incorporated into the mixtures in larger amounts when it is expected to replace part of their aggregate content. In this context, it is important to consider that part of this material can melt and change form, shape or even migrate to the binder phase. This will depend on the type of polymer and the exposition to high temperatures. In this case, the binder content would be higher than projected and the aggregate skeleton would be incomplete.

CHAPTER 3
MATERIALS FORMULATION AND PRODUCTION

This chapter presents a detailed description of the materials and of the procedure followed to produce binder or mixture specimens tested in all the experimental campaigns conducted during the development of this Thesis. Each campaign focused on investigating a specific objective and more details are given in the chapter 4 dedicated to the description of Method.

3.1 Introduction

This chapter provides an overview of the materials employed in this research study, detailing their preparation, and characterization processes. Figure 3-1 presents the flowchart of the method focusing on the steps that lead to the preparation of samples. The remaining sections of the flowchart are discussed in the next chapter (CHAPTER 4 - METHOD), where the procedure of each test performed with the samples is explained.

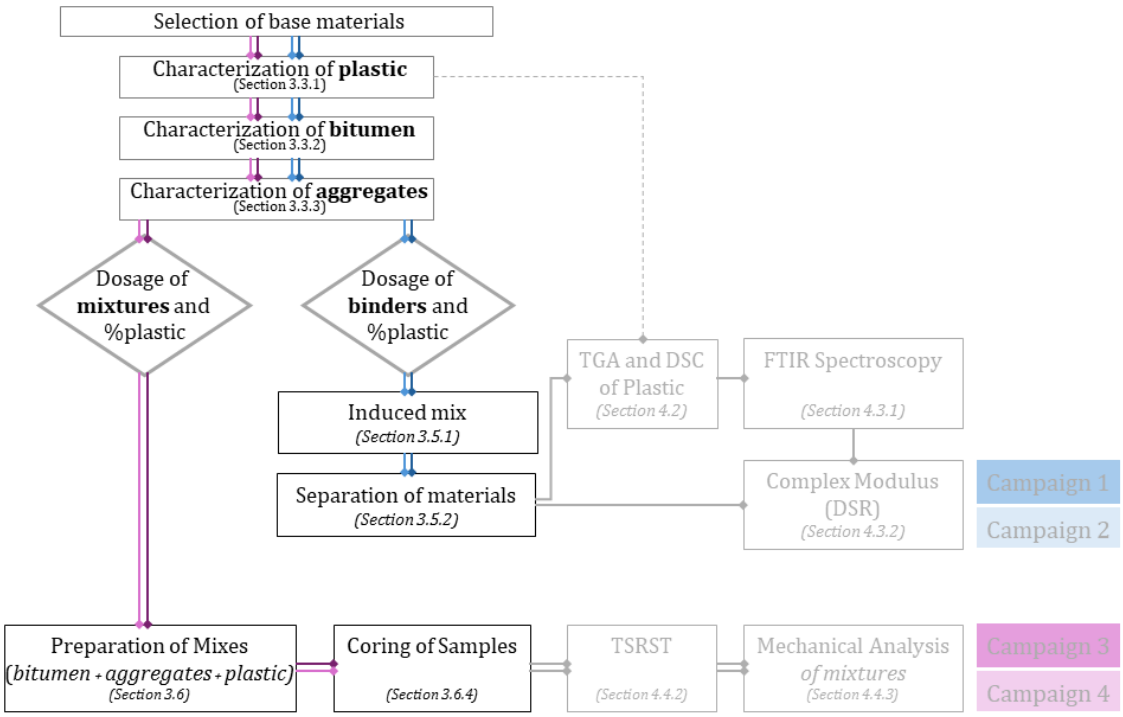


Figure 3-1 – Flowchart of experimental plan and production of samples

Within the framework of this research, four experimental campaigns were arranged. Each campaign is structured as an independent path and can be identified in the flowchart tracking the final output. Campaigns 1 and 2 refer to the tests carried out on the scale of bituminous binders while Campaigns 3 and 4 refer to those performed at the mixtures scale. A summary of all four campaigns is presented in the section 4.1.

Regarding the preparation of samples, the base materials (plastic waste, aggregates, and bituminous binders) were defined, and then the sources were selected. After collecting, the materials were characterized according to the features targeted in the scope of bituminous binders and mixtures.

Subsequently, two parallel paths were outlined. In the first place, there is the process for preparing samples of bituminous binders. This part of the experimental plan refers to the steps

of induced interaction between the binder and the waste plastic. In this phase, only the resulting bitumen was tested eliminating the solid plastic particles in suspension after interaction. This process outcomes in the method of campaigns 1 and 2.

Secondly, there is the path of the experimental plan that refers to the production of the samples of asphalt mixture. The samples were produced by laboratory mixing and compaction and then extracted and shaped in specific geometries for the tests. This path outcomes in the method of campaigns 3 and 4.

In the scope of this chapter, attention is given to the processes of sample preparation, ensuring that each specimen meets the required criteria for testing. In the following sections, the steps for the preparation of the samples are individually discussed. This discussion establishes a context for the subsequent chapters, where the effects of interaction and performances of these materials are explored.

3.2 Base Materials

The materials employed in this study were obtained through institutional partnerships and selected to reflect conditions relevant to practical applications in road engineering. The recycled plastic used corresponds to a multilayered food packaging waste, representative of a highly heterogeneous class of post-consumer polymers. The bituminous binder is a 50/70 penetration-grade bitumen, supplied and characterized according to European standards. A detailed description of all materials is provided in the following subsections.

3.2.1 Recycled Waste Plastic

A source of recycled plastic was chosen for all the experimental campaigns of this research. This material is derived from post-consumer food packaging waste and has been treated for re-insertion in the construction sector. The main supply of base material for this conditioning process was a multi-layered assembly of cardboard, polymer and aluminum used for the conservation of food and drinks. In its waste form, the base material is subjected to a process of densification and further shredding of the particles. After the shredding process the residue was tested to receive a recyclability certification.

Figure 3-2 presents the aspects of the neat shredded residue. In Figure 3-2 (b), it is shown a zoom in the texture of the particles, in which it is possible to observe the fibers in detail. In addition, in Figure 3-2 (c), it is shown examples of residues of PET found in the composition of the material. Concerning the analysis developed in this thesis, this residue is going to be referred simply as “plastic” in the further sections of this report.



Source: Author

Figure 3-2 – (a) Aspect of shredded plastic after obtainment; (b) Details of the fibers; (c) Particles of PET found in the neat plastic.

After the conditioning process, the composition of the plastic is targeted to be in majority (~ 90%) Low-Density Polyethylene (LDPE) and Linear Low-Density Polyethylene (LLDPE). High-Density Polyethylene (HDPE) and aluminum powder are expected to be around 5% each. In addition, due to the conditions of storage and production, it is expected that the plastic can be contaminated by residues of PET and cellulose. In the technical specifications, it is informed that the softening temperature is 110 °C. The melting temperature is going to be discussed in the discussion of the results of the chemical characterization of the plastic in the first campaign.

In the shredding procedure, the granular size of the particles is set to be under 10 mm. The gradation of the neat plastic was determined using a sieve analysis procedure (EN 933-1). A representative sample was selected and then mechanically shaken through a series of sieves of opening size: 16 mm, 12.5 mm, 10 mm, 5 mm, 2 mm, 1 mm, 0.5 mm, 0.2 mm, 0.106 mm, and 0.075 mm. The granulometry curve is shown in Figure 3-3.

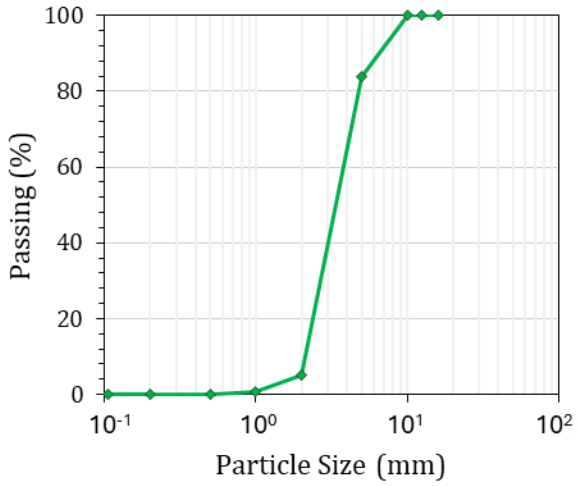


Figure 3-3 - Granular distribution of neat plastic

Based on the size distribution, it can be observed that the particle sizes are predominantly concentrated between 10 mm and 2 mm, with the majority (80%) situated within the range of below 5 mm, as indicated by the material that passes this sieve and it is retained on the sieve of 2 mm.

The density of the plastic was calculated using an adaptation of the pycnometer method (NF EN 1097-6). For this purpose, it was used a pycnometer of 1000 mL and distilled water to fill its volume. By default, it was observed that the content of plastic floated in the water, indicating a relative density below 1. Some particles remained in the bottom of the container, which might be a result of the presence of aluminum and PET in the composition of the plastic. The apparatus was carefully agitated in order to completely remove the air bubbles, and a filter was used to avoid the movement of the particles of plastic to above the level of water. Figure 3-4 shows the setup adapted for the test and the aspect of the sample. The procedure was repeated 3 times to check repeatability of measures. The relative density obtained for the plastic was 0.9.

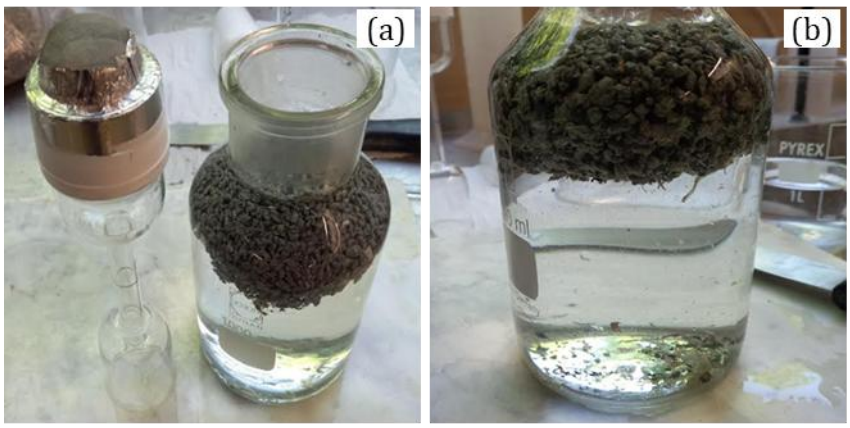


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Figure 3-4 (a) Setup of test of pycnometer adapted for plastic; (b) Aspect of the plastic when immersed in water.

3.2.2 Bitumen

The research involved three experimental campaigns, all of which required the use of asphalt binder in the experimental procedure. In order to focus only on the effects of the plastic when in contact with the bitumen and with the mixtures and eliminate the particularities of different type of binders, the same type of binder was maintained in all three campaigns.

The experimental design established the use of unmodified regular binders graded as 50/70 penetration grade binders (or PG 58-22 in the United-States Performance Grade classification), consistent with standard specifications for such materials. A different binder was used for each campaign, but all adhered strictly to the same grading and performance criteria. In the first campaign, the binder was obtained in the state of Ceará, in Brazil. In the second and third campaign the binder was provided by a producer in the region of Emilia Romagna, in Italy.

During all campaigns long periods of storage of the binder were avoided, ensuring that the materials retained their original properties and were not affected by prolonged storage time. Furthermore, each campaign included a step of mechanical characterization in its neat state using a Dynamic Shear Rheometer (DSR). This methodology provided a comprehensive and controlled evaluation of binder interactions and their implications for mixtures performance.

3.2.3 Aggregates

For the production of the mixtures, limestone aggregates and limestone-based fillers were used. The materials were provided in three fractions: coarse aggregate, sand, and filler. The filler is composed mainly by $CaCO_3$, as commonly employed in local reference mixtures. The coarse aggregate and the sand were sieved and separated following the order of sieves of EN 933-1: 16.0 mm; 12.5 mm; 10.0 mm; 5.0 mm; 2.0 mm; 1.0 mm; 0.5 mm; 0.2 mm; 0.106 mm; and 0.075 mm. The fractions were treated as individual materials in the composition of the mixtures.

The relative density was measured separately for each fraction. For this purpose, a vacuum equipment was employed as detailed in EN 1097-6:2022. This approach allows the more adequate calculation of the density of the aggregate and of the loose mixture during the mixture campaign. Table 3-1 presents the results of relative density measurement for the aggregates.

Table 3-1 – Relative density of aggregates by fraction

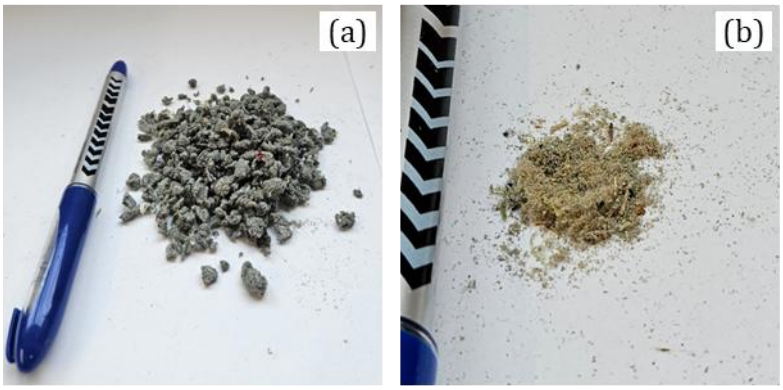
Fraction (*mm*)	**Relative density (-)**
12.5	2.715
10	2.717
5	2.728
2	2.749
1	2.737
0.5	2.723
0.2 0.106 0.075	2.722
filler	2.439

3.3 Preparation of plastic for chemical tests

The plastic can be described as a heterogeneous material with particles under 10 mm in neat condition. In order to prepare the sample of the material for the chemical tests performed in this thesis a pulverization process was proceeded to ensure a representative sampling even when separating small quantities. This is particularly important for the tests requiring small amounts of materials, such as the Thermogravimetric Analysis (TGA) and the Differential Scanning Calorimetry (DSC), conducted in this research.

The pulverization procedure involved immersing the plastic particles in liquid nitrogen, which was obtained at a temperature of approximately -90 °C, in order to facilitate the breaking of the particles and then transferring the material to a laboratory blender. All the contents of the neat plastic were kept inside the sample, even eventual contaminants such as PET and aluminum.

The cycles of nitrogen and blending were repeated until it was achieved particles in the form of a powder. Figure 3-5 presents an illustration of the plastic in powder form.



Source: Author

Figure 3-5 – Illustration of neat plastic after pulverization procedure. (a) Neat plastic in shredded form. (b) Neat plastic in powder form

3.4 Sample production: Interaction Bitumen-Plastic

In the scope of the experimental campaigns that targeted the influence of the interaction with the plastic in the behavior of the bitumen, a method to blend both materials, in which all the conditions could be observed and controlled, was proposed. Firstly, both materials were mixed in a High Shear Mixer with controlled shear rotation and then separated by sieving of solid content. The sieved bitumen was selected to produce samples used in tests while the solid content was not considered for analysis. This process ensures that only the bitumen that has potentially interacted with components from the plastic is considered for further analysis.

Figure 3-6 presents a scheme of production of the samples of bitumen considering the steps of mixing and sieving. These two steps are discussed in detail in the next sections of this chapter.

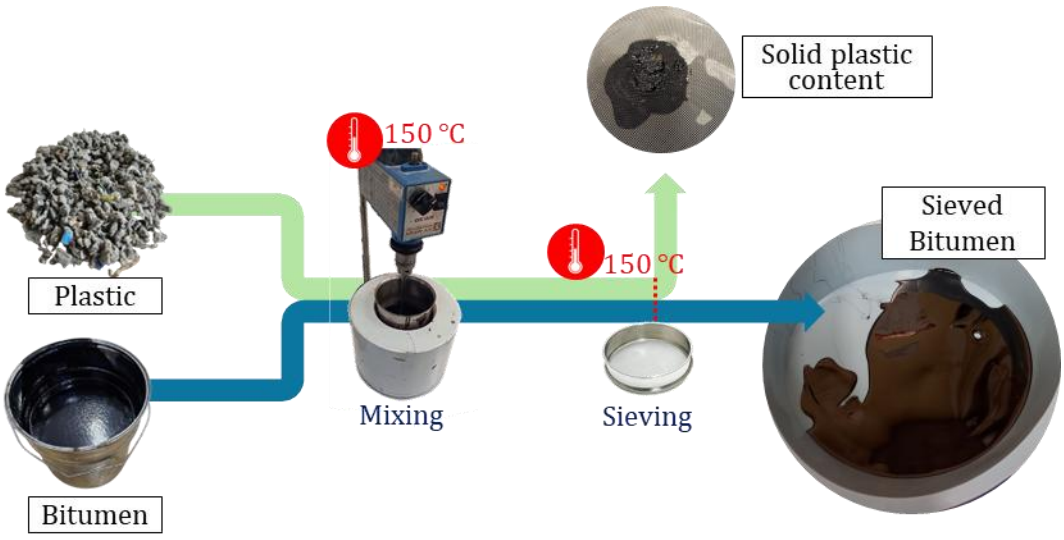


Figure 3-6 – Scheme of production of bitumen samples

3.4.1 Interaction Bitumen-Plastic: Mixing

As previously introduced, a laboratory High Shear Mixer was used to induce the interaction between bitumen and plastic. The mixing procedure was performed by heating the system at a constant temperature of 150 °C. The temperature inside the mix was monitored with a thermometer. This temperature was selected as a reproduction of the conditions that the plastics should normally be subjected to in the fabrication of Hot Mix Asphalt (HMA). Since the same temperature was set for all the samples, this variable could be removed from the experimental matrix.

The mixing time and the shear speed were set as variable parameters for the elaboration of the binders. The shear speed varied from a low-speed shear (200 RPM) and a high-speed shear (1000 RPM). The mixing time varies from 30 min to 60 min. These conditions were chosen in order to understand the potential impact of the variables of the mixing process on the interactions between bitumen and plastic. The selection of these specific mixing parameters is critical for elucidating the influence of these variables in the induction of contact between the two materials.

3.4.2 Interaction Bitumen-Plastic: Sieving

After mixing, the solid plastic phase was separated from the bitumen. For this purpose, the bitumen was filtered with the use of a laboratory sieve of 1.20 mm opening. The content was transferred to the sieve, and the system was then heated for 30 minutes at 150 °C in the oven. The decanted liquid was selected to test, and the solid phase was rejected.

3.4.3 Summary of Samples of Bitumen

Table 3-2 presents the list of all binders produced in the experimental program of this Thesis. The materials are divided into two groups. The first campaign refers to the phase of the experimental program that was carried out in the INCT-Infra, in Brazil. The second campaign refers to the binder campaign developed at ENTPE, in France.

In Campaign 1, the experimental matrix was determined to investigate the variables' influence in the interaction between the plastic and the binder. Based on that, 9 binders were designed, varying the plastic content, the mixing time, and the shear speed in different ways. Among

those, two materials of control were included. These samples were produced following the procedure explained in the section 3.4 Sample production: Interaction Bitumen-Plastic. However, no plastic was added to the system. In the data analysis, these samples will be used as a reference to compare results and understand which modifications of the binder occur under the influence of the plastic and which are a result of the thermal oxidation of the binder.

The content of plastic was defined by weight of bitumen. Two different contents were used in the mixing process: 5% and 20%. The first content (5%) was chosen in order to represent a realistic dosage for the Wet Method (Duarte & Faxina, 2021; Vargas & El Hanandeh, 2021). In contrast, the higher content (20%) was defined to maximize the contact between the two materials in a feasible proportion. The inclusion of both plastic contents provides valuable insights into the scalability of the interaction effects.

In the second campaign, the content of plastic in the interacting samples and the speed rotation were maintained the same and only the mixing time varied. These parameters were set the maximum in order to achieve the best interaction and the most evident effect of the interaction on the bituminous binders.

In Table 3-2 it is also presented the tests developed with each material. These tests are described in the next chapter with further details.

Table 3-2 – Mixing conditions of interaction bitumen-plastic

	#	Neat bitumen	Mix temperature (°C)	Plastic content (%)	Mixing time (min)	Shear Speed (RPM)	Tests
Campaign 1	01	50/70 (BR)	0	0	0	0	FTIR, G*
	02	50/70 (BR)	150	0	30	1000	G*
	03	50/70 (BR)	150	0	60	1000	FTIR, G*
	04	50/70 (BR)	150	5	30	200	G*
	05	50/70 (BR)	150	5	30	1000	G*
	06	50/70 (BR)	150	5	60	200	FTIR, G*
	07	50/70 (BR)	150	5	60	1000	G*
	08	50/70 (BR)	150	20	30	200	G*
	09	50/70 (BR)	150	20	30	1000	FTIR, G*
Campaign 2	10	50/70 (IT)	0	0	0	0	G*
	11	50/70 (IT)	150	0	30	200	G*
	12	50/70 (IT)	150	20	30	200	G*
	13	50/70 (IT)	150	0	60	200	G*
	14	50/70 (IT)	150	20	60	200	G*

The binder production process was followed consistently during both campaigns. However, it is worth noting that technical details varied due to the specific characteristics of the equipment used in each phase of the experimental program. Firstly, the sieve used in the first campaign

followed the specifications of the National Department of Transportation of Brazil (DNIT, 2006) while, for the second campaign, it was established in ISO 3310-1. Another difference was set in the spindle used for mixing the materials in the system. Figure 3-7 presents the two different tools.

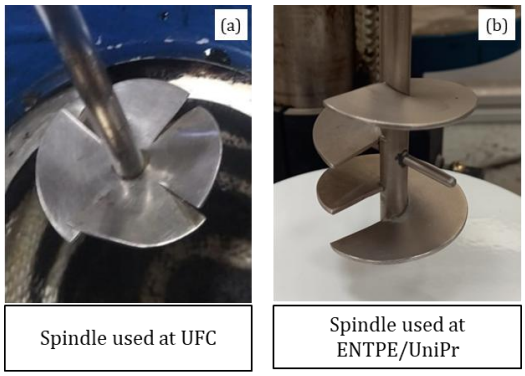


Figure 3-7 - Pictures of the spindles used for the mixing procedure with the electrical mixer; (a) Spindle used at UFC; (b) Spindle used at ENTPE/UniPr

3.5 Sample production: Mixtures

The mixture production followed the SuperPave protocol based on control of points (Cominsky, 1994). A gradation curve that meets these requirements was selected and used to design all the mixtures for the Mixtures campaign. Some prior investigations showed an experience with materials from the same mineral origin (Roberto et al., 2023; Romeo, 2013). The following sections describe the procedure for the selection of gradation curves, mixing, and compaction of the samples of mixtures studied in this research.

3.5.1 Compensation of Granulometry

As previously mentioned, the aggregate gradation used in this study was selected based on the Superpave protocol. This protocol establishes an interval of limit gradation curves where the mixture achieves optimal performance in terms of stability, durability, and workability. Based on that, a target gradation curve was determined. Figure 3-8 illustrates this target granulometry with the two limit curves. This gradation and its limits were set as reference for the designed mixtures in this experimental program.

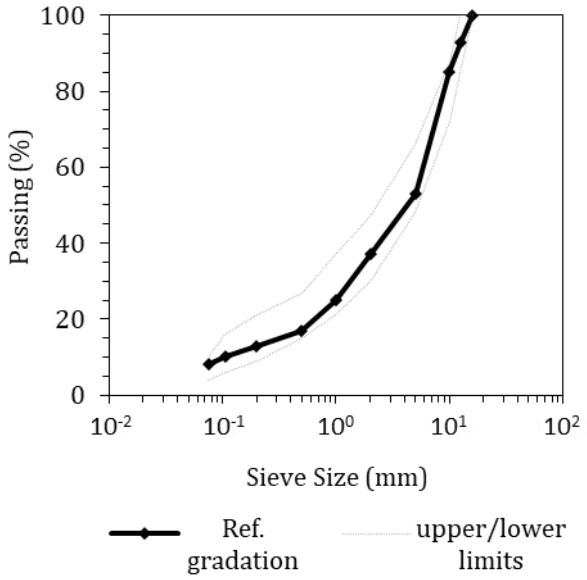


Figure 3-8 – Target granulometry of aggregates

The insertion of plastic in the modified mixtures was made under the definition of Dry Method, in which all the alternative materials are inserted in the system being comprehended as one of the aggregates and part of the structure of the mixtures.

Considering the different nature of the materials compounding the aggregates in these circumstances, two methods can be followed to define the granulometries of the modified mixture. In the first case, the mineral structure can be preserved, and the content of plastic is inserted as a supplementary component, as an add-on to the existing aggregates. A second approach is to include the plastic in the aggregate structure, adjusting the gradation curve of the ensemble mineral aggregate + plastic in order to correspond to the target reference curve. One key point to take into consideration in this approach is the fact that there is a significant difference in density between the plastic and the mineral aggregates.

In line with that, the mixture campaign was organized in order to evaluate the effects of the plastic as a component of the mixture and the two mentioned approaches of insertion of plastic in the mixtures when it comes to the Dry Method. Therefore, five mixtures were designed.

The first mixture, Mix 1, was designed without the insertion of plastic and following the targeted gradation curve. The content of bituminous binder defined for this mixture was 5.2% (in weight of aggregates). Mix 2 was designed with the same granulometry of mineral aggregate supplemented by 5% of its weight of plastic on top of the original curve. Mix 3, 4, and 5 were designed with the addition of - respectively - 5%, 2.5%, and 7.5% of plastic accounting the weight of mineral aggregate and preserving the target gradation curve. The same proportional content of bituminous binder was kept in the five mixtures. Figure 3-9 illustrates the composition of the five mixtures by proportion of materials.

	Composition Aggregate	Composition Mix			
	Plastic	Plastic	Filler	Mineral	Bitumen
Mix 1	0% (Reference)	0.0%	7.6%	87.5%	4.9%
Mix 2	5%	4.5%	7.2%	83.3%	4.9%
Mix 3	5%	4.8%	8.4%	81.9%	4.9%
Mix 4	2.5%	2.4%	8.0%	84.7%	4.9%
Mix 5	7.5%	7.1%	8.8%	79.2%	4.9%

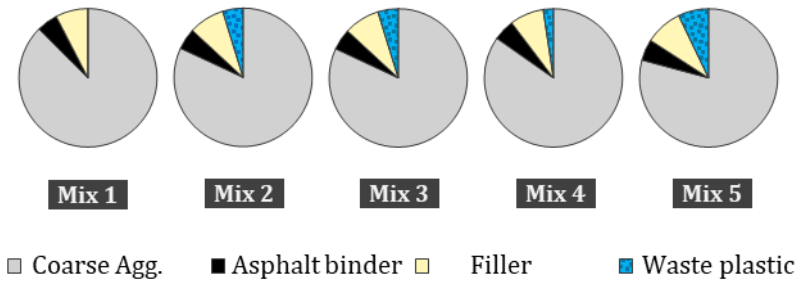


Figure 3-9 – Percentual representation of each material inside each Mix design

Taking into account the strong differences in density between the plastic and the mineral aggregate, the granulometric curve was converted to a curve of distribution of volume to guarantee that the particles of aggregate are replaced by the same volume of plastic. The notation of volume was considered for all mixtures in which the plastic was used to replace aggregates.

Also, one key point of the design process was to ensure that the plastic could be applied to the mixture in its neat gradation. Based on that, the proportions of fractions of mineral aggregate were balanced to reach the target curve. Figure 3-10 presents the gradation curves of the five mixes considering the distribution by weight and by volume.

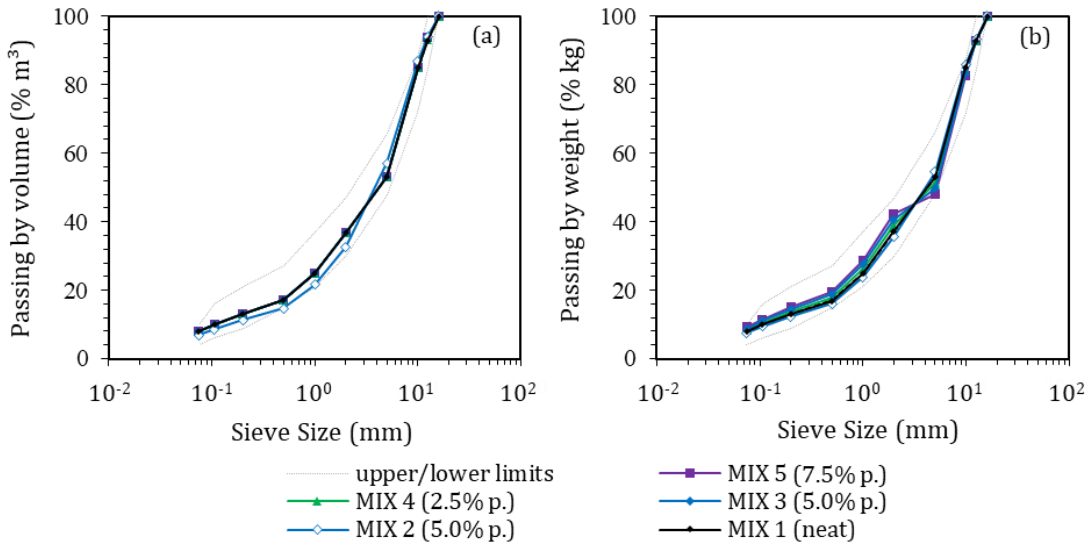


Figure 3-10 – Granulometry of aggregates in the slabs. (a) Granulometric curves by volume. (b) Granulometric curves by weight

All curves are consistently inside of the limits. However, it is relevant to notice that – considering the distribution by weight – the mixture designed with 7.5% plastic (MIX 5) reaches the lower limit curve for the 5 mm aggregates, which can represent a technical limit of plastic content as well for this design method. Alternatively, it is important to highlight that the approach used for Mixes 3, 4, and 5 assumes that the particles of plastic maintain their form and do not change in size and diameter, even with the heating and mixing process.

3.5.2 Mixing Procedure

The mixing procedure was first established for Mix 1, which was set as reference mixture without plastic and then adapted for the other mixtures aiming to ensure the correct application of the plastic in the mixture, considering the apparatus was set the same as unmodified mixtures. In this Mix procedure, the materials were inserted separately into the mixer following the order: (i) aggregates (all fractions including sand); (ii) bituminous binder; and (iii) filler. After each insertion of material into the mixer tank, the ensemble was mixed for 5 minutes at 150 °C. The mineral aggregates and fillers were pre-heated at a temperature of 175 °C for 2 hours before. After each mixing step, the content of the tank was analyzed visually in terms of homogeneity. If the homogeneity was not correctly reached one more mixing cycle of 2.5 minutes would be added in the procedure.

In Mix 2, the plastic was projected to be inserted as an add-on to the mineral aggregate. Based on that, the two materials were inserted together in the first step of the mixing process. The continuation of the procedure was maintained with other two steps of insertion of material followed by mixing for respectively, the binder and the filler. In this procedure the time of heating of the plastic comprehended the whole process of the mixture, which was between 25 and 30 minutes, considering the time to move the materials and the mixing tank.

In Mixes 3, 4, and 5, the plastic was considered in the granulometric structure of the mixtures. Taking that into account, it was included in the project an extra step for inserting the plastic only at the end of the mixing process, which reflected in a heating time of 5 minutes and would represent a decrease in melting and degradation of this material. Thus, in this procedure, the 3 first steps were preserved as the same as Mix 1 and the fourth was the insertion of the plastic. Figure 3-11 illustrates a summary of the 3 mixing procedures and the 5 mixtures.

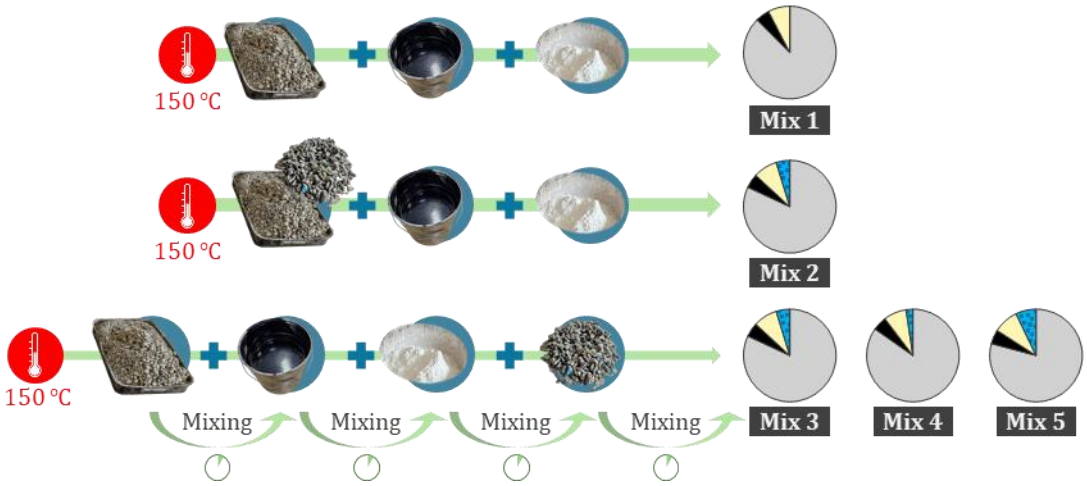


Figure 3-11 – Scheme for production of Mixes 1, 2, 3, 4 and 5

The mixing procedure was conducted using a laboratory mixer from InfraTest, designed for grain sizes below 16 mm. The mixture was prepared with a maximum tank capacity of 15 kg to ensure optimal performance within the recommended operating range of the equipment.

3.5.3 Compaction Procedure

For each mixture, a slab was compacted to enable the extraction of specimens for laboratory testing. Figure 3-12 illustrates the compaction procedure used for the production of the samples. The mixtures were constructed in the form of slabs of 50 mm × 50 mm shape (Figure 3-12b). The target height of the slabs was projected to 15 mm.

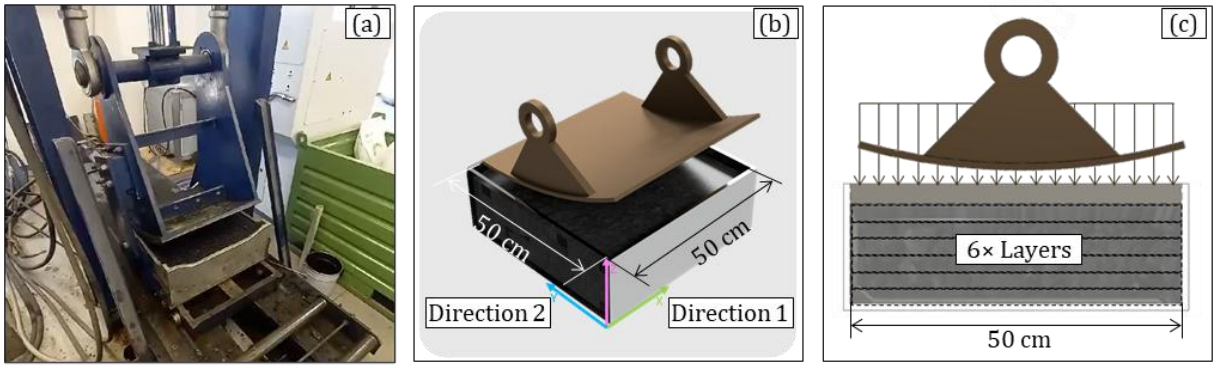


Figure 3-12 – Compaction of slabs. (a) Compactor used. (b) Representation of the size of slab and directions of compaction. (c) Representation of number of layers of compaction.

The compaction procedure was conducted using a pendulum compactor, as presented in Figure 3-12a. This type of compactor is designed to apply a uniform charge over large areas, ensuring the same level of density throughout all the points of the slab. Figure 3-12b and c present a scheme of the compaction. The slabs were compacted in two perpendicular directions. Firstly, the compactor was operated in the main axis of compaction and then the slab was rotated 90 degrees and then compacted in the second direction. The two directions approach were carried out aiming to ensure the uniform compaction.

Each slab weighed approximately 85-90 kilograms. Considering that and the mixing procedure previously explained, the material was divided into six layers, which were individually mixed and compacted. Each layer was subjected to four steps of four cycles of compaction.

3.5.4 Coring of Samples

The samples used for thermomechanical tests were extracted from the slabs. Following their construction, a coring plan was developed to determine the positions and the dimensions of the specimens. Figure 3-13 illustrates the coring plan applied to the slabs.

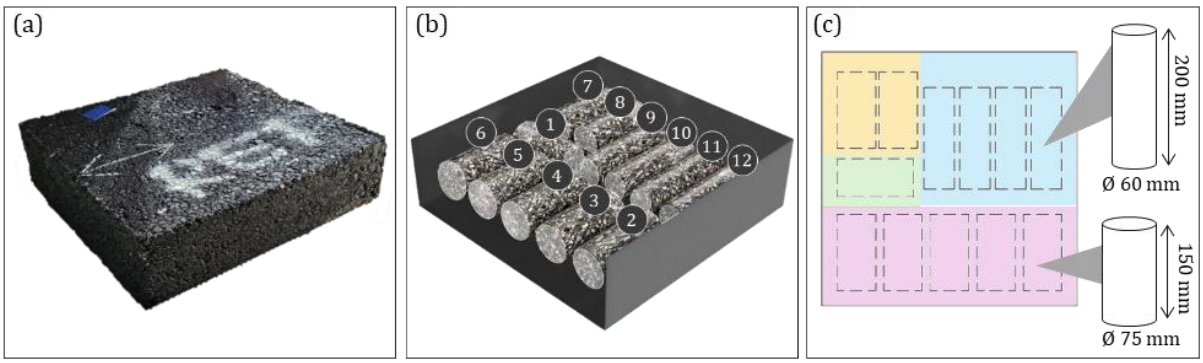


Figure 3-13 – Coring plan of slabs. (a) Example of slab made in laboratory. (b) Illustration of position of specimen. (c) Details of coring and size of samples

Figure 3-13a illustrates one of the slabs after construction, from which a total of 12 specimens were extracted. The position of the specimen was determined based on the direction of the first cycle of compaction, defined in the phase of preparation. Figure 3-13b shows the specific positions of the specimens within the slab.

Two different specimen geometries were prepared. Specimens 1 to 8 have a diameter of 75 mm and a height of 150 mm, while specimens 9 to 12 have a diameter of 60 mm and 200 mm height. The slab was divided into four sections, and the samples were extracted accordingly.

CHAPTER 4
METHOD

This chapter discuss the performance tests performed in each experimental campaign that compounds this Thesis. In the following sections of this chapter, a summary of the scope of each campaign and the procedures for the tests are presented.

4.1 Introduction

4.1.1 Overview of Campaigns

This research was structured around the specific objectives outlined in section 1.4.2 Specific Objectives. To achieve the objectives, four independent experimental campaigns were designed for the development of this research. Figure 4-1 highlights the parts of the flowchart of the conception of the study concerning the laboratory tests performed, with the data of each campaign as an outcome. The first part of the flowchart, focusing on the production of materials and samples, was highlighted in Figure 3-1.

In the flowchart, each box represents a step of an experimental process. The four colored paths represent the campaigns. In the following sections, each campaign is described separately.

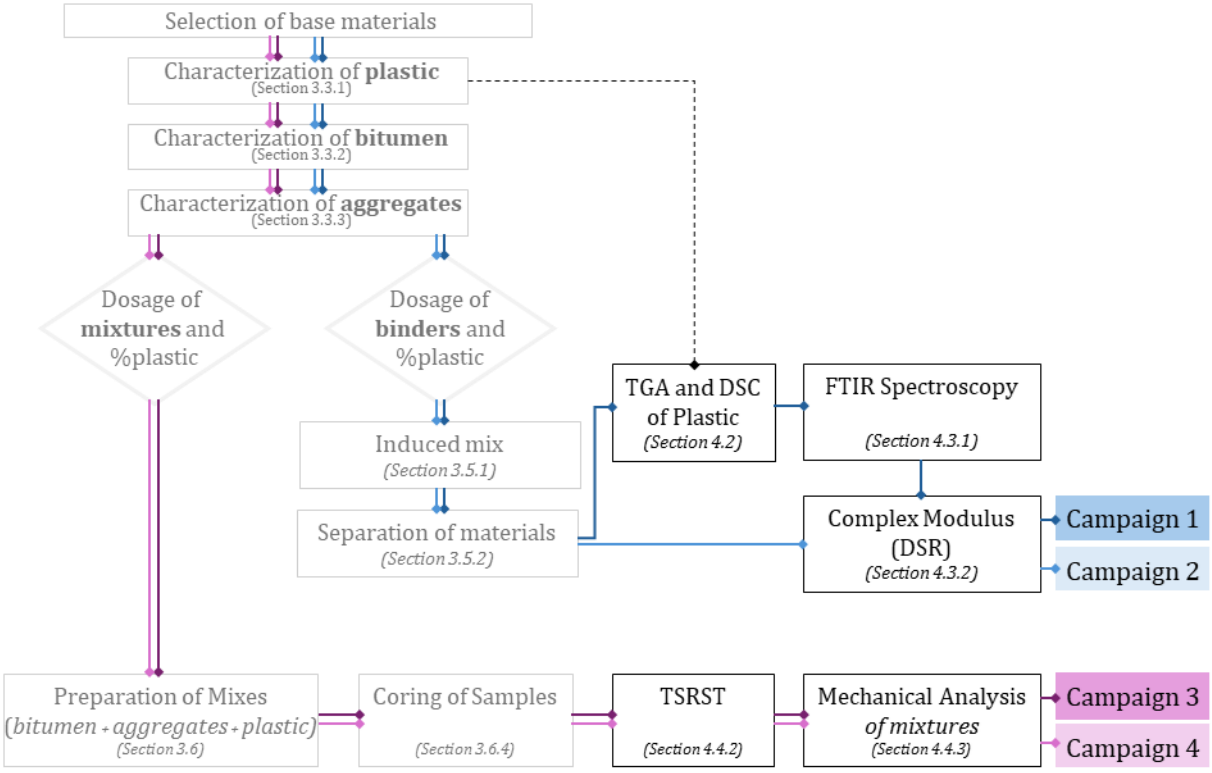


Figure 4-1. Flowchart of method with focus on the four experimental campaigns and the experimental methods

After the steps concerning the selection and characterization of base materials (highlighted in Figure 3-1), the diagram is divided into two main branches, the first related to the tests with bituminous binders, referring to the first two campaigns of the research, and the second,

referring to the tests with the mixtures and the other two campaigns. Due to the interconnected nature of the research, some steps are connected and exchange information.

The experimental work for this study was conducted across multiple institutions: Universidade Federal do Ceará (UFC, Brazil), ENTPE (France) and Università di Parma (UniPr, Italy). This chapter focuses on the characterization and performance tests carried out in the experimental plan of this research after the preparation of samples. The following subsections explain the scope of each experimental campaign individually.

4.1.2 Campaign 1: analysis of interaction between the recycled plastic and the bitumen (UFC, UniPr, ENTPE)

In the first campaign, the nature of the interaction between the plastic and the bituminous binder was investigated under controlled laboratory mixing conditions. At this point of the research, the key point was understanding if a potential mobilization of plastic components would occur in the scale of the bituminous binder, meaning a (partial) blend between the two materials, or if the interaction would be purely mechanical with grains of plastic in suspension in the bituminous phase, as acting like small aggregates in a mortar.

For this purpose, the samples for this campaign were prepared in conditions designed to approximate from those found in plant facilities when in the preparation of wearing courses and bituminous mixtures used for other layers. In the preparation of the specimens found in these samples, the mixing parameters were individually altered to establish those that reflected more impactfully in the blend between plastic and binder. Although this campaign aims to address whether interaction occurs, it is important to highlight that the selected conditions were also designed to provide indications of this phenomenon under the specific conditions to which these materials are typically subjected.

Materials produced and used in this testing campaign underwent chemical characterization through FTIR spectroscopy and rheological characterization at intermediate and high temperatures using the DSR. The goal was to understand whether any change is observed on physic-chemical and mechanical properties of bitumen after it stays in contact with plastic in various conditions (namely mixing temperature, duration, and speed). Eventual variations of these properties would suggest that potential migration of plastic components into the binder occurs.

4.1.3 Campaign 2: effects of the interaction in the thermomechanical behavior of the bitumen (UFC, UniPr, ENTPE)

The second campaign was conceived with the purpose to further investigate the rheological behavior of the binders after interaction with the waste plastic. In this phase, the thermomechanical tests were conducted both at intermediate to high temperatures, as done in the first campaign, and also at low temperatures.

The additional test temperature aimed to provide information on the behavior of the materials over a wider range of frequency and temperature, including the region corresponding to the glassy elastic plateau. Such information is essential in order to properly model the viscoelastic behavior using a rheological model, such as the 2S2P1D model used (see section 4.6). This allowed verifying which model parameters are affected by the interaction of bitumen with plastic, i.e., the mobilization of plastic components into the binder.

4.1.4 Campaign 3: analysis of production of mixtures through dry processes (UniPr, ENTPE)

In the second branch of the experimental plan, the focus moved from the scale of the binder to the scale of mixtures. The main scope of the experimental plan in Campaign 3 was to investigate the use of recycled plastic in bituminous mixtures by dry method.

To achieve this, two different methods of incorporation of polymers into the mixtures were explored, as detailed in chapter 3 about materials. The effectiveness and feasibility of each method was investigated and compared to a reference mixture designed without plastic. The physical (density, air voids) and thermomechanical properties of the various mixtures produced provided information about the effect of the production procedures on the final performances of Hot Mix Asphalt (HMA) materials in laboratory conditions. This phase provided insights into the practicality of using recycled plastic in bituminous mixtures for use in dry processes and its operational implications.

4.1.5 Campaign 4: effects of plastic content on the thermomechanical behavior of mixtures (UniPr, ENTPE)

Based on the results of Campaigns 1 and 2, suggesting that interaction with plastic affects the behavior of bitumen even in the absence of complete blending, and of Campaign 3, showing

the feasibility of producing mixtures containing plastics by dry method, Campaign 4 aimed at studying the effect of plastics, in different dosages, on thermomechanical behavior of mixtures produced by dry method.

The goal of this campaign is to investigate the LVE behavior of mixtures and its relationship with the LVE behavior of corresponding binders, using the results of the previous Campaigns.

4.2 Thermal Characterization of Plastic: Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

As discussed in the previous sections, the shredded plastic was pulverized into a powder with a small particle size to be adequate for the devices used for chemical characterization, including the thermal characterization of the base material. For this purpose, the Differential Scanning Calorimetry (DSC), and Thermogravimetry analysis (TGA) were carried out.

The use of thermal analysis aims to describe the characteristics of the polymers when exposed to a variation of temperature. In the DSC, the sample is confined in a controlled atmosphere and the amount of heat required to increase the temperature to a specific level is measured. The sample is subjected to a linear rate of increase of temperature, and it is possible to identify the temperature ranges in which endothermic and exothermic processes occur, such as phase transitions of any component of the sample. In this test, the sample was heated in a controlled atmosphere and the variation of heat flow required to increase its temperature from 0°C to 300°C at 20 °C/min was measured. This test aimed to identify particularly the temperature ranges where each polymer composing the base plastic started to either melt or to reach a glassy transition.

In parallel, the TGA is a test that measures the loss of mass of the material while it is heated. This test measures the mass loss of the material as it is heated, which can be attributed to phenomena like decomposition or evaporation of components. During the test, the plastic was heated at a rate of 10 °C/min and the weight of the sample was constantly monitored until total loss of weight.

This test identifies a range of temperature in which the plastic vaporizes into the atmosphere of study and the speed of this process. Similarly to DSC, TGA allows estimating the heterogeneity of the material by identifying the presence of distinct polymers with different thermal susceptibility, based on the trends observed in the degradation curves of the material. Together, these techniques provide valuable insights into the thermal susceptibility of the plastic.

4.3 Chemical characterization of plastic and binders: Fourier Transform Infrared Spectroscopy (FTIR)

Fourier-Transform Infrared (FTIR) Spectroscopy was applied to identify the functional groups present in the components of the materials. In particular, this test was performed firstly to the neat plastic and subsequently to the bituminous binders produced in the first campaign after interaction with plastic and filtering of solid content, in order to verify the potential migration of some functional groups from plastics to the binders.

In the procedure for this test, the samples were exposed to a range of infrared light with wavelengths varying from 2.5 μm to 25 μm (corresponding to wavenumbers from 4000 to 400 cm^{-1}).

As the beam passes through the tested material, the different frequencies are absorbed, and the intensity of absorption is measured and recorded at each wavelength. Each band of the spectrum can be associated with a specific chemical bond or functional group that can be found in the molecules of polymer or the components of the bitumen. Variations in the absorption spectra provide information about the relative importance of the different functional groups within the tested material.

Concerning the plastic, this analysis allows identifying which polymers compose the material as well as the potential contamination found in the sample collected. When this test is applied to bituminous binders before and after interaction with the plastic, it is possible to identify the functional groups inside the binders, potentially due to the mobilization of components from the plastic in the interaction process. FTIR tests were performed at UFC (binders) and UniPr (neat plastic).

Having in mind that the heating process may oxidize the binder, control samples were produced using the unmodified binder, processed under the same conditions but without plastic addition, in order to isolate the effects of polymer mobilization. Table 4-1 presents a summary of the samples that were submitted to the FTIR analysis.

Table 4-1 – Summary of samples submitted to FTIR Spectroscopy

Sample	Base Material	Mix Temp (°C)	Plastic (%)	Duration (min)	Rotation (RPM)
01	Plastic	0	100	0	0
02	Binder 50/70	0	0	0	0
03	Binder 50/70	150	0	60	1000
04	Binder 50/70	150	5	60	200
05	Binder 50/70	150	20	30	1000

4.4 Rheological characterization of binders: Dynamic Shear Rheometer Analysis (DSR)

The rheological characterization of the bituminous binders was carried out by performing complex modulus tests at various frequencies and temperatures using a DSR equipment.

Tests were performed by applying an oscillatory loading in strain-controlled mode, using a plate-plate configuration, following the method proposed by Nguyen et al. (Nguyen et al., 2013a). Three temperature ranges were studied, and for doing so, three different models of spindles with distinct geometries were employed, as shown in Figure 4-2.

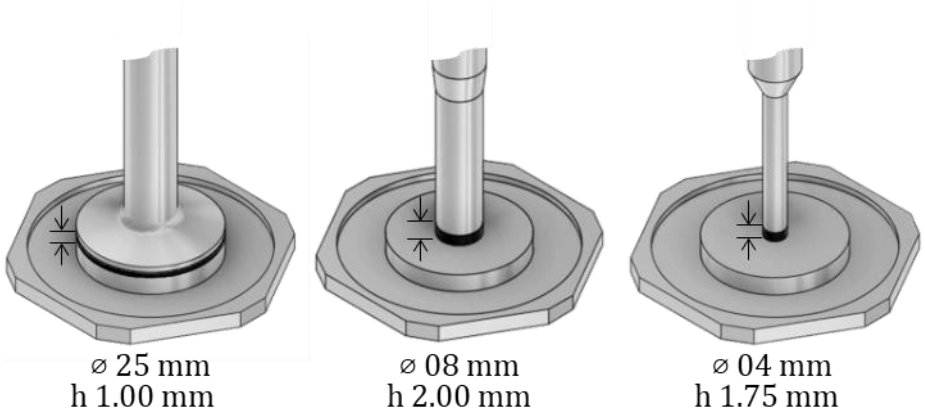


Figure 4-2 – Illustration of geometries of test with different spindles

Taking into account the three chosen geometries, The range of temperatures defined for studying were the following:

i. For high temperatures (T > 40 °C): A plate with 25 mm diameter and a 1.00 mm gap;

ii. For intermediate temperatures (10 °C < T < 30 °C): A plate with 8 mm diameter and a 2.00 mm gap; and

iii. For low temperatures (T < 0 °C): A plate with 4 mm diameter and a 1.75 gap.

In the first binder campaign (Campaign 1) it was studied the effects of the interaction between the plastic and the bituminous binder at high temperatures, considering that the effects of the modification with plastic are better observed at this range of temperature (Vargas & El Hanandeh, 2021). Based on that, all tests were performed only at high temperatures and consequently with the first geometry of the test (25-mm diameter, 1-mm gap). Taking into account that this test focused only on one range of temperature, the tests were performed in intervals of 6 °C, starting by 46 °C (46, 52, 58, 64, 70, 76, and 82 °C). For this campaign, tests

were conducted using a TA instruments equipment, as part of the experimental plan held in UFC.

In the second binder campaign (Campaign 2), a full range of temperatures was analyzed. Based on that, the three geometries were tested. The tests were performed in intervals of 10 °C, as presented in Table 4-2. In the limit temperatures (0, 10, and 30 °C) the test was performed in more than one geometry in order to investigate the effect of the geometries in the encounter of the curves. For this campaign, materials were prepared in UniPr, and tests were conducted in ENTPE.

Table 4-2 – List of temperatures tested in the DSR by range of temperature (low, intermediate, and high) and geometry of spindle

Temperature	***⌀ 25 mm***	***⌀ 08 mm***	***⌀ 04 mm***
-20			×
-10			×
0		×	×
10		×	×
20		×	
30	×	×	
40	×		
50	×		
60	×		
70	×		

The tests were performed by applying an oscillatory shear strain of 0,1% amplitude in cycles of decreasing frequencies (10, 3, 1, 0.3, 0.1, 0.03 and 0.01 Hz), in ascending temperatures. During the majority of the cycles, the temperature was stabilized for 30 minutes before applying the shear strain. The conditioning time was extended to 12 hours for the tests at – 20 °C, in order to take into consideration the physical hardening. The number of measured points varied for each frequency as shown in Table 4-3.

Table 4-3 – Number of measured points by frequency in DSR tests

Frequency (Hz)	***Number of points***
10	80
3	60
1	30
0.3	16
0.1	12
0.03	8
0.01	6

After the execution of the tests, the acquired data were accurately verified, aiming to exclude from the analysis incorrect data associated with potential measurement errors. Following the equipment specifications, the verification involved the following criteria: (i) torque oscillation within the range of 0.5 nNm to 230 mNm; (ii) deflection angle below 0.05 rad; (iii) frequency confined to the range of 10^{-7} to 100 Hz; (iv) normal force between 0.005 and 50 N; and (v) normal force resolution below 0.5 mN. Any data points failing to fit one of these limits were excluded from further analysis. In sequence, another data processing step was implemented, regarding the statistic distribution of the considered data. The steps for this data processing will be detailed in the next chapter.

4.5 Thermomechanical characterization of mixtures: complex modulus tests

4.5.1 Setup for mechanical tests

All complex modulus tension-compression tests performed on mixtures were carried out at ENTPE, using a hydraulic press equipped with a load cell capable of handling a maximum force of 25 kN either tension or compression. The mechanical tests were carried out with cylindric samples cored from slabs produced in laboratory, as described in Section 3.5.4.

The specimens were placed vertically, with the parallel faces glued to the two metal plates of the press using a two-component epoxy resin. After coring, the cylindrical specimen is subjected to a 15-day drying period on a sand substrate, during which their weight is monitored are regular intervals in order to ensure proper evaporation of water. Subsequently, the real dimensions of the specimen are measured, with three height measurements and nine diameter measurements in total - three at the top of the specimen, three in the middle, and three at the base. The arithmetic mean of these measurements determines the specimen's final dimensions for future calculations of density and voids.

The testing system allows control over key parameters for the test, including the position of the piston, the load and torque applied to the sample. This ensures that testing conditions can be controlled during the application of deformation. Additionally, in order to control the temperature during the test, the testing system is equipped with a thermal chamber and a Pt100 temperature probe is used to monitor the temperature on the surface of the specimen.

For this experiment, three extensometers and four contactless sensors were utilized to capture measurements. The extensometers were separated by 120 degrees in the external surface of the specimens.

The output data collected from the testing system includes axial and radial strain measurements. To obtain this information, the system was equipped with additional sensors. Axial strain was obtained using three extensometers applied on the surface of the central part of the sample at 120° from each other. The average value of the three extensometers was retained as axial strain and was used to control the test. To measure the radial deformation, four contactless eddy-current sensors were used. The sensors were arranged in pairs, with each pair placed in two opposite aligned points along the diameter of the sample, close to its surface, between 80 and 120 µm. One pair was aligned along the direction of compaction of the slab from which the sample was cored. The second pair was positioned on the same radial plane, along the direction

perpendicular to the direction of compaction of the slab. Each sensor provides the distance to a metallic tape attached to the specimen. Data from each pair of sensors are used to calculate radial strain of the sample in the corresponding radial direction during the whole test.

Figure 4-3 and Figure 4-4 show schematic illustrations of the placement of each sensor on the specimen and of the whole test set-up with the three extensometers and the four contactless sensors, respectively. Figure 4-5 shows a close-up of a sample equipped with all described sensors placed inside the thermal chamber of the testing system: the temperature probe, a contactless sensor and an extensometer are visible.

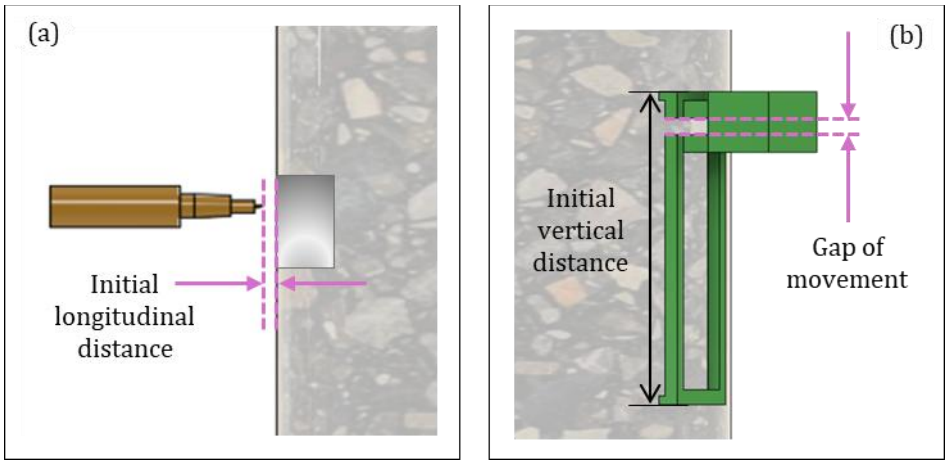


Figure 4-3 – Scheme of setup for measuring deformation in the specimen of mixture. (a) Illustration of contactless sensor. (b) Illustration of extensometer

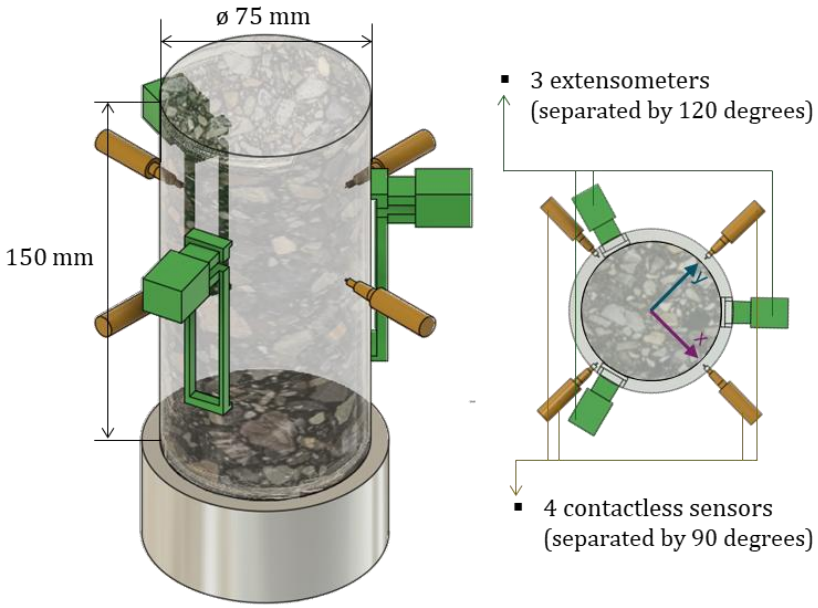


Figure 4-4 – Scheme of setup of mechanical test of mixtures representing position of extensometers and contactless sensors

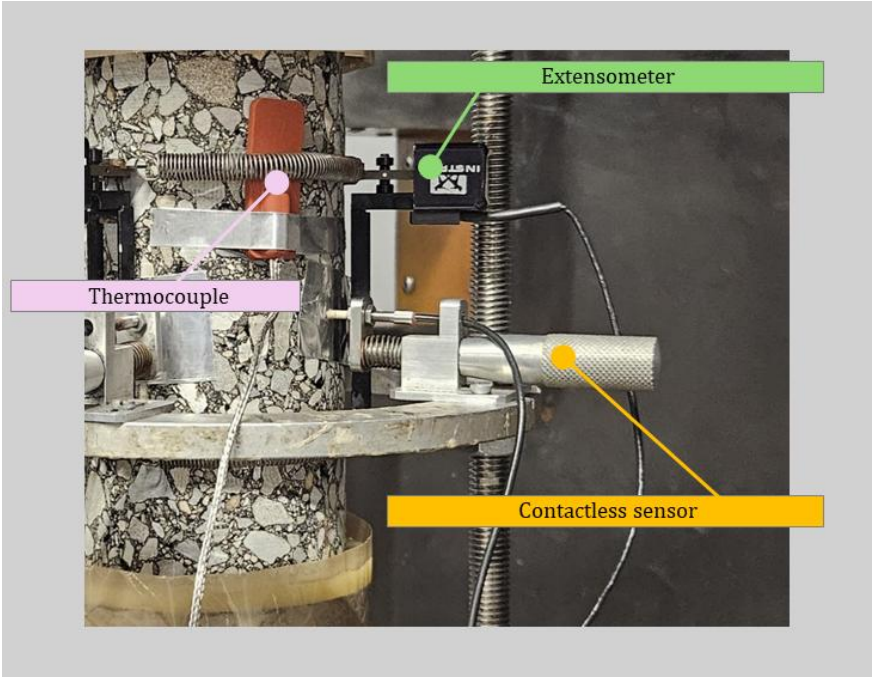


Figure 4-5 – Positioning of extensometer, contactless sensor, and thermocouple in the test

4.5.2 Complex Modulus test procedure

In parallel to the experimental campaign proposed for the bituminous binders, the analysis of the Complex Modulus was also carried out for the specimen of mixtures. The tests were conducted in tension-compression configuration, in a range of temperatures selected to accommodate the thermal chamber's operational limits while encompassing low, intermediate, and high-temperature intervals. The graph presented in Figure 4-6 summarizes the temperatures at which the samples are submitted during the duration of the test.

The test procedure is carried out from -25 °C to 45 °C, starting at the lowest temperature, with temperature increments of 10 °C between two consecutive temperatures. In addition, in this procedure, the specimen is tested at an intermediate reference temperature of 15 °C both before and after the main test in order to monitor its behavior and ensure the structural integrity of the material throughout the process. Prior to each testing cycle, the system is maintained at the testing temperature for four hours to achieve a uniform temperature distribution across the material.

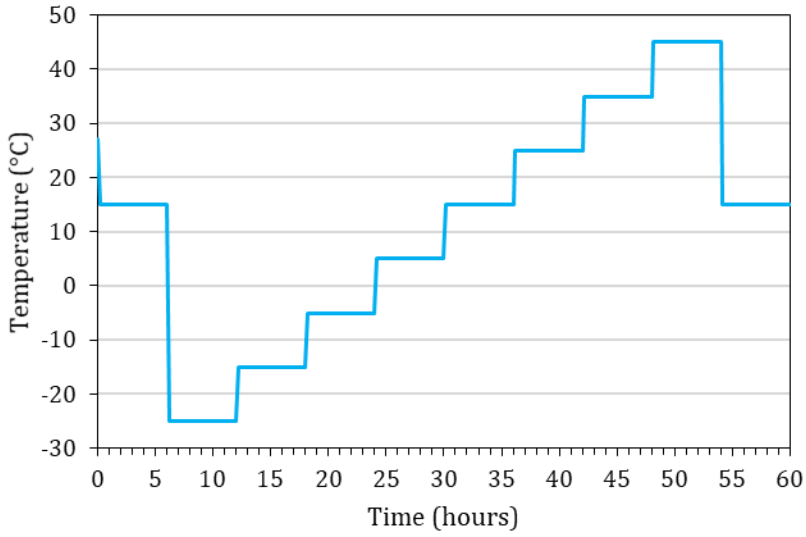


Figure 4-6 – Temperature evolution in Complex Modulus tests of mixtures

For each temperature, eight sinusoidal loading sequences were applied at frequencies from 0.003 Hz to 10 Hz, separated by 5 s of rest. Table 4-4 presents the list of the frequencies and the corresponding number of loading cycles applied. The number of cycles was defined in order to allow for dissipation of viscoelastic effects due to the application of cyclic loading.

Table 4-4 – Frequencies and number of points of tested in each cycle of temperature of tests with mixtures

Frequency (Hz)	***Number of loading cycles***
10	50
3	40
1	30
0.3	16
0.1	12
0.03	8
0.01	6
0.003	4

The samples were tested in tension-compression, in strain control mode. An axial strain amplitude of 32 μm/m (corresponding to a 2.38 μm average displacement of the three extensometers) was applied. This value falls within the LVE range commonly considered for bituminous mixtures (Di Benedetto et al., 2004).

A Proportional-integral-derivative (PID) controller is implemented in the servo-control system to control the feedback of the sinusoidal wave applied to the sample. This feedback continuously modulates the load (input) based on the difference between the targeted and measured strain (output). The post-acquisition data processing is detailed in the Results section dedicated to the analysis of the mixtures (CHAPTER 6).

4.6 Mechanical Modeling - 2S2P1D model

The use of a mechanical model to simulate the experimental results obtained on materials can provide interesting insights about their mechanical behavior under different conditions. Moreover, applying the same model to corresponding bituminous binders and mixtures helps verifying the relations between the behaviors of these materials at different scales.

If complex modulus results align along unique curves when plotted in complex planes (Black and Cole-Cole diagrams), then effects of loading frequency and temperature on can be confounded. As a consequence, the materials are said to present a thermorheologically simple behavior and time-temperature superposition principle (TTSP) can be assumed as validated.

The 2S2P1D model is a well-established representation for bituminous materials (Di Benedetto et al., 2004). This is an analogical LVE model that consists of an assembly of two springs (2S), two parabolic elements (2P, on-linear flow elements) and a linear dashpot (1D). In its representation, one of the springs is associated in parallel with the other elements that are associated in series, as shown in Figure 4-7. Both for binders and mixtures, the model can simulate complex moduli E* and G* (axial and shear) if the corresponding parameters (E_{00} and E_0 or G_{00} and G_0, respectively) are used. This model was already successfully used in the past to simulate the behavior of binders, both neat and PMB, and mixtures (Cai et al., 2019; Di Benedetto et al., 2004; Nguyen et al., 2013b; Olard & Di Benedetto, 2003).

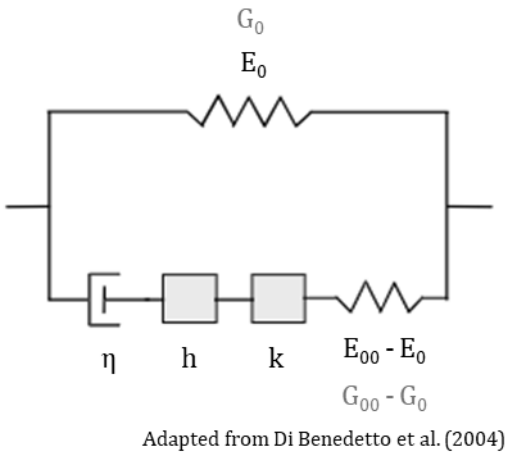


Figure 4-7 – Representation of the 2S2P1D model

In the next subsection the parameters and the representative equation of the model are presented. In addition, it is discussed how each parameter impacts and changes the shape of the

Black Diagram and the Cole & Cole curves, as well as the implications to the master curves of the materials. In this research the 2S2P1D model was applied as a tool to compare materials from same nature and validate the results found for modified binders and mixtures.

4.6.1 Parameters of the model

The 2S2P1D can be mathematically represented by the Equation (1). given for G* as an example.

$$G^*(i\omega\tau_G) = G_{00} + \frac{G_0 - G_{00}}{1 + \delta(i\omega\tau_G)^{-k} + (i\omega\tau_G)^{-h}(i\omega\tau_G)^{-1}} \quad (1)$$

The equation is based on seven parameters, G_0, G_{00}, k, h, δ, τ and β. In general, for neat binders it is common to fix $G_{00} = 0$ with the high temperature/low frequency asymptote corresponding to Newtonian flow. Among the 2S2P1D parameters, characteristic time τ is the only parameter depending on temperature. If the material shows a thermorheologically simple behavior, isotherms of norm and phase angle of E* and G* can be shifted along the frequency axis to build master curves at the reference temperature T_{Ref}. The shift factors of each isotherm can be obtained as the ratio of τ values at the corresponding temperature and at the reference temperature, as in Equation (2):

$$a_T = \frac{\tau(T)}{\tau(T_{ref})} \quad (2)$$

Shift factors at all test temperatures were fitted using the WLF law (Williams et al., 1955), explained in Equation (3).

$$\log(a_T) = -\frac{C_1(T - T_{ref})}{C_2 + T - T_{ref}} \quad (3)$$

Where a_T is the shift factor, T is the tested temperature, T_{ref} is the temperature of reference for plotting the master curve, and C_1 and C_2 are constants that fit the shape of the curve.

4.6.1 Elaboration of master curve

Figure 4-8 shows a representation of the process of shifting the isotherms into the master curve based on one example of results of tests performed with a neat binder between 10 and 70 °C. The procedure for calculating the reduced frequencies were chosen based on each material and are presented in the section of the results of each campaign in the next chapters.

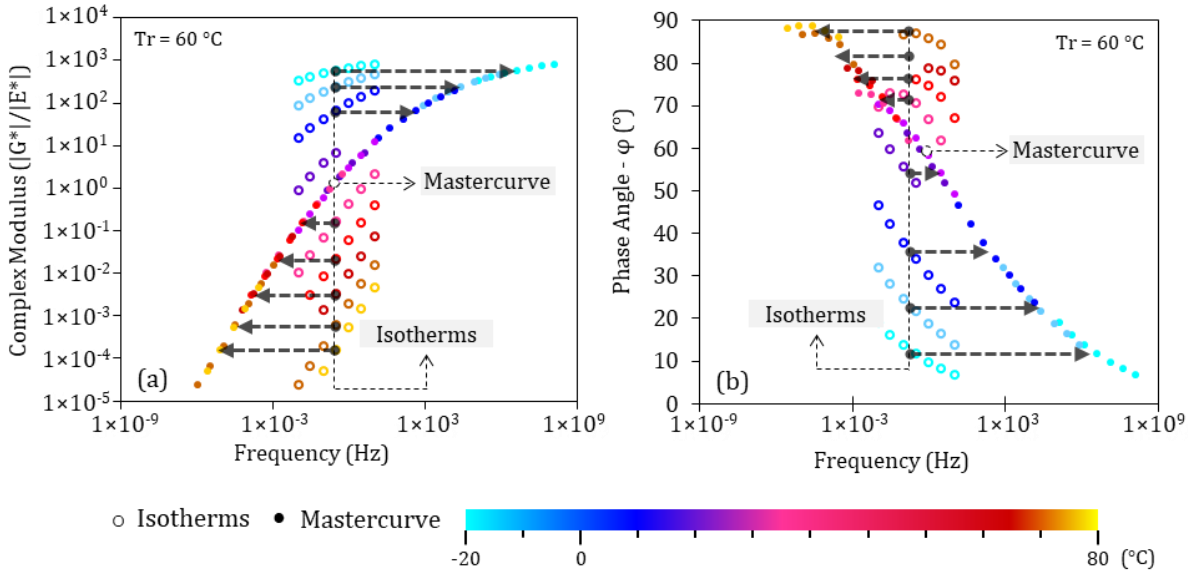


Figure 4-8 – Illustration of plotting of master curve by shifting of isotherms. (a) Example of master curve of Complex Modulus (|G*|). (b) Example of master curve of Phase Angle (°)

The effect of various 2S2P1D constants on the trends observed in the Cole-Cole and Black diagrams are represented in Figure 4-9. It is noteworthy to recall that in the Cole-Cole plot the data relative to low temperatures/high frequencies are highlighted. For this reason, the effects of constants G_0, k and δ can be better observed on this plot. On the other hand, the Black Diagram can be used to highlight the behavior at high temperatures/low frequencies (Figure 4-9b). Therefore, the shape of the curve described by the 2S2P1D model in this plot is more influenced by the constants G_{00}, h, and β. For the neat binder, it was adopted $G_{00} = 0$.

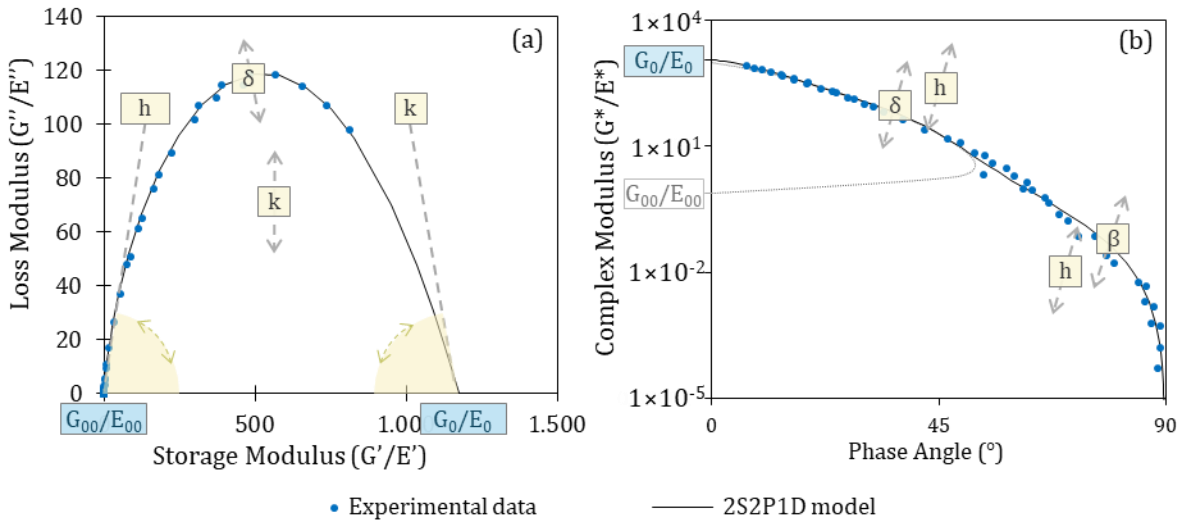


Figure 4-9 – Parameters of 2S2P1D presented in graphs. (a) Example of Cole & Cole plot with 2S2P1D curve. (b) Example of Black Diagram with 2S2P1D curve

The constants were determined as those that minimized the error after multiples iterations. For the neat binder it was adopted $G_{00} = 0$. The same procedure was applied to the binders that interacted with the waste plastic in the HSM procedure. These models are discussed later in this report.

CHAPTER 5
RESULTS ON BINDERS

This chapter presents the results from Campaign 1 and Campaign 2, discussing them from the perspective of the mechanical behavior of the bituminous binders. The following sections describe the main findings and analyses derived from the experimental investigations.

5.1 Summary of Campaign 1 and Campaign 2

In the experimental plan designed for this research, the first and the second campaigns comprise the tests carried out with the bituminous binders. This chapter presents the discussion of results obtained from the outputs of this part of the experimental plan. Both campaigns focused on the analysis of effects of the interaction between the recycled plastic from waste food packaging and the bituminous binder, in order to assess the potential use of this resource as a component of bituminous mixtures.

In the first campaign an introductory focus was placed on the physic-chemical characterization of the neat plastic. This characterization was assessed by means of Differential Scanning Calorimetry (DSC), Thermogravimetry Analysis (TGA), and Fourier-Transformation Infrared (FTIR) Spectroscopy. Following this preliminary analysis, the focus of the campaign moved to the rheological behavior of the bituminous binders after interaction with the plastic, with particular attention to the observations of the FTIR spectroscopy. The results of Campaign 1 are described in sections: (i) 5.2 - Thermal analysis of recycled plastic (TGA and DSC); (ii) 5.3 - Chemical characterization (FTIR Spectroscopy; and 5.4 - Campaign 1: Rheological analysis of binder (DSR, from 46 to 82 °C, results from UFC).

The second campaign followed up on the thermo-mechanical analysis of the bituminous binder after induced interaction with plastic. In this phase, the attention was moved to the mixing time, with an expanded range of test temperatures encompassing intermediate and low temperatures. The expansion of the range of temperatures allowed modelling the data by means of the 2S2P1D model. The results of Campaign 2 are described in sections: (i) 5.5 - Campaign 2: Rheological analysis of binder (DSR, from -20 to 70 °C, results from UniPr/ENTPE); and (ii) 5.6 - 2S2P1D modeling (Campaign 2).

After discussing individually, the insights obtained from each campaign were looked upon jointly in order to draw some conclusions about the effect of plastic on binder, as a component of paving materials. The effects of the interaction with plastic on thermomechanical properties of the bitumen presented similar characteristics as those observed with more conventional binder modification. Examples of mechanical and chemical impacts of the interaction of bitumen with plastic were, respectively, the loss of a purely viscous (Newtonian flow) asymptote at high temperature and the reduction of the indicators of oxidation generated by the heating during the mixing stage. These results indicate the potential use of the studied plastic as a material for asphalt mixtures.

5.2 Thermal analysis of recycled plastic (TGA and DSC)

As explained in previous sections, tests for physic-chemical characterization of plastic (both the thermal analysis through TGA and DSC and chemical analysis through FTIR spectroscopy) were carried out in an interlaboratory experiment held in UFC and UniPr. The material was tested in powder form, obtained from the processing of its shredded form with liquid nitrogen. It is assumed that the contact with nitrogen did not influence the chemical properties of the plastic. This assumption is supported by the fact that nitrogen is chemically inert and does not react with polymers in an isolated system and under these temperatures.

Figure 5-1 shows the curve of decrease of weight of plastic as a function of the temperature in the system, obtained from TGA. The maximum values and ranges of temperature used in the experimental plan of this research for the production of mixtures and the rheological tests, respectively, are also marked.

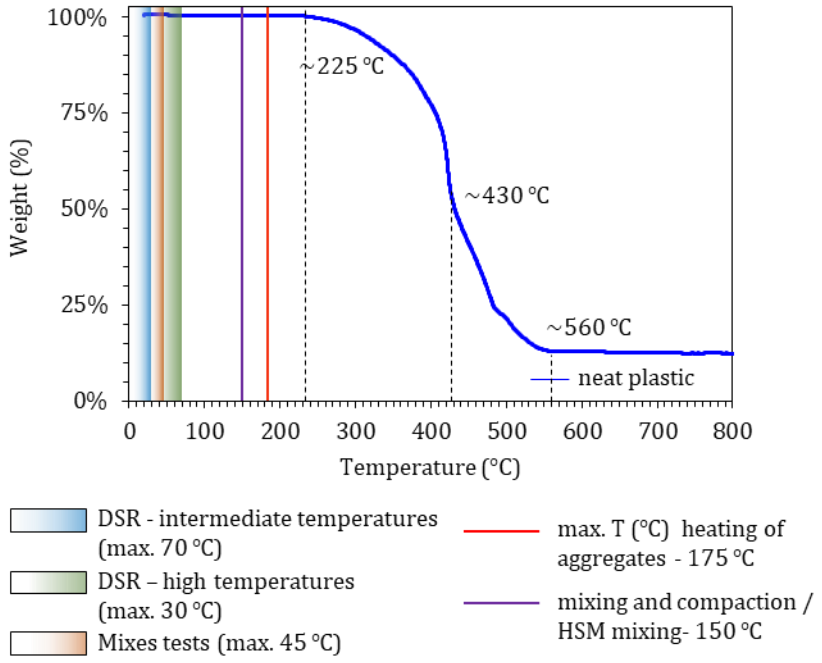


Figure 5-1 - Thermogravimetric analysis of weight × temperature

The curve of weight against temperature presents a wide interval of temperature (225~560 °C) of decrease of mass, suggesting that various components with different temperatures of degradation are present inside this material. An important decrease in weight can be observed around the temperature of 430 °C. This temperature is also inside the range of sharp degradation of polyethylene (Miandad et al., 2019; Su et al., 2004), which can indicate the prevalence of this polymer. In fact, in a nitrogen atmosphere oxidative degradation and loss of

mass begins at 350 °C for polyethylene and at 250 °C for polypropylene and polystyrene (Peterson et al., 2001).

The exact range of temperatures of loss of mass of each component depends on the thermal exchanges inside the material. It is worth highlighting that for temperatures below 225 °C the curve of TGA is quite flat, indicating low degradation, evaporation, and production of gases. Considering that the experimental procedures performed in this study (both material production and testing) involve temperatures below 225 °C, it is possible to assume that the chances of material degradation regarding the plastic are negligible within the temperature range where bitumen and bituminous mixtures are either processed or used.

Figure 5-2 shows the output of the DSC test, with the heat flow plotted as a function of the temperature. As for TGA results, the figure shows the temperature ranges of the rheological tests and maximum temperatures of material production experimental procedures to which the plastic and the other materials in this research are subjected.

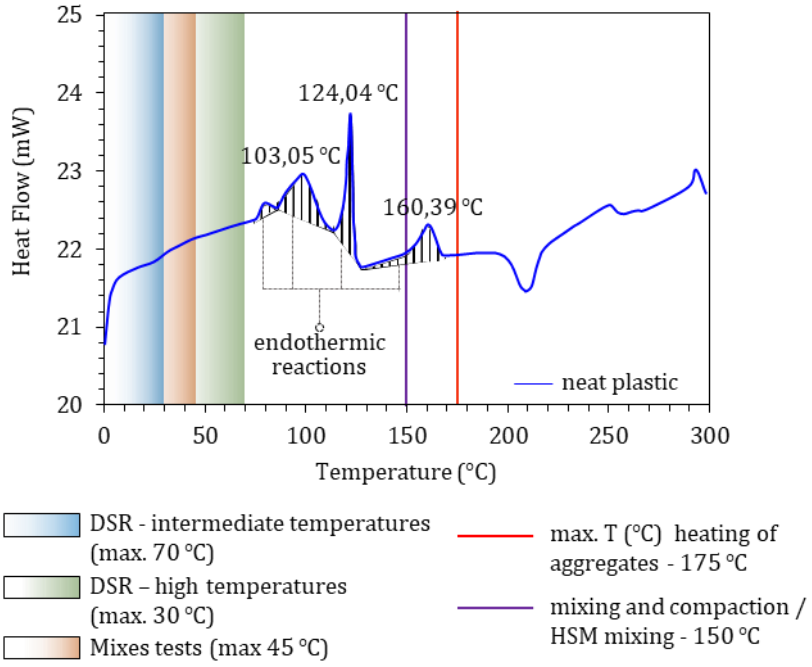


Figure 5-2 – Calorimetry graph of heat flow × temperature

From the analysis of the heat flow, four endothermic reactions – represented by peaks in the curve - were observed before the sample reach the temperature of 200 °C. Among these peaks, those at 103°C, 124°C and 160 °C present remarkable areas, indicating that some components of the material might melt or reach the glass transition at these temperatures.

Taking into consideration the potential use of this plastic within bituminous mixtures, which can usually reach heating procedures with temperatures of nearly 175 °C during production, there is the possibility that some components might change the physical state under these circumstances. This implies that during the mixing procedure bitumen comes in contact with plastic components beyond their glass transition temperatures, which can facilitate migration and blending phenomena. As an example, glass transition of materials composed by a blend of polystyrene and polypropylene can occur at about 100 °C, although the melting points of these polymers are typically around 240 °C (Thirtha et al., 2005). Such information must be given careful consideration for the interpretation of the results of this study and, more in general, for the use of recycled plastics in bituminous mixtures.

5.3 Chemical characterization (FTIR Spectroscopy)

This section presents the results obtained from FTIR tests. The tests presented in this section refer to part of the experimental plan carried out in UFC. First, the absorbance spectrum of the neat plastic is discussed, providing further information about the composition of this material. Then, the discussion moves to the analysis of the samples of bituminous binder prepared after interacting with the plastic. This second part focuses on modifications of the chemical signatures emerging from the interaction process.

5.3.1 FTIR of carton plastic

Figure 5-3 shows the spectrum of the neat plastic obtained by absorbance in KBr atmosphere. The spectrum was smoothed and then normalized with respect to the strongest band, with a wavelength of 2920 cm^{-1}, which can be associated with the group CH present in the polymers. Based on that, the bands can be observed by their occurrence rather than the size of their peaks.

The presence of multiple bands at varying wavelengths alongside the spectrum indicates that several different types of chemical groups can be found in the composition of this material, corroborating the idea that different polymers compose the plastic. This aligns with the expectations, given the nature of this material and its storage conditions.

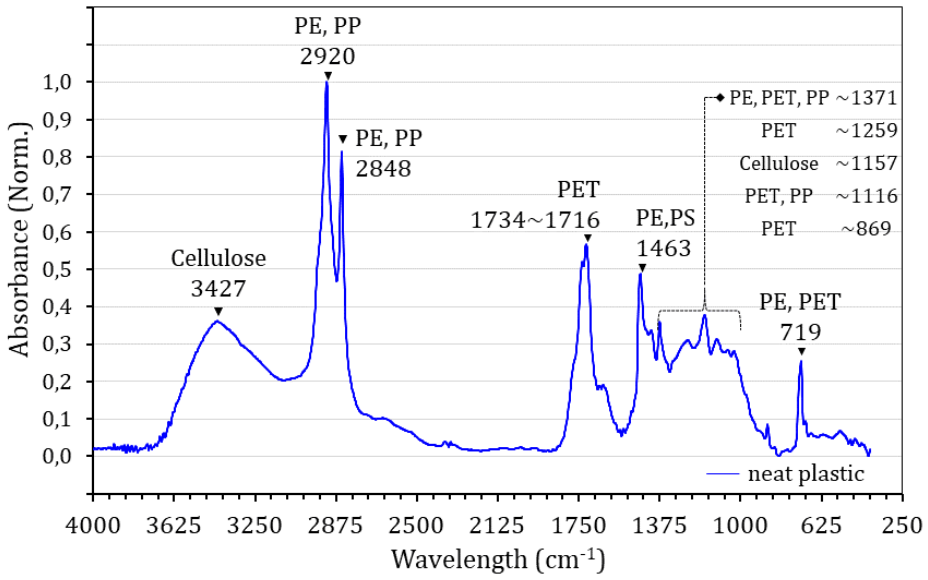


Figure 5-3 – FTIR spectrum of the neat plastic

The bands with strongest absorbance are specified in the graph and based on their wavelength, they were associated with the groups commonly identified in some polymers. The interval of wavelength between 2000 and 4000 cm^{-1} represents the first half of the spectrum. This region is characterized by strong and spaced functional groups. As mentioned before, there are bands common to the polyethylene, associated to the CH groups, at 2920 and 2848 cm^{-1}. A well-defined band at 3427 cm^{-1} is also observed, which can be associated with OH or NH groups. In this case, it is possible to associate this band to the group OH present in cellulose (Poletto et al., 2013). The traces of cellulose can be associated to contamination of the material in the storage facilities and/or that the production process of shredded plastic before its storagin is insufficient to perfectly segregate the polymer from the paper/cardboard layers present in the origin food packaging source.

In the middle of the spectrum, between 2500 and 2000 cm^{-1} low prominent bands were obtained. In the second half of the spectrum (where the wavenumber is lower than 2000 cm^{-1}) it is possible to observe a higher concentration of peaks. The corresponding bands can be associated to functional groups characteristic of some polymers - such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) – and to groups commonly found in the celullose, such as the C-O-C asymmetrical stretching, represented by the band at 1157 cm^{-1} (Fan et al., 2012).

5.3.2 FTIR of bitumen before and after contact with plastic

As discussed in chapter 3, the bitumen-plastic mixing process was conducted at 150°C. At this temperature, it is possible that the bitumen oxidizes, which implies the formation and increase of carbonyl (1700 cm^{-1}), sulfoxide (1032 cm^{-1}) and aromatics (1600 cm^{-1}) functional groups (Banja et al., 2018).

Among the molecules formed during the oxidative process, those containing the carbonyl and sulfoxide groups, respectively mostly present in converted ketones and the result of the oxidation of organic sulphides, can be associated to the hardening of binders after ageing (Petersen & Glaser, 2011; Tauste et al., 2018). These modifications are also related to changes in the proportions of SARA components, which also might change the chemical arrangement of the molecules inside the binder. For these reasons, the analysis of the effect of interaction with plastic on binders was made by comparison with the control binder rather than with the neat binder.

Besides the control binder, heated at 150°C for 60 minutes and mixed at 1000 RPM, two other materials were considered in the investigation including FTIR results. The first one is the bitumen exposed to 5% of plastic for 60 minutes with a mixing speed of 200 RPM. The second one is the bitumen exposed to 20% of plastic for 30 minutes with a mixing speed of 1000 RPM.

Figure 5-4 shows the FTIR spectroscopy analysis obtained from the samples prepared with induced interaction with the plastic. The samples were analysed having in perspective the spectra of the neat binder and of the sample of control that passed through the HSM procedure without contact with plastic. This approach aims to isolate the ageing effects on the chemistry of the binder from those generated by the contact with the plastic.

The data was normalized following the same procedure used in the FTIR analysis of the plastic to allow a better understanding of the bands formed in each process and a comparison of the materials. This process was carried out by qualitative contrast of the format of the bands and its position.

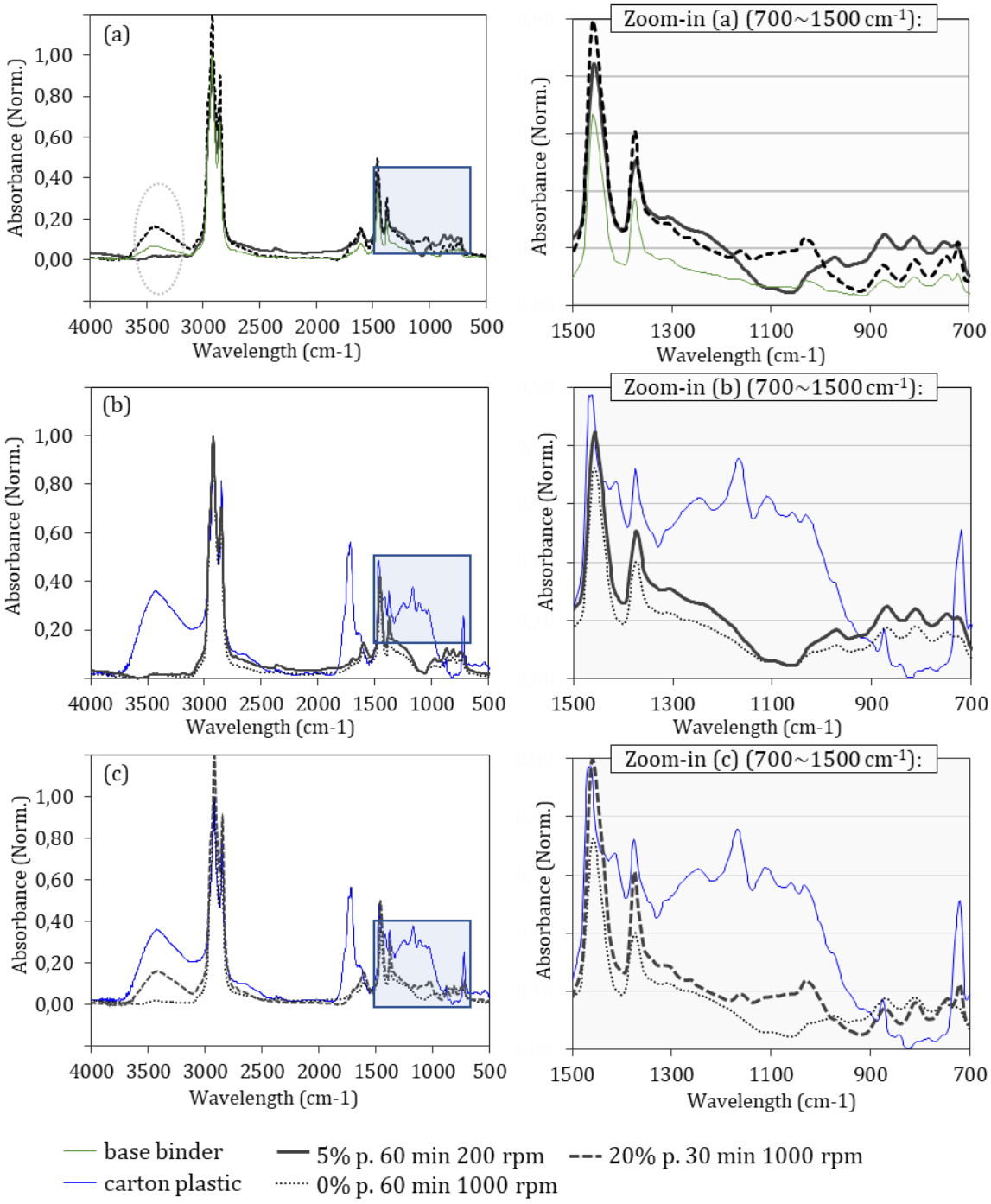


Figure 5-4 – FTIR spectra of plastic and bitumen after mixing and separation, with different plastic contents (0%, 5% and 20%): (a) Comparison between the neat binder and binders after contact with plastic (5% and 20% plastic). (b) Comparison between plastic, control binder (0% plastic), and binder after contact with plastic (5%). (c) Comparison between plastic, control binder (0% plastic), and binder after contact with plastic (20%)

As previously discussed, the oxidative conditions imply the formation and increase of groups carbonyl – C=O (1700 cm^{-1}), sulfoxide – S=O (1032 cm^{-1}), and aromatics (1600 cm^{-1})

functional groups (Banja et al., 2018). In the first graph (Figure 5-4a), it is possible to observe the formation of a functional group in the sample produced with contact to 20% plastic placed in a wavelength of around 1030 cm^{-1}. If this band is associated with oxidation, its presence would represent the formation of sulfoxide in this sample. However, considering the same was not observed in the material prepared with 5% plastic, it can be also the result of the stronger presence of plastic in the production phase. It is also possible to observe a smaller band placed in a wavelength of 1160 cm^{-1} that was only observed in the sample prepared with 20% plastic, which might not be related to the oxidative effect.

When it comes to aromatics and carbonyls, it is possible to observe that the samples presented an increase in prominence in the wavelength of 1600 cm^{-1} and a formation of a small band around 1700 cm^{-1}. Those differences do not indicate a level of oxidation that would impact the performance of the binder.

In Figure 5-4b, the spectra of the control binder and the sample exposed to 5% plastic are compared, together with the spectrum of the plastic itself. It is possible to observe in this binder, and in the control sample, a formation of a band in a wavelength 990 cm^{-1} in comparison to the neat binder, which does not evidence the presence of plastic in the sample. Regarding the preparation of the binder with 5% plastic, it is possible to infer that this process does not change the chemical characterization when in contrast to the same process carried out without the addition of plastic.

Based only on the FTIR analysis, it was not possible to observe strong evidence of mobilization of any specific component of the residue of plastic, since there is no particular band that was created in the sample of binder exposed to the plastic. It is relevant to consider that the control binder (0% plastic) was mixed at a different mixing speed (1000 RPM instead of 200 RPM). However, little modification is expected in the spectrum since the temperature of heating was kept the same and the bitumen is not subjected to a modifying agent.

When it comes to the sample prepared with exposition to 20% plastic, some variations can be observed in some bands taking into perspective the control sample without plastic. The analysis of this material is presented in Figure 5-4c, together with the one of the control binders (0% binder) and of the plastic. Remarkable differences can be noticed between the spectra of the two binders. In particular, the band observed around the wavelength of 3400 cm^{-1} indicates the presence of some residue of cellulose in the material. The sample prepared with 20% presented a strong alteration in this band when compared to the control sample and the sample prepared

with 5% plastic. This suggests that the higher rotation speed, combined with the type of spindle used might be abrasive enough to reduce the size of these particles creating a suspension of smaller particles inside the binder that could not be separated by the sieve used. The higher plastic content likely played a significant role in making this effect more pronounced. Smaller bands formed around both wavelengths of 1500 cm^{-1} and 700 cm^{-1} were also observed, associated with the presence of PE, PET, and/or PP in the sample.

Considering the possibility of mobilization and blending between the neat plastic and the neat binder, it is not possible to state specifically which of these polymers have migrated to the binder since the polymers achieve the glass transition at temperatures below their melting points, and simultaneously. It is also possible that these points reflect the presence of micro filler particles that after 1 hour of mixing are smaller than 1.20 mm and can pass through the sieve, and that behave differently from those that are not associated with the asphaltenes modifying the SARA proportions (Porto et al., 2019).

5.4 Campaign 1: Rheological analysis of binder (DSR, from 46 to 82 °C, results from UFC)

In this section the analysis and interpretation of the results obtained from DSR tests of Campaign 1 are presented. The raw data were initially verified to exclude points obtained outside the acceptable ranges of tolerance of the equipment. The procedure was first validated for the results obtained on the neat binder and then applied for data processing of the results for all other materials.

5.4.1 Data processing and cleaning

Multiple measurements were made at each frequency. The protocol of test was set as gap control. In addition, all data points acquired in conditions not complying with the following criteria were not considered in the analysis:

i. gap (plate to plate distance) variation with respect to imposed value lower than 4.00 μm in absolute value;

ii. axial force lower than 1.00 N in absolute value;

iii. torque lower than 0.100 μN.m;

iv. temperature variation with respect to imposed value lower than 0.50 °C (in absolute value).

The limiting values were chosen based on the specifications of the equipment and on experience (commonly accepted test conditions). The standard dispersion of the data points acquired for each combination of frequency and temperature was used as an additional criterion to discard measurements showing excessive dispersion.

5.4.2 Black diagram

In Figure 5-5 the outputs obtained for each test are presented in two graphs. The graphs show the norm (|G*|) and phase angle (φ) of complex modulus G* plotted in a Black diagram.

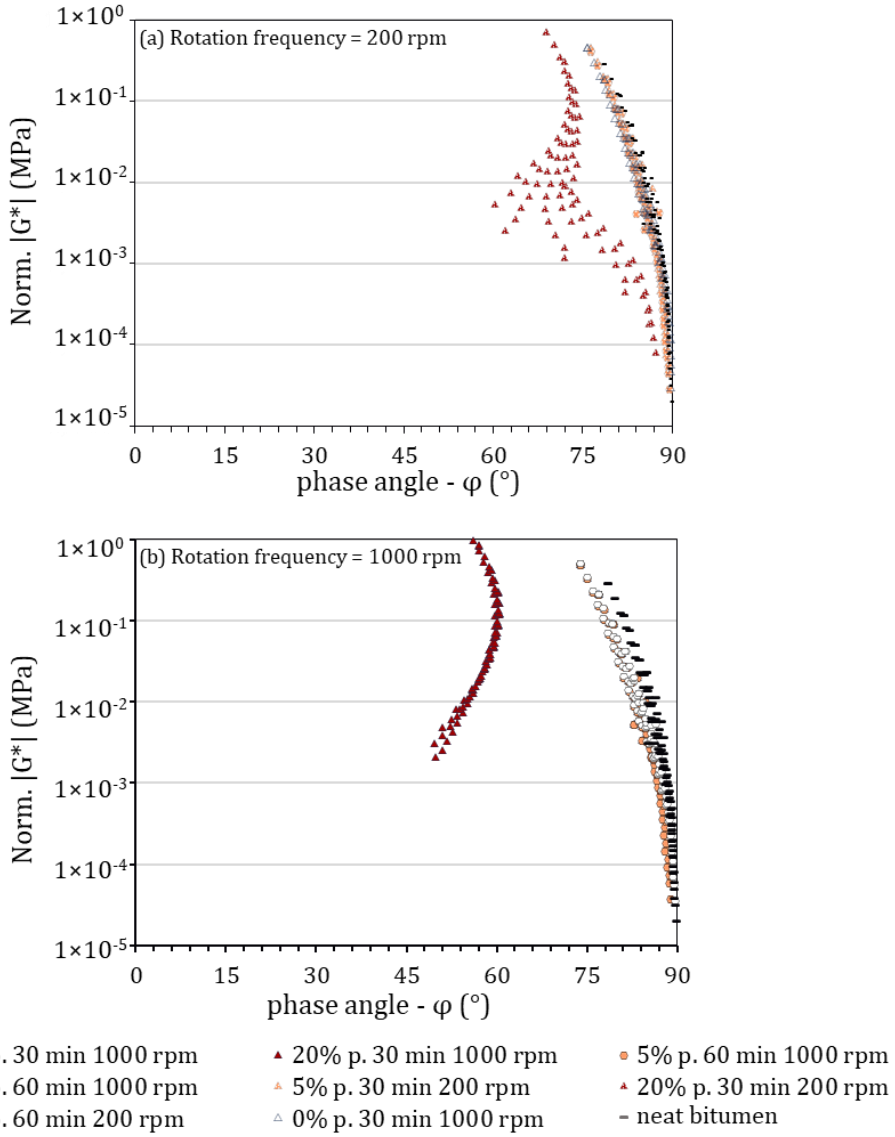


Figure 5-5 – Campaign 1: Black diagram of DSR results for bitumen after mixing (200 and 1000 RPM) and separation, with different plastic contents (0%, 5% and 20%) at UFC: (a) Results on materials mixed at 200 RPM; (b) Results on materials mixed at 1000 RPM.

The first graph (Figure 5-5a) shows the data of the materials produced at a mixing speed of 200 RPM, while the second one (Figure 5-5b) shows those of the materials produced at a mixing speed of 1000 RPM. In both figures, data obtained for the neat binder and for the control binders (mixed with 0% plastics) are plotted to provide a comparison.

With respect to the behavior of the control binder samples, the binders exposed to 5% plastic did not present notable variation in their viscoelastic properties, maintaining a thermorheologically simple behavior close to the one obtained from the control bitumen prepared without plastic. This similarity suggests that no substantial retention of polymeric

material occurred during the exposure phase for this material, which means minor interaction. This hypothesis is supported by the fact that both materials exhibited similar thermorheological behavior throughout the tested temperature range. When submitted to lower frequencies (and high temperatures), these two binders tend toward a Newtonian flow, indicated by their curves approaching the phase angle of 90°.

On the other hand, significant alterations in the linear viscoelastic behavior were observed for the binders exposed to 20% plastic (Figure 5-5b). In particular, the binder exposed to 20% plastic for 30 minutes at 200 rpm does not show a smooth and continuous Black curve, although still tending towards a 90° phase angle asymptote. This binder presents a notably narrow Black curve, in contrast to the previous binder, with isotherms practically superposed and a lower phase angle range. In both graphs, it is possible to imply an effect of interaction and compatibility with the plastic. In addition, it is also possible to find points out of the main trend which could represent the presence of inclusions (potentially plastics, which do not integrate the compatible system or remaining fibers of cellulose) within the sieved bitumen.

5.4.3 Elaboration of master curves (for range of temperatures from 46 to 82 °C)

For all binders (including those exposed to 20% of plastic), the isotherms of |G*| and φ were shifted for a reference temperature (T_{ref}) of 58°C in order to build master curves of norm and phase angle of complex modulus. The time-temperature superposition principle (TTSP) was assumed to allow for the horizontal shifting of the isotherms with respect to the T_{ref}. Firstly, a preliminary shift was obtained by adjusting the experimental frequency to a corresponding reduced frequency, according to Equation (4).

$$\log(a_T) = \log\left(\frac{f_G}{f_{GTref}}\right) \quad (4)$$

where f_G is the loading frequency of the experimental data and f_{GTref} is the reduced frequency based on reference temperature T_{ref}. The shifting of the isotherms was adjusted based on the dispersion of the experimental data points and the smoothness of the resulting curve.

Figure 5-6 shows the isotherms and master curves obtained for norm and phase angle of G*, while Figure 5-7 shows the values of the shift factors found plotted as a function of the corresponding temperature. The same set of shift factors was used for |G*| and φ.

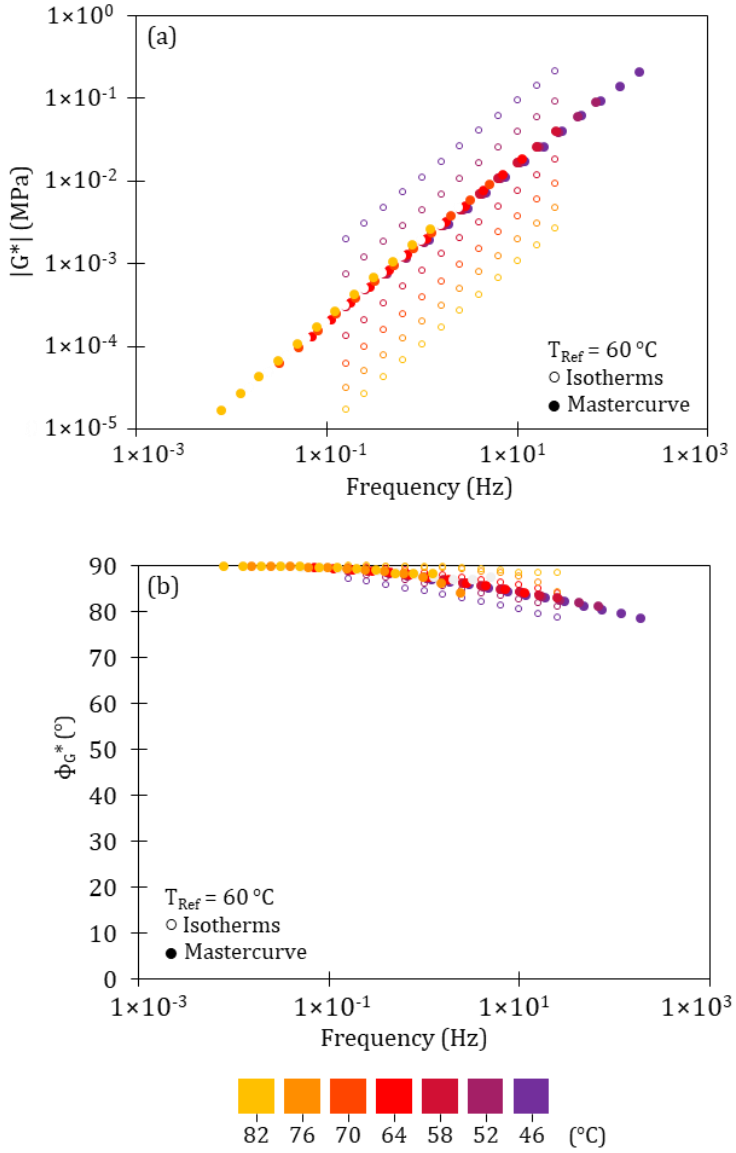


Figure 5-6 – Campaign 1. Master curves of neat binder (T_{ref} = 60 °C): (a) norm |G*| and (b) phase angle φ of shear complex modulus

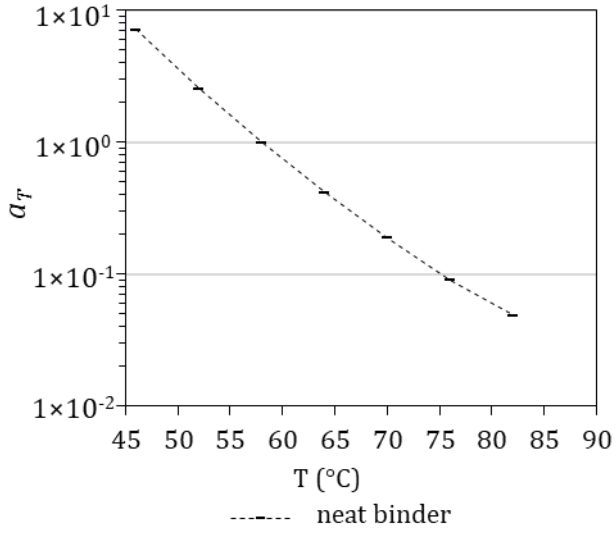


Figure 5-7 – Campaign 1: Shift factors determined for neat binder (T_{ref} = 60 °C)

Although it is expected that these shift factors are reproducible to other parameters of the frequency sweep analysis, it is important to highlight that the parameters determined in an analysis of the complex moduli were the same used to plot the master curve of the phase angles.

Figure 5-6 shows the master curves plotted with the determined reference shift factors. In the graphs, the isotherms are also individually represented. In Figure 5-6a the complex modulus curve is presented while Figure 5-6b shows the curve for the phase angle.

It is possible to observe that for both the complex moduli and the phase angles the shift factors provide adherence to the isotherms, resulting in a smooth curve. For the neat binder, it was not observed outliers, and/or points that were dispersed out of the natural tendency of the curve.

5.4.4 Analysis of binders prepared at 200 and 1000 rpm

Figure 5-8 and Figure 5-9 show the master curves of the norm |G*| and phase angle φ of shear complex modulus and corresponding shift factors obtained for the binders mixed to plastic at a rotation speed of 200 rpm and for the control binder (binder mixed without with plastic for 30 minutes at a rotation rate of 1000 rpm). Similarly, Figure 5-10 and Figure 5-11 show the master curves of |G*| and φ and corresponding shift factors obtained for the binders mixed to plastic at

a rotation speed of 1000 rpm and for the control binder (binder mixed without with plastic for 30 minutes at a rotation rate of 1000 rpm).

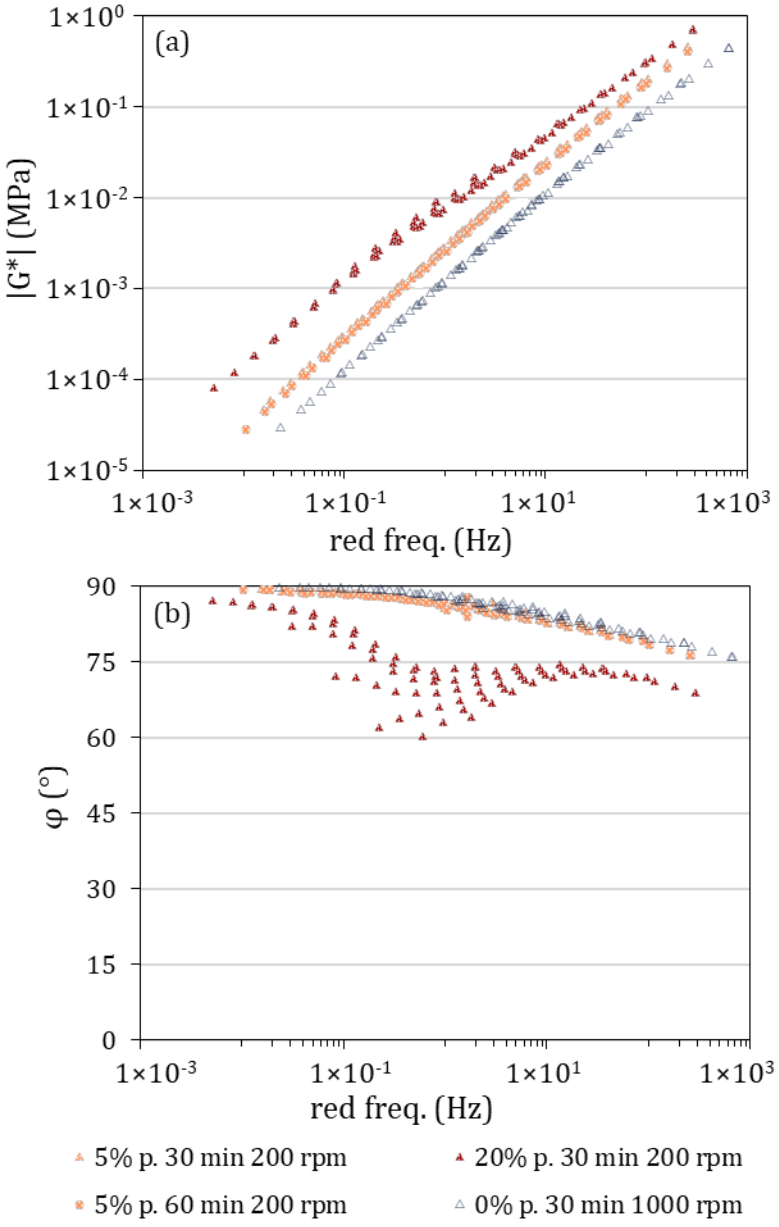


Figure 5-8 – Campaign 1. Master curves (T_{ref} = 60 °C) of the binders exposed to plastic with a rotation rate of 200 rpm and of the control binder (0% plastic, 30 minutes, 1000 rpm): (a) norm |G*| and (b) phase angle φ of shear complex modulus

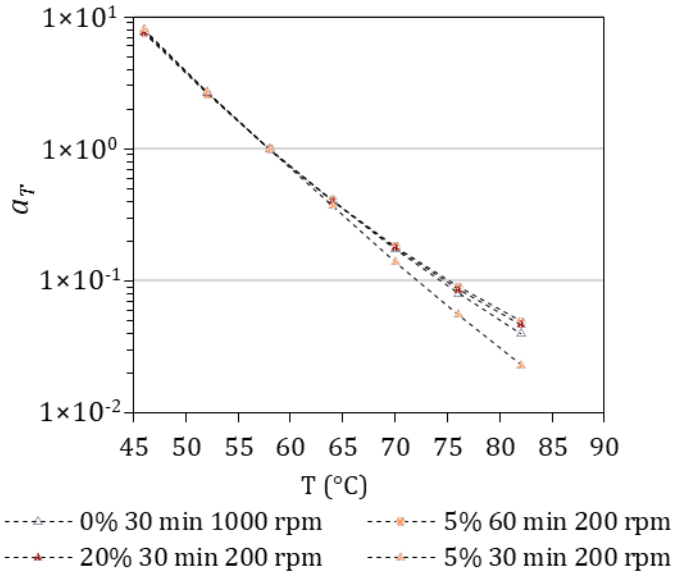


Figure 5-9 – Campaign 1. Shift factors (T_{ref} = 60 °C) determined for binders exposed to plastic with a rotation rate of 200 rpm and for the control binder (0% plastic, 30 minutes, 1000 rpm)

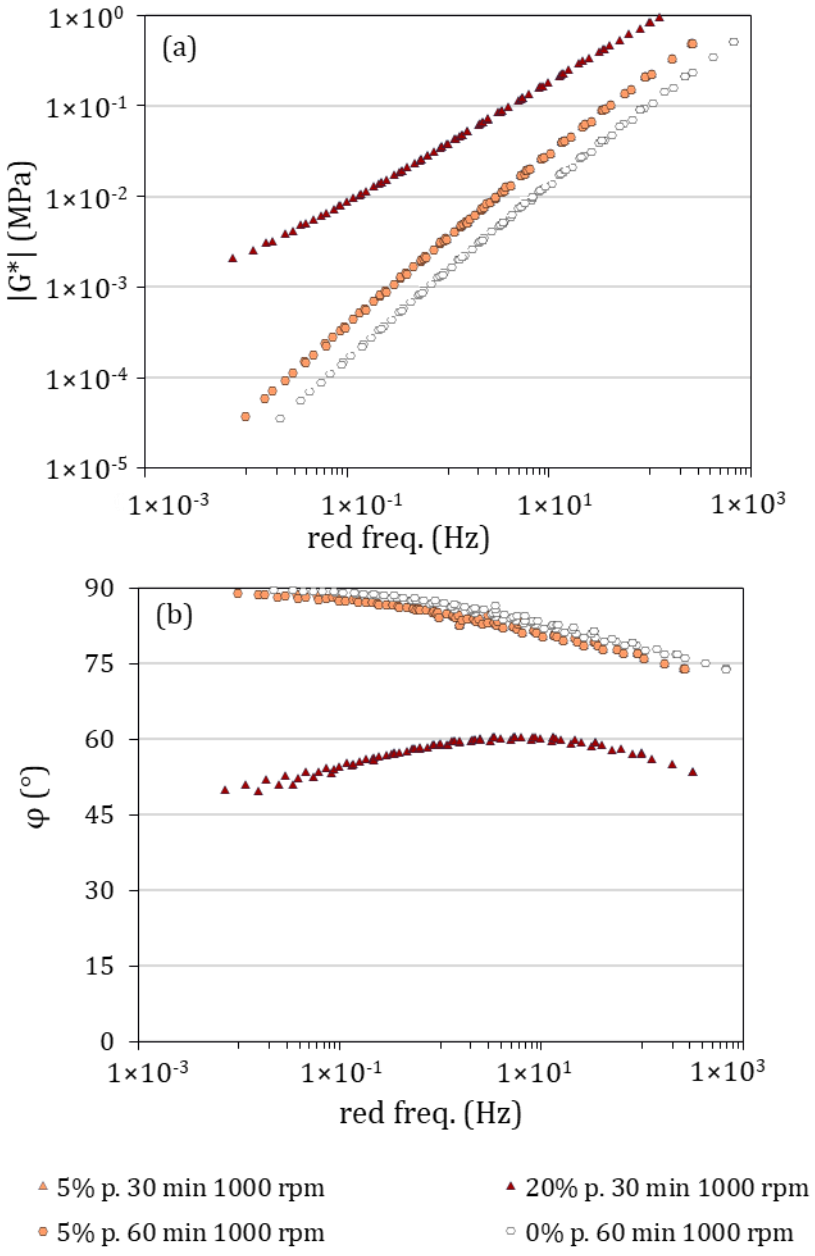


Figure 5-10 - Campaign 1. Master curves (T_{ref} = 60 °C) of the binders exposed to plastic with a rotation rate of 1000 rpm and of the control binder (0% plastic, 30 minutes, 1000 rpm): (a) norm |G*| and (b) phase angle φ of shear complex modulus

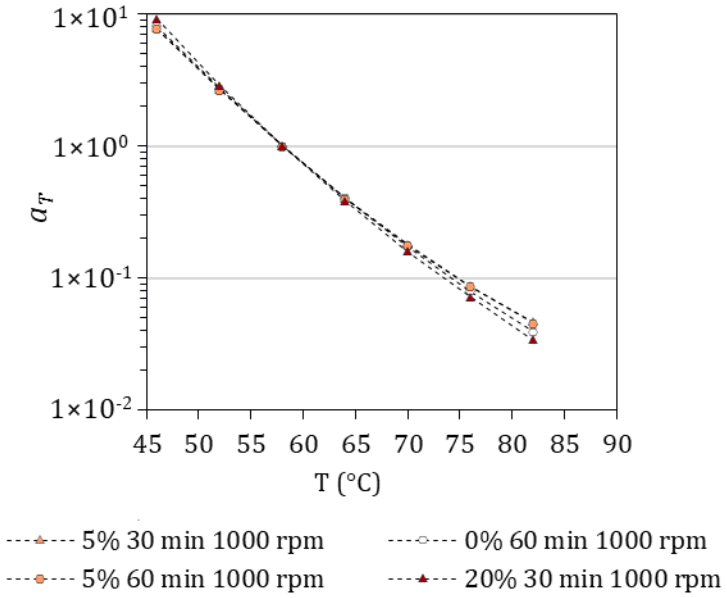


Figure 5-11 - Campaign 1. Shift factors (T_{ref} = 60 °C) determined for binders exposed to plastic with a rotation rate of 1000 rpm and for the control binder (0% plastic, 30 minutes, 1000 rpm)

It is possible to observe that, for temperatures higher than 60 °C, the shift factors were gradually dispersed. This dispersion may be attributed to an increased thermal sensitivity of the material at higher temperatures that was also potentially influenced by the presence of the polymer in the compatible system. This indicates that at higher temperatures the materials present more dispersed isotherms when put in comparison, which might indicate that in some aspects they are not the same. Regarding the samples prepared at 1000 rpm, it is possible to observe that at 46 °C, the lowest temperature in this analysis, there was also a difference between the shift factors. This indicates that the isotherms at these temperatures might present a slight difference in form or position.

When it comes to the analysis of |G*|, it is possible to infer an increase in the stiffness of the material in the materials prepared with the addition of plastic, illustrated by the displacement of the position of these curves above the control sample. It is relevant to remark that, considering the samples prepared with 5% plastic, both samples presented a relatively approximate position when compared to the others, even though they were mixed for different times (30 and 60 minutes). It would be possible to assume that, under these conditions, the

proportion of plastic adopted for the preparation was a more influential variable in the increment of stiffness at high temperatures than the oxidation due to the heating process.

The analysis of the phase angle through the master curves part from the discussion proposed in the analysis of the Black Diagram concerning the viscoelastic behavior of the sample prepared with contact to 20% plastic. The master curve obtained for this sample presented multiple tendencies rather than a smooth format and evolution. In the lower frequencies, which correspond to the higher temperatures, the curve seemed to be directed to a 90-degree phase angle. However, in the intermediate frequencies, it is possible to observe a dispersion of variable trends of behavior. Among those, some seemed to present a decrease of the phase angle, which would represent an increase in the elastic behavior promoted by the mobilization of plastic content into the binder.

Some similarities could be found when comparing the samples prepared with the two different speeds (200 and 1000 rpm) and isolating the effect of this variable. Among the second group of materials (produced at 1000 rpm), the binder that interacted with a content of 20% plastic for 30 minutes presented the highest increase in stiffness. At the same time, the two binders prepared with 5% plastic were placed relatively in the same position when putting into perspective the distance between the control binder and the one with highest increment of stiffness.

It would be possible to infer that the elevation in stiffness was more expressive in that sample due to a higher exposition of the plastic content promoted by the higher rotation rate. This effect was also observed when analyzing the master curves of phase angle, presented in Figure 5-11.

Taking into analysis the curves of phase angle, it is possible to observe a very well outlined divergence of behavior when it comes to the sample of binder exposed to 20% of plastic. In one of the extremities, this curve presents a clear tendency to decrease as the frequency decreases. This gives an indication of elastic behavior at higher temperatures, where unmodified binders are conditioned to behave as Newtonian fluids.

It is possible to observe that, independently from the mixing speed, an increase of the plastic content leads to an increase of |G*|, with no sensible differences between the master curves of the binders exposed to 5% plastic mixed for 30 and 60 minutes. Moreover, negligible variations of the phase angle master curves of all binders exposed to 5% plastic were observed with respect to the control binder.

Only the binders exposed to 20% plastic shows considerable differences with respect to the control binder, both for |G*| and φ. In fact, as already noticed from the analysis of the Black diagram, the phase angle of the binder exposed to 20% of plastic shows presented an unexpected behavior at high temperatures, not presenting a constant tendency towards 90 degrees as the temperature increases. This result indicates a clear effect of the interaction between bitumen and plastic. However, it is not possible to exclude the possibility that the observed impact on the linear viscoelastic properties of binder after exposure to plastic is due to the presence of dispersed plastic that does not integrate the structure of the binder. Under these circumstances, it should be considered a scenario of low compatibility in which the particles of plastic that migrate to the binder structure have diameter slightly below 1,20 mm (sieve opening), acting as fillers dispersed in a solution.

5.5 Campaign 2: Rheological analysis of binder (DSR, from -20 to 70 °C, results from UniPr/ENTPE)

From the results obtained in Campaign 1, the interaction between plastic and bitumen was better observed when binders were exposed to 20% of plastic by weight at a mixing speed of 1000 rpm. These conditions were adopted for the preparation of materials in Campaign 2, carried out at ENTPE with the support of UniPr.

In this phase of study, the rheological characterization was carried out at a wider range of temperatures, varying from -20 to 70 °C, using different plate-plate geometries according to the temperature, as already explained in Section 4.4. Neat binder, binders mixed without plastic (0%) and binders exposed to 20% plastic were tested in this campaign. The purpose of this part of the study was to further investigate the effects of potential interaction with plastic in the conditions where the most significant changes were observed during Campaign 1. The 2S2P1D model was used to simulate the linear viscoelastic behavior of the tested materials.

5.5.1 Data processing and cleaning

The procedure of data processing and cleaning was further refined with respect to the one followed for processing data on Campaign 1. Three replicates were obtained for each material.

As mentioned in Section 4.4, for each test temperature, the number of cycles performed varied according to the loading frequency. Figure 5-12 presents an example of unprocessed data obtained from a complex modulus test on the neat binder at 50°C. Values of |G*| and φ obtained are plotted as a function of the number of loading cycles and presented by frequency.

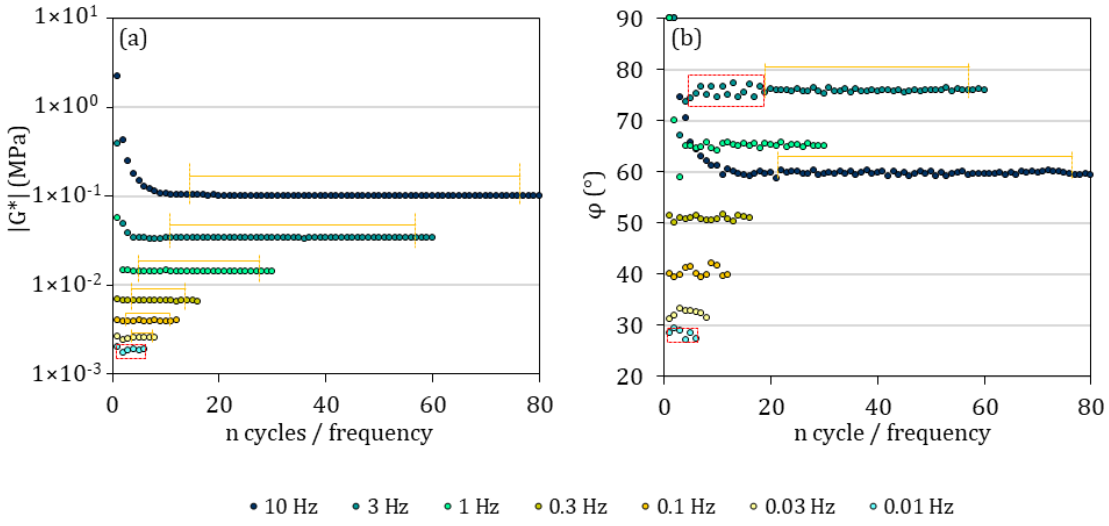


Figure 5-12 – Campaign 2. Example of raw data obtained for |G*| (a) and φ (b) on neat binder at 50° C

The first step of the data processing was to discard all the cycles within the transient regime affected by viscoelastic effects, showing variable values of |G*| and φ. Depending on the frequency, the number of cycles concerned varied between 1 and approximately 25. For additional safety, the first 10% + 1 and the last 5% + 1 of all the cycles recorded for each frequency were discarded regardless of the values found. For example, the yellow bars in Figure 5-12 indicate the cycles retained for each loading frequency. In addition to this verification, similarly to what done for DSR data obtained in Campaign 1, all the cycles showing values of normal force, strain amplitude, and torque outside of the tolerances given by the specifications of the equipment were also discarded. The remaining data were averaged in order to obtain |G*| and φ values for each combination of frequency and temperature.

As already mentioned, three samples were tested for each material. The following process aimed to identify discrepancies between the data obtained on the three samples and validate values for analysis. Figure 5-13 presents an example of three repetitions of test carried out on the reference binder (neat) at 20°C, 40°C and 60°C, using a 25 mm geometry. For each combination of frequency and temperature, the arithmetic mean of the values of the three repetitions was calculated and retained for the analysis. An acceptance criterion was established to reject the data showing a coefficient of variation higher than 0.15. In the figure, it is possible to observe that data obtained at 20°C at 1, 3 and 10 Hz10 presented excessive differences and were ignored for the analysis carried out.

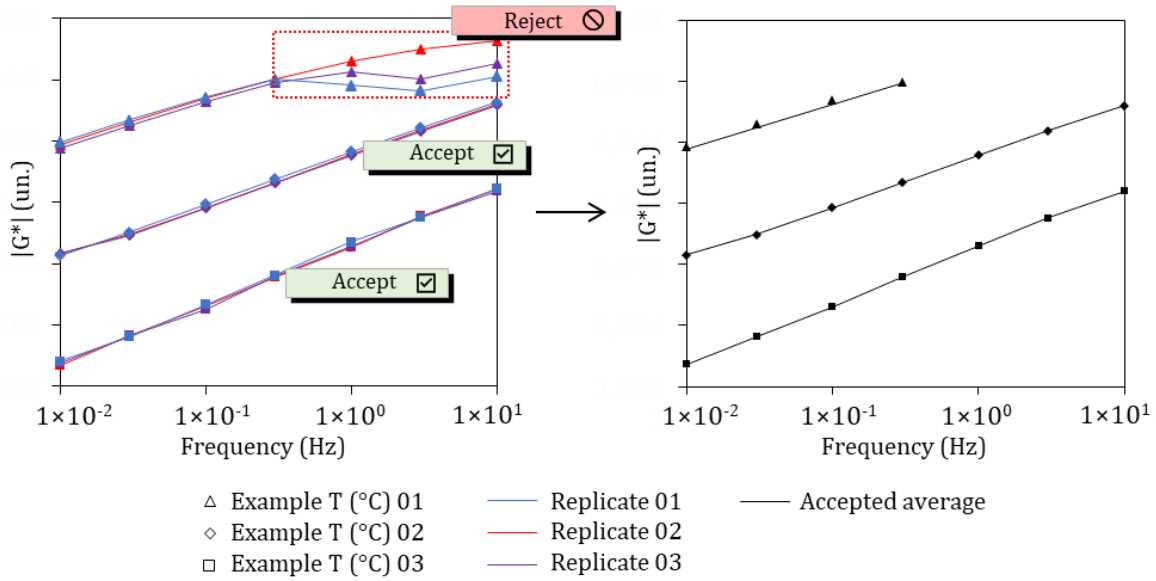


Figure 5-13 – Campaign 2. Example of comparison of three repetitions carried out on reference binder at 20°C, 40°C and 60 °C

5.5.2 Results and analysis

Figure 5-14 shows the dispersion of the data obtained in the DSR tests after cleaning and statistical analysis, obtained in Campaign 2. The points are presented in a Black Diagram, where the x-axis is the phase angle (φ) and the y-axis is the norm of the Complex modulus (|G*|). the 2S2P1D modeling. The detailed procedure for the calculation of the 2S2P1D simulation and its interpretation is discussed later in this section. As already explained, three different DSR geometries (4 mm, 8 mm, and 25 mm) were used to obtain data over a large range of temperatures. Data obtained with different spindles are plotted in different colors in the figure.

In the plots, it is possible to observe three regions. The first region refers to tests performed at low temperatures with the plate spindle of 4 mm diameter. Secondly, there is a region of intermediate temperatures, where the diameter of the spindle was set as 8 mm. And the third region is the one where the tests were performed at high temperatures and spindle of 25 mm diameter. The results in the third region are more expected to reproduce the behavior of the materials designed for in Campaign 1, where all tests were performed at these conditions. It is possible to observe that in the region of low temperatures and most parts of the region of intermediate temperatures the materials presented a tendency of fitting in a well-shaped curve, without dispersion. Based only on the Black Diagram it was not possible to observe effects of the interaction plastic-bitumen in these regions.

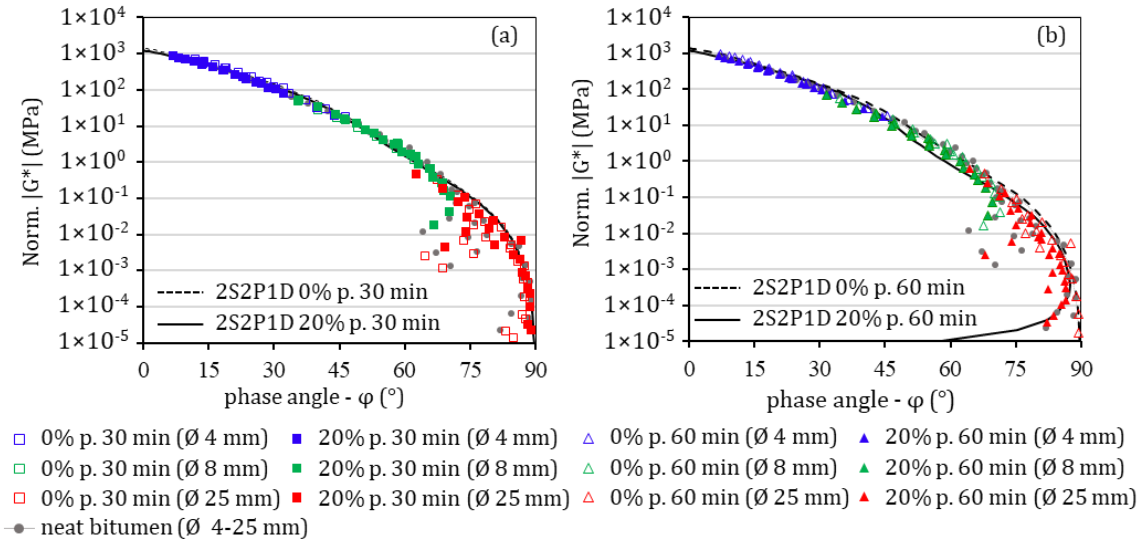


Figure 5-14 - Campaign 2. Black diagram of DSR results for bitumen after mixing (1000 RPM) and separation, with 20% plastic content at ENTPE: (a) Results on materials mixed for 30 minutes; (b) Results on materials mixed for 60 minutes.

Some scatter is observed for the data obtained at the lower tested frequencies (0.01, 0.03, and 0.1 Hz) at 30, 40, and 50 °C. Considering the trend was observed in all the samples, it was assumed that this dispersion was probably related to the geometries used for the tests and the data points concerned were not considered in the analysis.

For the binders mixed for 30 minutes, (Figure 5-14a), negligible differences can be observed between the data obtained for the binder that interacted with the plastic and the control one that was heated and mixed without contact with plastic. In both cases, the 90°-phase angle asymptote is observed at high temperature/low frequency. This point suggests a preliminary indication that the base binder used for Campaign 2 was less prone to interaction with plastic than the binder used for Campaign 1. In Figure 5-14b, the binder exposed to plastic for 60 minutes exhibits slightly lower phase angle values at high temperature than the binder mixed with no plastic (that shows a viscous Newtonian asymptote). However, the scatter of the data does not allow defining clear tendencies.

Figure 5-15 shows the data of the bituminous binder tests in Cole-Cole plots. Data from binders mixed for 30 and 60 minutes are presented in Figure 5-15a and Figure 5-15b, respectively. As

for Black diagrams, data obtained with different DSR geometries are plotted in different colors in the figure.

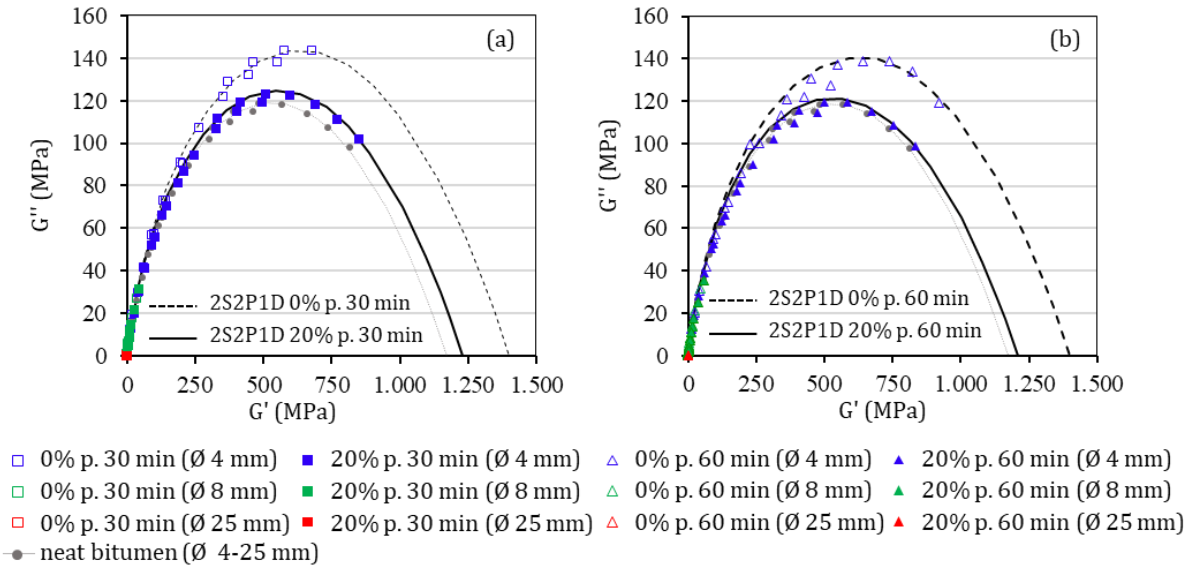


Figure 5-15 – Campaign 2. Cole-Cole plot of DSR results for bitumen after mixing (1000 RPM) and separation, with different plastic contents (0% and 20%) at ENTPE: (a) Results on materials mixed for 30 minutes; (b) Results on materials mixed for 60 minutes

Independently of the mixing duration (30 or 60 minutes), the control binders mixed and heated without interaction to the plastic show higher asymptotic values of their storage modulus at low temperature/high frequency, G_0, than the neat binder. The effect of the interaction of binders with plastic is clearly visible in both graphs (for both mixing speeds) as a reduction of the value of the glassy modulus.

5.5.3 Elaboration of Master curves (for range of temperatures from -20 to 70 °C)

Differently from Campaign 1, the wide range of test temperatures used in Campaign 2 allowed modelling the outputs of the tests (G*) using the 2S2P1D model. All the tested binders (neat, with and without interaction with plastic) show a thermorheologically simple behavior on complex planes, validating the time-temperature superposition principle (TTSP). Isotherms were then shifted to build master curves of norm and phase angle of complex modulus at the reference temperature T_{Ref} equal to 20°C. Shift factors used for the translation of the isotherms

could be calculated according to τ values of 2SP21D model, as in Equation (1) presented and explained in Section 4.6.

For this matter, this constitutes an additional step with respect to the procedure followed in Campaign 1. Shift factors calculated at all test temperatures were then fitted using the WLF law.

The whole procedure of 2S2P1D simulation and obtention of the master curves of |G*| and φ was first validated on the neat binder and then applied for the analysis of the other materials. Figure 5-16 and Figure 5-17 show the master curves with the 2S2P1D model simulation and the shift factors with the WLF fit calculated for the neat binder, respectively.

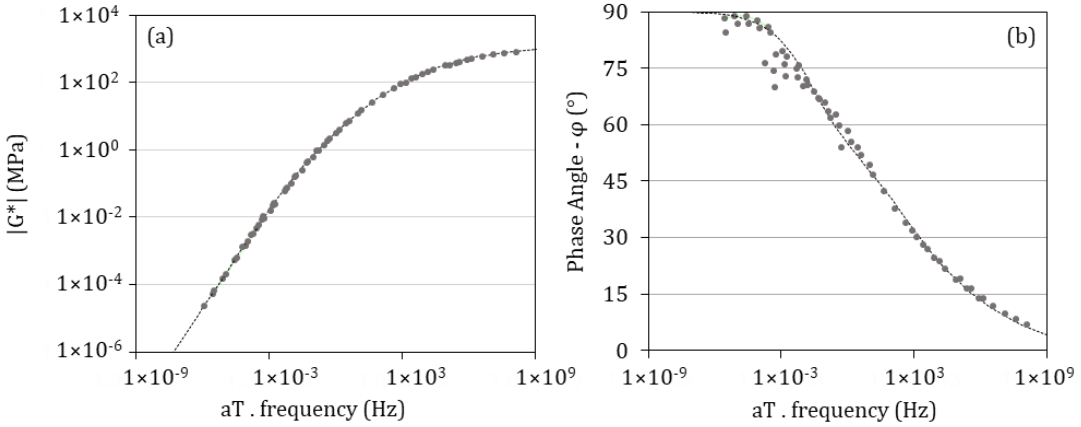


Figure 5-16 – Campaign 2. Master curves of |G*| and φ for neat binder and 2S2P1D model: (a) master curve of |G*|. (b) master curve of φ

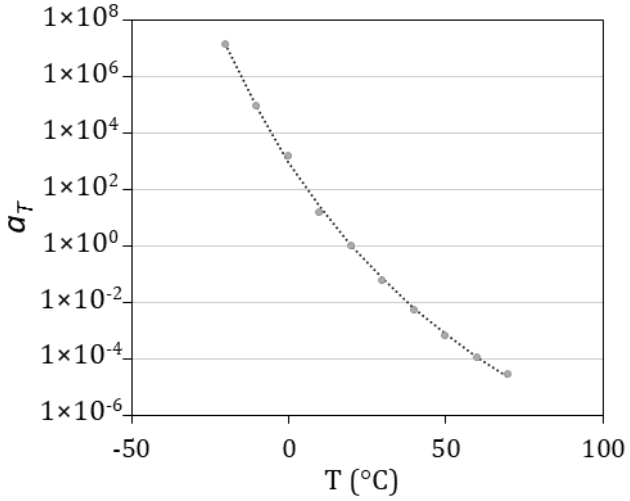


Figure 5-17 – Campaign 2. Shift factors and WLF curve calculated for neat binder

Table 5-1 reports all the obtained values of 2S2P1D model and WLF parameters C_1 and C_2 for all the tested binders. Initial trends observed among the parameters are presented, and their implications to the mechanical performance are subsequently addressed in the specific subsections when applicable. The value of G_{00} is equal to 0 MPa for all binders, except for the one exposed to 20% plastic. This result is in line with previous 2P2P1D modeling of polymer-modified binders (Airey, 2004; Sengoz and Isikyakar, 2008; Zhu et al., 2014).

The obtained values of G_0 for all binders follow the previous observation about the effect of short-term aging. The values of G_0 of the binders mixed without plastic are higher than the value of G_0 of neat binder. Time of mixing does not appear to play a role with respect to this aspect since the binder mixed for 60 minutes has the same G_0 as the one mixed for 30 minutes. Both binders exposed to 20% plastic have lower G_0 values than the control binders mixed without plastic, highlighting an effect of the interaction in the low temperature/high frequency region domain of the rheological behavior of the materials.

Among the other constants, it was observed that k, h and δ presented low variation or remained the same, indicating that the shape of the master curve in the 2S2P1D model remains similar. On the other hand, a stronger difference was observed in the material conditioned with plastic for 60 minutes. In this case, β changed (by more than double) from a value that was constant in all other samples. This reflects the change in shape of the curve in the Black diagram in the high frequency/low temperature region.

Table 5-1 – Campaign 2. Summary of 2S2P1D and WLF constants for the binders tested in Campaign 2 (modeled at 20°C)

Binder	G_{00} ***(MPa)***	G_0 ***(MPa)***	***k (-)***	***h (-)***	***δ (-)***	τ ***(s)*** $_{20°C}$	***β (-)***	C_1 **(-)**	C_2 **(°C)**
neat binder 1000 RPM	~0	1174	0.238	0.580	3.40	1×10^{-05}	280	17.71	138.98
0% 30 min 1000 RPM	~0	1400	0.240	0.580	3.40	1×10^{-05}	280	19.15	148.20
20% 30 min 1000 RPM	~0	1230	0.238	0.580	3.40	1×10^{-05}	280	21.08	163.45
0% 60 min 1000 RPM	~0	1400	0.236	0.580	3.40	1×10^{-05}	280	17.86	140.40
20% 60 min 1000 RPM	1×10^{-05}	1210	0.230	0.560	2.90	1.4×10^{-05}	620	22.06	173.81

The sample conditioned with 20 % plastic for 60 minutes presented the highest values of both C_1 and C_2, respectively 22.06 and 173.81 °C. This demonstrates that this material is the one with strongest variation of a_T in function of temperature among the samples. The value of C2 also demonstrates that the material phase is preserved for a wider range of temperature. Considering the effects of the polymer when modifying the binder, the comparative analysis of

these constants suggests that the contact with the plastic can increase the distance between the shift factors as one of the effects. For example, comparing two binders conditioned for similar time with and without plastic, the stiffness observed in the experimental temperature of 10 °C (10 °C lower than T_{ref}) would correspond to a higher load frequency in the sample with plastic. It is also relevant to observe that, although no strong difference was obtained between the materials after 30 minutes, evidence of the interaction plastic-binder is already observed.

5.5.4 Analysis of bitumen after 30 minutes of HSM procedure

In this part of the analysis the master curves of the materials produced in a mixing time of 30 minutes will be discussed individually. Figure 5-18 shows the plot for the shift factors calculated for each material in this group. The WLF curves were also presented in the graph. The parameters C1 and C2 calculated for each curve will be discussed in detail after the discussion of the master curves.

In this part of the study the discussion was centered on the effects of the plastic. For this purpose, a bitumen prepared with the same mixing time and conditions but without exposition to the plastic was set as reference.

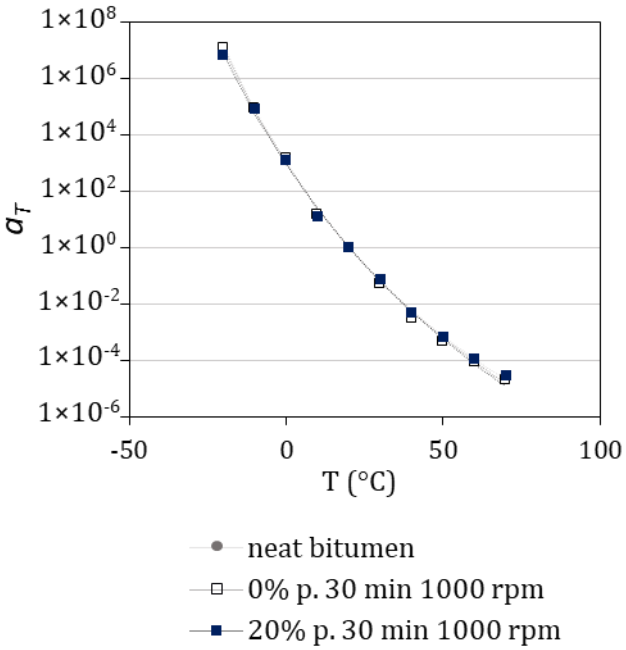


Figure 5-18 - Shift factors calculated for materials prepared with an interaction duration of 30 minutes

The shift factors of the two materials are relatively in the same positions, indicating that in the temperatures located in the extremities, the isotherms are situated at a similar distance and might present an approximate shape. Taking into account the shift factors used to plot the neat binder it is possible to affirm that both binders did not change expressively from their base material.

Figure 5-19 shows the master curves of complex modulus plotted for a reference temperature (T_{ref}) of 20 °C using the shift factors calculated for each material. The curve is presented in three different sectors, corresponding to each geometry and temperature range of the test.

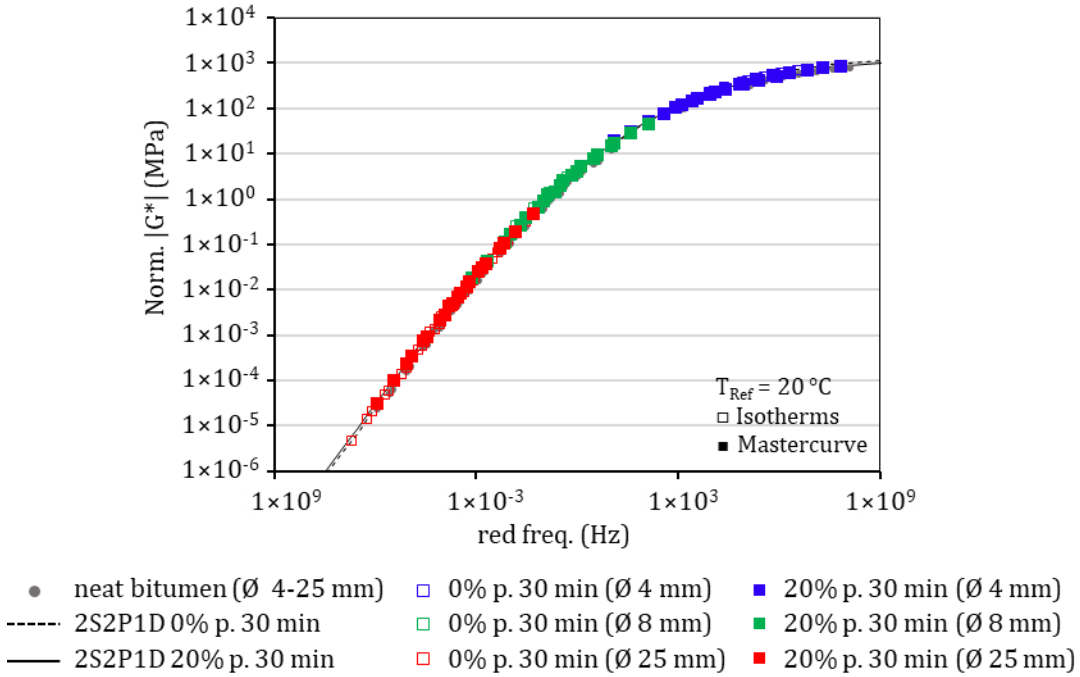


Figure 5-19 - Master curve of Complex Modulus (|G*|) (T_{ref} = 20 °C) of materials prepared with an interaction duration of 30 minutes

Almost no significant differences can be observed between the control binder and the one produced with exposition to the plastic regarding the stiffness. Taking into account the region of high temperatures, represented by the lower frequencies, it was not possible to observe the effect of the plastic in the increment of stiffness of the binder. This highlight that the compatibility is not the same when put in perspective the interaction between the plastic and the base binder used in campaign 2 and the interaction promoted by the same process when considering a binder from a different source.

The investigation of the effects of the interaction with the plastic was also proceeded by the analysis of the master curves of the phase angle, presented in Figure 5-20.

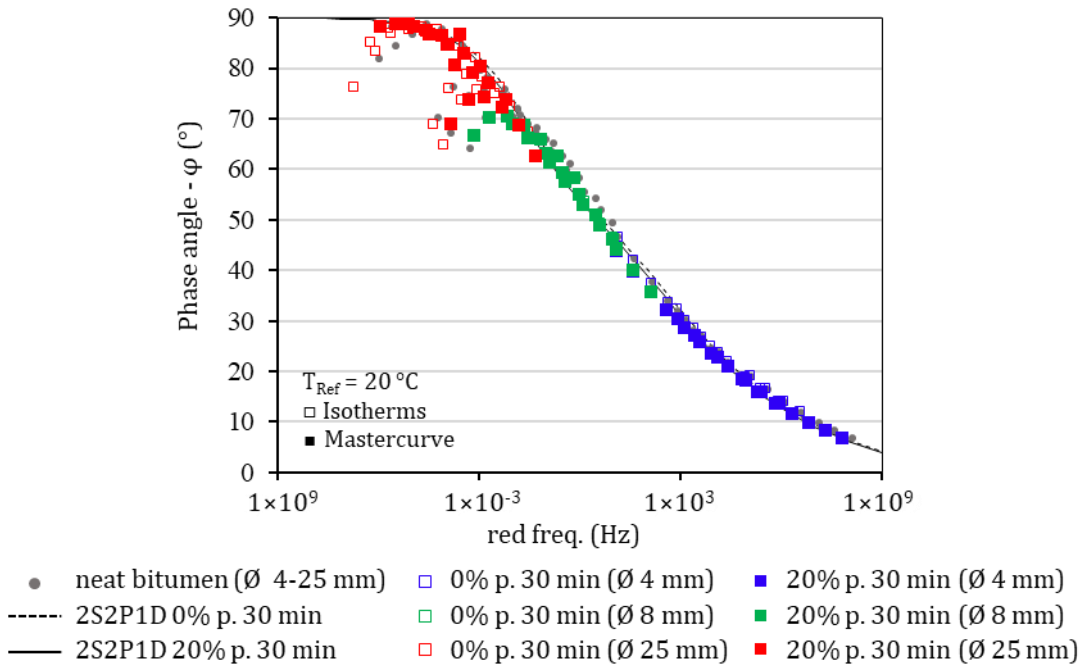


Figure 5-20 - Master curve of phase angle (φ) (T_{ref} = 20 °C) of materials prepared with an interaction duration of 30 minutes

In general, it can be observed that, as the temperature increases, the phase angle of the materials approaches 90, indicating the behavior characteristic of a Newtonian fluid. This response reflects the absence of a significant elastic component, suggesting a non-expressive presence of polymeric content within the binder. The difference in phase angle between the various binders is of a few degrees at most.

5.5.5 Analysis of bitumen after 60 minutes of HSM procedure

Figure 5-21 shows the disposition of the shift factors calculated for the plotting the master curves of |G*| of the materials prepared in an extended time of 60 minutes of contact with the plastic content during Campaign 2.

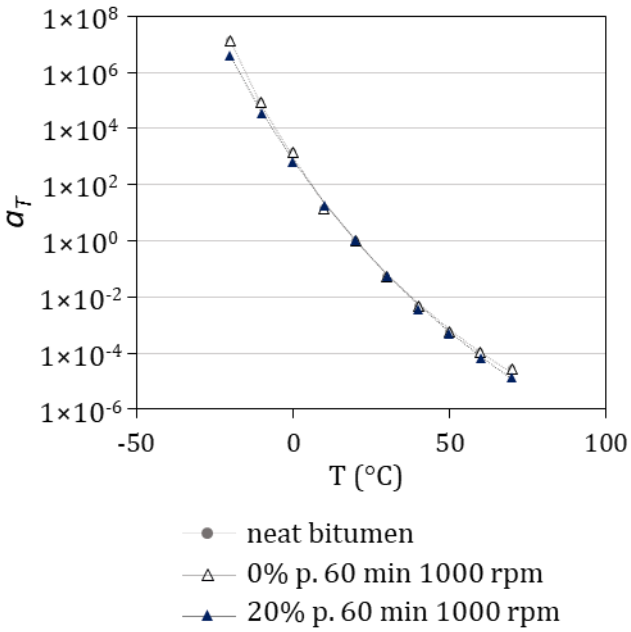


Figure 5-21 - Shift factors calculated for materials prepared at an interaction duration of 30 minutes

Taking into perspective the samples produced in half of the time of production, shown in the previous analysis, it is possible to observe divergences between the WLF curve in the extremities when comparing the control material to the tested samples. This indicates a possible divergence between the isotherms regarding their positions and shapes.

Considering that stronger effects of the interaction are expected in higher temperatures, it is possible to predict that even central isotherms used as reference for plotting the master curves at 20 °C changed under these conditions. Figure 5-22 presents the master curves of |G*| representing the three ranges of temperature investigated during the test, for T_{ref} = 20 °C.

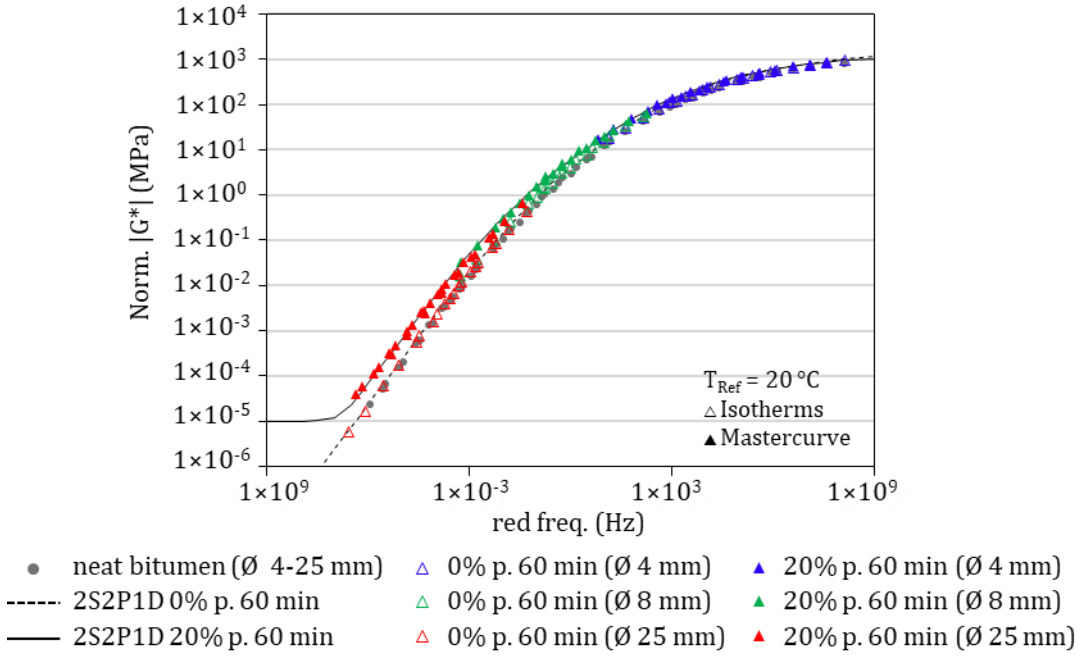


Figure 5-22 - Master curve of Complex Modulus (|G*|) (T_{ref} = 20 °C) of materials prepared with an interaction duration of 60 minutes

As expected, the master curve of the material that interacted with the plastic presented a different shape when compared to the control material, with a tendency of gradually increasing the stiffness as the frequency decreases. This observation reflects the effect of the interaction when the binder is subjected to elevated temperatures. In the graph, it is possible to notice the effects starting by the region of intermediate temperature.

Comparing the analysis of complex modulus of the materials prepared with 30 and 60 minutes under the conditions specified for their production, it would be possible to assume that the extended time promoted a stronger interaction plastic-binder, enough to change its stiffness at high temperatures, while the same was not observed when the mixing was proceeded for only 30 minutes.

Figure 5-23 shows the master curves of phase angle plotted following the same procedure and shift factors.

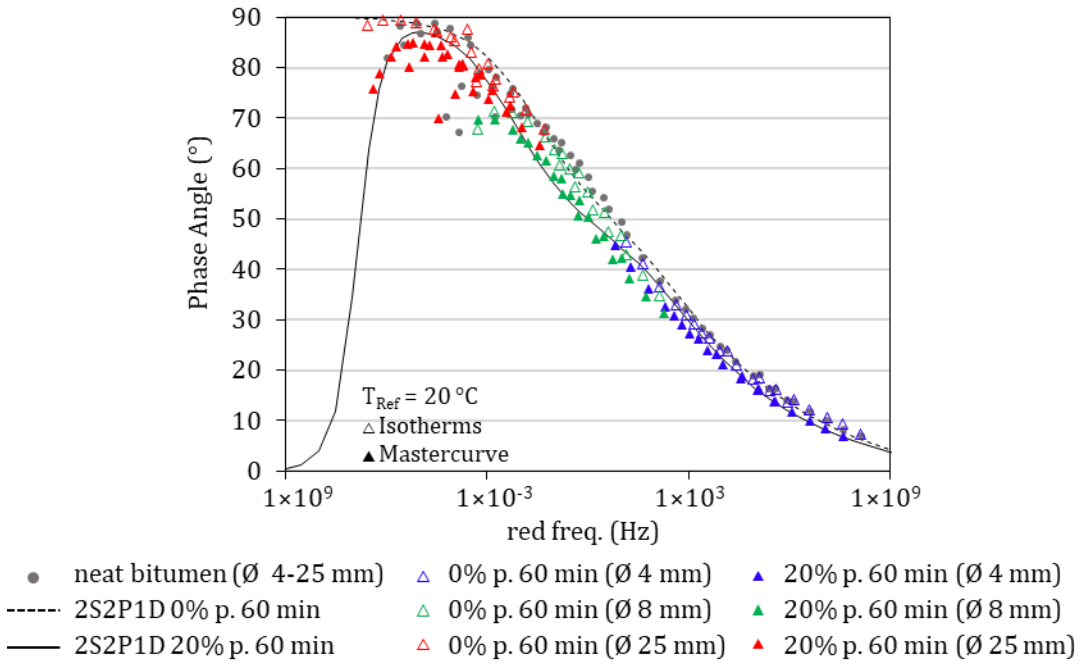


Figure 5-23 - Master curve of Phase Angle (φ) (T_{ref} = 20 °C) of materials prepared with an interaction duration of 60 minutes

Although the curves present strong dispersion in the data. The phase angle master curve of the bituminous binder exposed to plastic presents values that are 3 to 5-degree lower than those of the control material in the range of frequencies of this graph. In higher temperatures this difference was stronger. The reduction of phase angle illustrates the presence of an elastic component in the viscoelastic behavior of the binder, suggesting a chemical modification in its constitution.

This difference can be more rigorously interpreted as a horizontal frequency shift in the master curve, which is directly related to the difference in characteristic relaxation time (τ) of the binder containing 20% plastic compared to the other binders.

From this perspective, the gap observed between the master curves corresponds to a difference of reference temperature of ~1°C, based on the WLF fit of the obtained shift factors. This implies that the incorporation of plastic alters the temperature-frequency dependency in the binder's rheological behavior.

In the high temperature/low frequency region, the binder exposed to plastic appears to exhibit an elastic asymptote instead of a Newtonian flow. This observation is in line with findings reported in the literature for binders modified with Styrene-Butadiene-Styrene (SBS) polymers,

which tends to exhibit similarly phase angle reduction and the development of an elastic asymptote(Airey, 2004; Sengoz & Isikyakar, 2008; Zhu et al., 2014).

In perspective of this data, it is possible to infer that the conception of a polymeric modified bitumen via interaction with this recycled plastic would only be possible if some conditions were respected, such as the right choice of base bitumen; the correct preparation of the shredded plastic; and the use of a temperature and mixing procedure that allows the exposition of the binder to a maximum area of plastic.

5.6 2S2P1D modeling (Campaign 2)

The previous section presented the discussion of the mechanical behavior of samples of the bituminous binder produced in campaign 2 putting into perspective the experimental data. In that analysis the experimental data was used to promote an analysis on the evidence of effects of the polymer. The data was plotted using a 2S2P1D model to enrich the comparison and have a clear notion of the behavior of the materials under different conditions and ignoring the outliers of the experiment.

In the bituminous binder, the arrangement of the elements of this model allows a representation of both the viscous and the elastic aspects, assigned respectively by the 2 parabolic elements and the 2 springs (refer to section 4.6 - Mechanical Modeling - 2S2P1D model). In complement, the dashpot represents the flow behavior of the binder. From the discussions set in the previous section, it was possible to observe that one of the effects of the incorporation of the plastic was observed in the change of the Newtonian flow assumption at higher temperatures for an elastic recovery. The equations for the model were also changed to include these changes.

This section focuses the discussion on the parameters that were calculated to accommodate the changes brought by the incorporation of the plastic. Firstly, the parameters for all materials are presented as they were calculated and then a test of adherence is presented to estimate the efficacy of the model on representing the modified samples.

5.6.1 Calculation of parameters

For describing the behavior of the 5 elements, the 2S2P1D model consists of seven constants (G_{00}, G_0, k, h, δ τ and β) that were optimized to fit the curve to the experimental data (the equation is presented in the subsection 4.6.1 - Parameters of the model). In unmodified binders it is common to adopt a value for static modulus (G_{00}) close to 0, since this modulus is the representation of the modulus at very low frequencies and in this state the binder tends to a Newtonian flow. This assumption was adopted prior to the first iteration for fitting the curve. Considering one of the effects of the PMBs in the curve is the creation of an elastic recuperation at low frequencies, an alteration on this constant might be a sign of interaction plastic-binder. (This phenomenon is discussed in the subsection 2.6.4 - Which mechanical differences are expected when mixing mineral and polymeric aggregates?).

In contrast, the glassy modulus (G_0) represents asymptotic of the modulus at very high frequencies tending to infinite. The second elastic element is associated with the difference between these two moduli. Based on that, a change in the elastic character of a material might be reflected in a variation of both constants.

The parabolic elements are associated with the constants k, h and δ. While k is related to the creep behavior at lower frequencies, h is linked to the creep behavior in high frequencies. Since no changes were observed in high frequencies, it is expected that the model matches this observation with constant values of h. Similarly, an alteration of the Newtonian flow can also affect the constant β, that is linked to the dashpot.

The model was optimized through an analysis of fitting point-by-point of the experimental data when placed in a Black Diagram and in a Cole & Cole plan. In Table 5-2 the constants of the model are presented for all the materials studied in Campaign 2.

Table 5-2 – Optimized 2S2P1D-model constants for bituminous binders tested during Campaign 2

Binder	G_{00} ***(MPa)***	G_0 ***(MPa)***	***k (-)***	***h (-)***	δ ***(-)***	$\tau_{\varepsilon 20}$ ***(s)***	β ***(-)***
neat binder 1000 RPM	~0	1174	0.238	0.580	3.40	1×10^{-05}	280
0% 30 min 1000 RPM	~0	1400	0.240	0.580	3.40	1×10^{-05}	280
20% 30 min 1000 RPM	~0	1230	0.238	0.580	3.40	1×10^{-05}	280
0% 60 min 1000 RPM	~0	1400	0.236	0.580	3.40	1×10^{-05}	280
20% 60 min 1000 RPM	1×10^{-05}	1210	0.230	0.560	2.90	1.4×10^{-05}	620

The most perceptible difference among the constants was observed in the model of the binder designed with 60 min of mixing time and with contact with the plastic. Comparing the effects on the model among samples with similar heating times, it was observed that the constants did not vary significantly in samples heated for 30 min. However, samples heated for 60 min showed greater divergence in the constants.

In a detailed observation, the material conditioned for this time in contact with plastic was also the only sample that presented a G_{00} greater than 0.

In the 2s2p1d model, the values of G_{00}were estimated by extrapolating the asymptotic trend of the curves based on iterative minimization of error. For the mastercurve of samples mixed for 60 minutes, this estimation was performed without experimental data obtained from this region

of the curve. Considering this deviation, it would be relevant to adjust it using experimental measurements on this region of the curve to more accurately characterize the material response. This region corresponds to high temperatures and very low frequencies, which would require cycles with extended duration (such as 24h by cycle) under temperatures at which the material remains stable and undegraded. For the purpose of this analysis, the asymptotic behavior was inferred from the observed trend of the curve.

Considering only this constant, it would be possible to assert that at 60 minutes of conditioning with 20% plastic in the environment, this bitumen starts to show the first signs of modification. In contrast, given its magnitude (11×10^{-05} MPa), it is possible to assume that this modification is not strong, and not sufficient to reach the plastic compatibility.

Regarding G_0, it was observed that this constant increase in all samples when compared to the neat bitumen. However, this variation was less pronounced in the two materials heated with plastic when compared to the control samples. Two assumptions could be formulated based on that. Firstly, associating the increment of this constant to the oxidative effect promoted by the conditioning temperature, it would be possible to suggest that the presence of the plastic could act retarding the aging of the material. In a second perspective, this observation could also be related to a decrease of stiffness at lower temperatures.

Although identifying the phenomenon that leads to this result is not the focus of this analysis, it is possible to assume that at lower temperatures the two binders that interacted with the plastic tend to present lower stiffness, which is favorable to avoid failure by cracking. In a further evaluation, this observation eliminates the hypothesis that there is no effect of the binder after 20 minutes. However, the magnitude of this effect does not reflect in a strong impact in the performance of this material.

Regarding the analysis of the other constants, it was observed a variation on δ in the last sample. However, k and h kept approximated constant values. This effect illustrates a slight modification in the viscoelastic response of this sample simultaneously to little modification of the viscous aspects. In parallel, a change was also observed in β. The change in this last parameter seems to be connected to the elastic recuperation incorporated into the mechanical behavior of this binder.

5.6.2 Adherence of the model

For asserting the reliability of this model and of the parameters calculated for each sample an adherence test was proceeded to verify the level of fitting between the experimental data and the modelized data in similar frequencies. For that purpose, values of |G*| and φ were extracted from the experimental master curve and from 2S2P1D model.

The fitting test followed two procedures. The first procedure was the test of adherence between the target value (experimental) and the calculated value (model). In this phase the quadratic variation in each point was calculated followed by a measure of the coefficient of determination (R^2) of this error. After that, a test of normality of the residues was carried out to observe if they followed an aleatory tendency. These two procedures allow the investigation whether the errors are distributed along all the model or in a particular area. Figure 5-24 presents the graphs of comparison between the experimental values and the model for the materials tested during this campaign. The R^2 calculated are presented in Table 5-3.

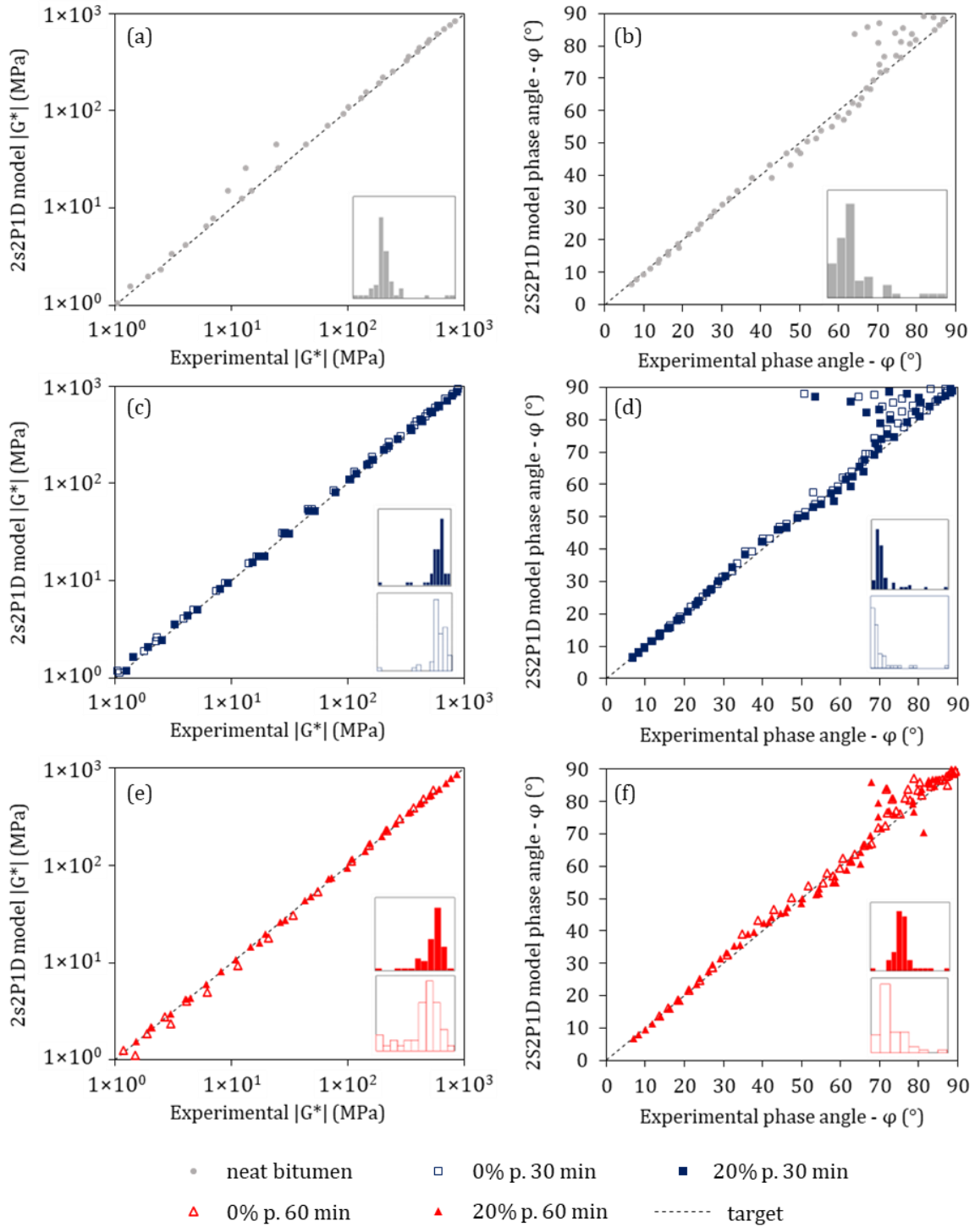


Figure 5-24 – Analysis of adherence of 2S2P1D model to experimental data of |G*| and φ. (a) analysis of neat binder - |G*|. (b) analysis of neat binder – φ. (c) analysis of binders conditioned for 30 min - |G*|. (d) analysis of binders conditioned for 30 min – φ. (e) analysis of binders conditioned for 60 min - |G*|. (f) analysis of binders conditioned for 60 min – φ.

Table 5-3 – coefficient of determination of adherence test (bituminous binders)

	R^2	
	|G*|	**φ**
neat bitumen	0.996	0.954
0% p. 30 min	0.996	0.918
20% p. 30 min	0.998	0.927
0% p. 60 min	0.991	0.978
20% p. 60 min	0.998	0.973

In a comparative analysis of the data and of the graphs from Figure 5-24, the most dispersed points were located in the graphs of φ in angles above 70 degrees. In fact, in these samples the residues presented a lower tendency of following a normal distribution. The dispersed points coincide with lower frequencies, revealing a trend of this material at high temperatures.

Among all samples the R^2 was above 0.90, which indicates that the model is more than 90% reliable to all samples. Based on that it is possible to estimate that the constants calculated are led to a shape of curve that fits well to the experimental data and gives a good understanding of the behavior of these materials. It was also possible to confirm that the model can be used with samples that interact with plastic without a procedure of modification.

5.7 Final considerations about the blending procedure

When included as base materials in a mixture designed by a dry process, the plastic and the binder are heated and are mixed with the aggregates in the same mixing tank. During this process it is not possible to control whether the two will get in contact or not. Within the scope of Campaign 1 and Campaign 2 the effects of a rapid interaction between these materials in the same mixing temperature of an HMA were investigated in laboratory conditions using a HSM apparatus.

It is important to highlight that the objective of these two first campaigns was not properly to modify the binder but investigate if this was a phenomenon to be considered under the mixing conditions commonly found in construction projects. In the scope of these campaigns, the effects of this interaction and possible modifications were evaluated from the viewpoint of three variables: the heating time, the plastic proportion, and the rotation speed of the mixer.

Logically, the interaction occurs through various mechanisms and is also influenced by the scale of the equipment where the contact occurs. In the scale of a mixing tank employed in plant, for example, the exposure of the binder may be intensified, and therefore a direct correlation between this method and laboratory-scale mixing is not feasible or encouraged. However, it is still pertinent to verify which among these variables, make the rate of blending of these materials be more sensible.

5.7.1 Effects of time and rotation on blending

In the first campaign, the experimental matrix considered the different values for the three variables. Assuming the proportion of plastic is constant, the heating time and the rotation speed rest as parameters of the mixture that can be controlled and modified during its production. In the second campaign the rotation speed was also maintained constant among all samples, which led the heating time to be the singular variable parameter.

Considering firstly the heating time, the variation between 30 min and 60 min reflected in little modification, when considering the samples with plastic content of 5%. The stiffness of these materials was approximately similar, and no variation of phase angle was observed, which indicates that the viscoelastic behavior also did not change. In contrast, when the same analysis was conducted with 20% plastic, mechanical modifications were observed, as evidenced by the increase in stiffness.

However, these differences were more pronounced when isolating the heating time and comparing different rotation speeds. When testing a percentual of plastic of 5% and heating time of 60 min, a difference could be observed when varying the configuration of the mixer from 200 to 1000 RPM. This result raises a premise that for targeting a stronger blending is eventually more effective to raise the rotation speed than the time of exposure of the binder. Moving to the viewpoint of the dry process, this might indicate that even when the plastic is heated for a short period of time, a certain content might mobilize into the binder interface if the mixing tank works at a high rotation speed.

This difference was even stronger when testing the proportion of plastic of 20%. In this case, the differences were not only observed in the high temperature performance but in the viscoelastic behavior, indicating that at some proportion the content of plastic inside the binder was already able to increase the elastic aspect of the material.

5.7.2 Effects of the plastic content on blending

Concerning the interaction between plastic and binder, one difference to be considered between the wet and the dry process is the proportion between the two materials. While an optimum blend in wet process occurs when the proportion of plastic rests below 10% of the weight of binder, in a dry process this material replaces part of the aggregate content. This indicates that this proportion might exceed this limit by a significant margin, reaching around the same proportion of binder content.

In the previous analysis, it was demonstrated that the proportion of plastic is an important factor for the interaction, being eventually a key parameter that determines whether the blending will occur or not. However, from a dry mixture point of view rather than a binder-focused approach, the aggregate is present in the highest proportion, while plastic is also significantly present. Given the complex interactions among these three components, it is not possible to discard the hypothesis of plastic blending with the binder.

CHAPTER 6
RESULTS ON MIXTURES

This chapter presents the results from Campaign 3 and Campaign 4, discussing the mechanical behavior at the mixture scale. The following sections analyze the performance of the samples developed and tested during these campaigns.

6.1 Recapitulation of Campaigns 3 and 4

Completing the scope of the experimental plan, the third and the fourth campaigns comprise the tests carried out with bituminous mixtures. Both campaigns studied the mechanical behavior of mixtures, focusing on the possible effect of the presence of plastic. This chapter continues the discussion of the results obtained in this research and the approach moves to this corresponding part of the experimental plan.

All samples designed for these campaigns were constructed following the idea of Dry Process. In the third campaign, the same proportion of plastic (5 %) was tested, investigating two different techniques of Dry Process. In parallel, the fourth campaign tested the methodology of Dry Process where the plastic is incorporated as the last mixing material comparing two different proportions (2.5 and 7.5 %).

For proceeding with mechanical tests, 50 × 50 cm slabs were prepared in laboratory and then cored in laboratory (refer to section 3.5 Sample production: Mixtures). This chapter presents the observations made during procedures for preparing the slabs and choosing the specimen for test. In sequence, the raw data is discussed and the procedure for processing the data from the mechanical tests. After data processing and cleaning the mechanical outputs are presented and discussed in the perspective of the performance of the mixtures. The results reinforce the potential use of three-layer recycled plastic in road construction. Particularly, when applied following a Dry Process.

6.1.1 Discussion about mix, compaction, and extraction of specimen

The preparation of materials for the mechanical tests was carried out through a process that included mixing, compaction, and extraction of samples in the geometry of the test. This procedure is presented and detailed in the Chapter of materials. This section discusses the observations made in this process and possible problems to be solved in plant.

Regarding the workability of the plastic, the main difference to be considered is that at 150 °C this material is around its glass transition. This means that, in terms of viscosity, this material is not as fluid as the plastic and not as solid as the aggregates. Considering that, the effort required for mixing might be higher than what conventional HMA requires. In the preparation of samples for this experimental plan, it was observed that, after the insertion of the plastic, the mixer was not as efficient for mixing all the contents of the tank as when dealing only with

conventional binder and aggregates. In general, it was observed that the mixer requires more time to reach a homogeneous mix. Therefore, it is important to observe how this is reflected in plant.

Another point to observe is the compaction of the mixtures after mixing. Considering the temperature of compaction of 150 °C, it is relevant to predict that the workability can also be a problem. In a first perspective, it is important to observe that the material is correctly spread in the mold. In addition, verifying that the compaction load is applied consistently with conventional mixtures is fundamental. A feature of the plastic to be observed is that mixtures with plastic might return to the non-compacted form after the application of load. In construction, it would be relevant to calculate the percentages of load that are returned and absorbed by the sample and apply a compensation of load.

Figure 6-1 presents the density of the specimen extracted from the slabs produced in this experimental plan. The graph presents separately the Gmm, the maximum density projected of each mix.

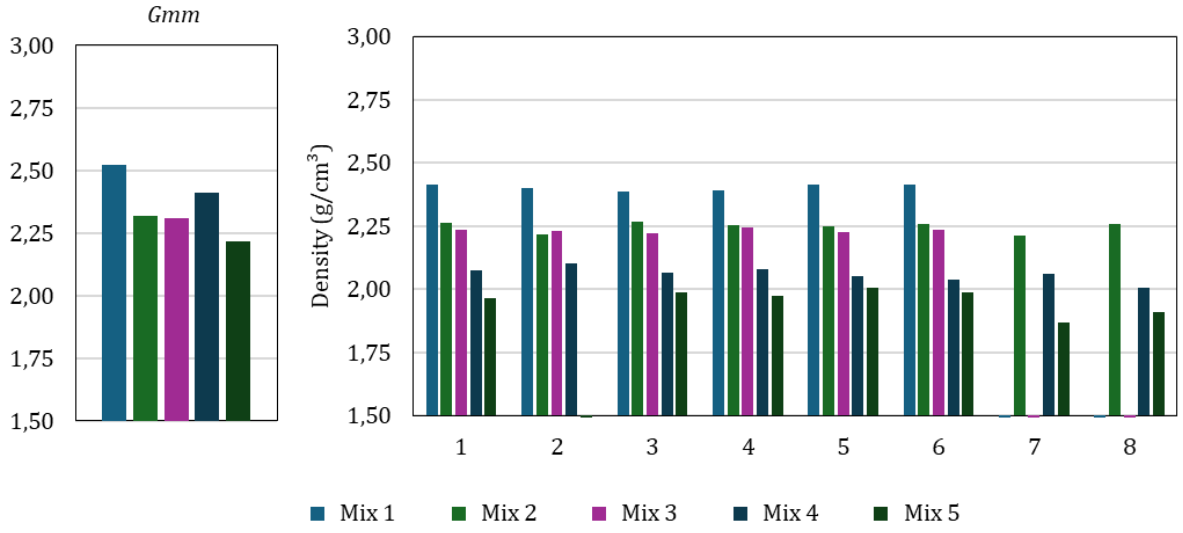


Figure 6-1 – *Gmm* and density of specimens extracted from slabs

As detailed in the Materials chapter, the coring process is carried firstly with the separation of the slab into smaller pieces from where the specimen was cored. During the separation of the pieces, some specimens presented brittle behavior, making them unsuitable for testing. These were identified and discarded to ensure the reliability of the results. In the previous graph these samples are not shown, since they were eliminated from analysis.

In relation to density, it was observed that the presence of the plastic impacted on the workability of the mixture. In some of the specimens, the density was notably lower than the Gmm, indicating that the mixture was harder to compact than the reference mixture without plastic.

6.2 Data processing point-by-point

Following the criteria of density and shape, specimens from each slab were selected and submitted to the mechanical evaluation of Complex Modulus. The setup for the test and the procedure are both detailed in the section 4.5 Thermomechanical characterization of mixtures: complex modulus tests.

As previously discussed, the Complex Modulus test was carried out under different temperatures. In each temperature, a controlled strain was applied in different process stages corresponding to increasing frequencies (from 0.003 to 10 Hz). The number of load cycles varied in function of the frequency and the duration of a cycle. For example, it was applied 4 cycles in the stage of 0.003 Hz while, for 10 Hz, the number of cycles was 50. A statistical analysis was carried out in order to determine the average from all cycles in the same stage.

All mechanical analysis was conducted using average data for each frequency. Based on that, a procedure for processing the data and eliminating outliers that would not lead to a representative statistical mean was followed. The data processing was divided into two parts. Firstly, a visual inspection, and then, a statistical analysis of the points accepted for a specific frequency.

During the visual inspection, the shape of the hysteresis cycle and the sinusoidal of application of load and displacement were individually evaluated.

In some cycles it was observed that the hysteresis cycle would not have coinciding points in the beginning and end of the cycle, or even would have a shape different from the targeted cycle. These are two examples of cycle that were disregarded from the following analysis. When it comes to the inspection of the sinusoidal signs it was also observed if they corresponded to the targeted sign. In relation to the displacement, the smoothness of the sign was observed, to guarantee there would not be a strong difference of positioning of the piston in a short interval. Similarly, the inspection of the sinusoidal of the force also considered occasional points of the curve where a force above the maximum requested for each material was reached.

Figure 6-2 presents examples of elements that were inspected parting from the specimen studied in this research. Two examples from each graph are presented, in the right a wrong example from a cycle that was rejected from the analysis and in the left an example that attended to the targeted sign. All cycles that had at least one of the examples of not corresponding graph were excluded from the statistical analysis.

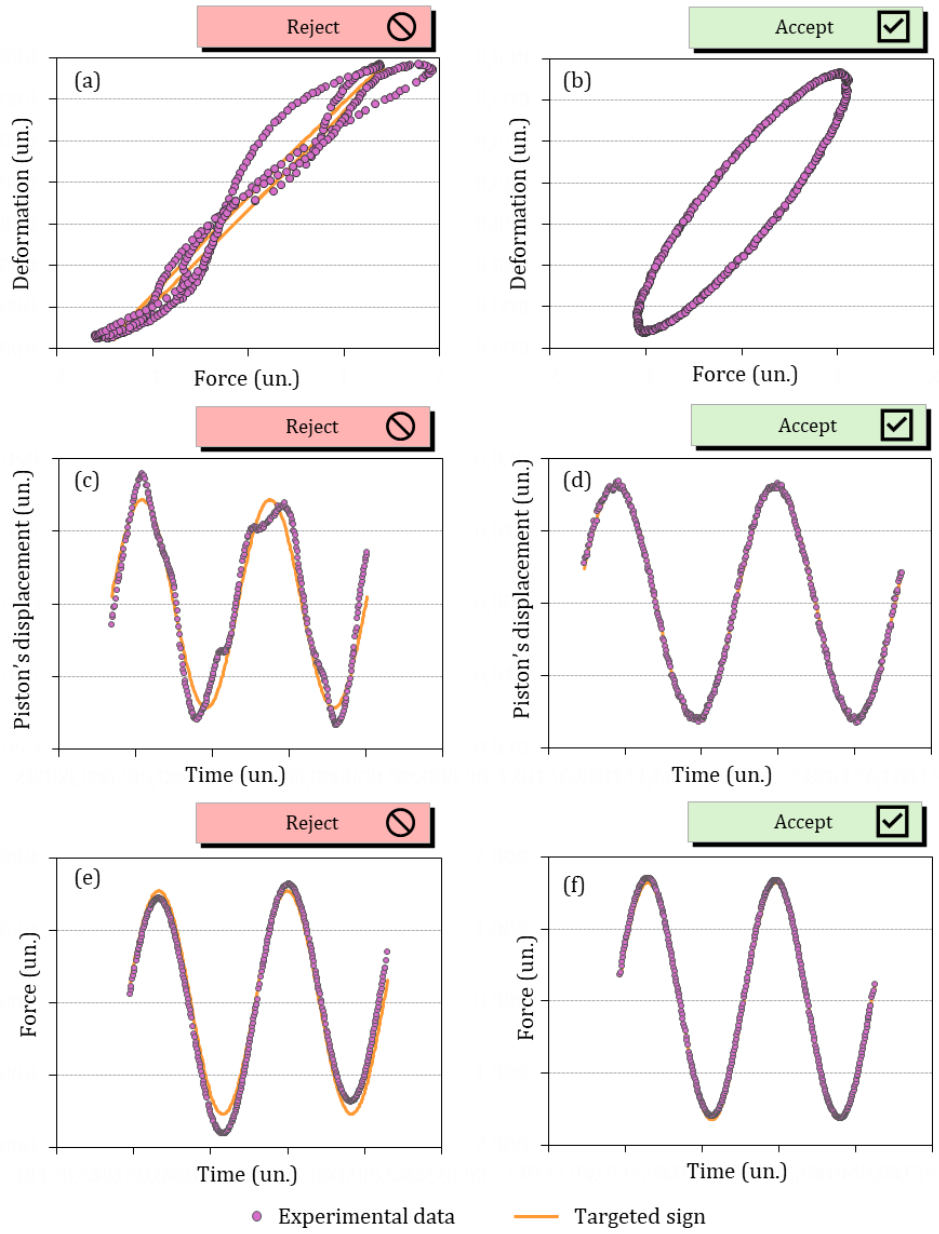


Figure 6-2 – Examples of processing for accepting points. (a) Ex. of rejected hysteresis cycle; (b) Ex. of accepted hysteresis cycle; (c) Ex. of rejected displacement sinusoidal; (d) Ex. of accepted displacement sinusoidal (e) Ex. of rejected force sinusoidal; (f) Ex. of accepted force sinusoidal

Once all data was visually inspected, all the remaining cycles were plotted, evaluating the strain amplitude, the complex modulus, and the phase angle from each cycle. All points that did not correspond to a main tendency were rejected from the calculation of the mean. In addition, starting from the stages of 0.3 Hz, the 3 first and last cycle were also automatically ignored to avoid considering in the analysis the interval of frequencies in which the equipment is adapting

the sinusoidal shape. After that, the arithmetic means of all outputs were calculated and referred in further analysis in this research.

6.3 Mechanical Analysis – Campaign 3

This section presents results obtained from Campaign 3. Firstly, details on the mechanical outputs of specimen after their extraction are introduced. For each slab, two specimens were selected based on their density, surface, and form. Each specimen was submitted to the mechanical procedure described in the Chapter of Method.

The following subsections detail the analysis of the mechanical tests. Firstly, the criteria for processing and pre-analyzing the outputs of the tests are explained. In sequence, the isotherms are adjusted in a master curve relative to the reference temperature of 15 °C. Lastly, the mechanical characterization of the samples is compared focusing on their evolution of stiffness and viscoelastic behavior. The procedure used for preparation of each material in Campaign 3 was discussed as the main parameter to be observed in this section.

6.3.1 Reference Mix (Mix 1 – without plastic)

From the cored samples, specimen 1 and 6 were selected for the mechanical analysis. The two specimen present similar density, which can be relevant to avoid dispersion of results between the two analyses.

Figure 6-3 shows the disposition of the output of the two samples after processing and cleaning disposed in a Cole & Cole plot and in a Black Diagram. The points are individually presented by tested temperature.

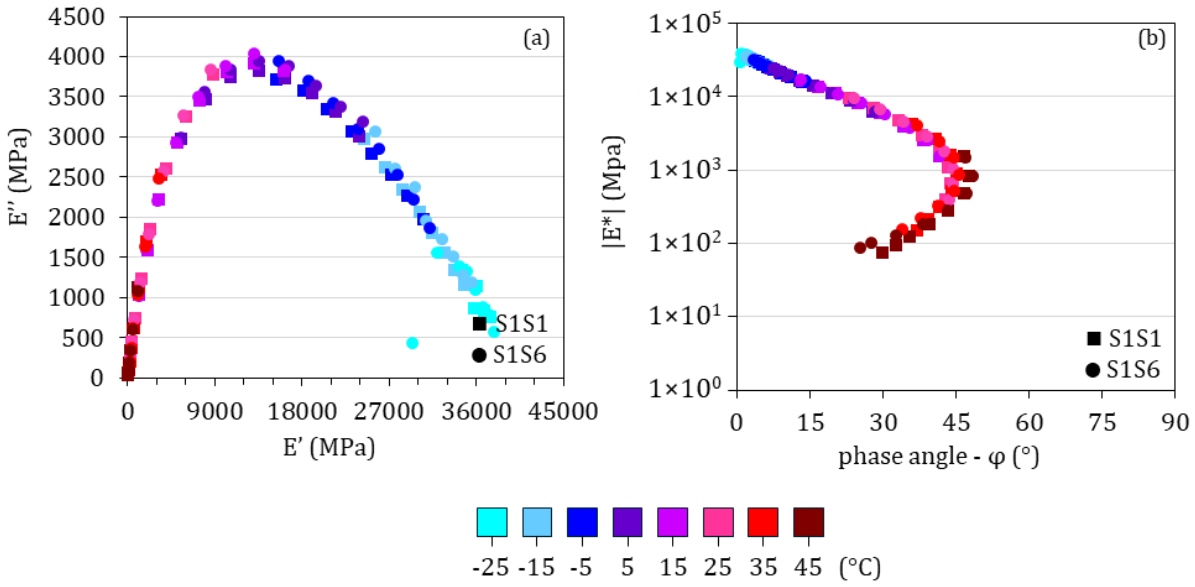


Figure 6-3 – Dispersion of the cleaned data of mechanical tests by specimen - Slab 1 (reference). (a) Cole & Cole plot. (b) Black Diagram of Complex Modulus (|E*|)

It is possible to observe by the disposition of the points that the test is reproductible, and that the form of the curves in the Cole & Cole plot and in the Black Diagram reflect the same behavior. The Cole & Cole plot presents the relation between the real part and the imaginary part of the complex modulus. In the asymptote it is possible to observe that the maximum value of the loss modulus (E'') is placed around 4000 MPa. This value will be used as reference for the next analysis of the Cole & Cole plot.

The mechanical performance in higher temperatures can be better observed in the Black Diagram of the complex modulus. In this Diagram it is possible to observe that, in tests performed around 35 and 45 °C, the sample reaches its maximum phase angle, which is placed in around 45-degree. After that, the phase angle tends to decrease due to the elastic behavior of the aggregate skeleton.

The master curves were plotted based on the shift factors calculated for shifting the isotherms of complex modulus (|E*|) to the reference temperature of 15 °C. Figure 6-4 shows the shift factors and the WLF curves calculated for the interval of temperatures of this test. The constants C_1 and C_2 from the WLF model are presented in Table 6-1.

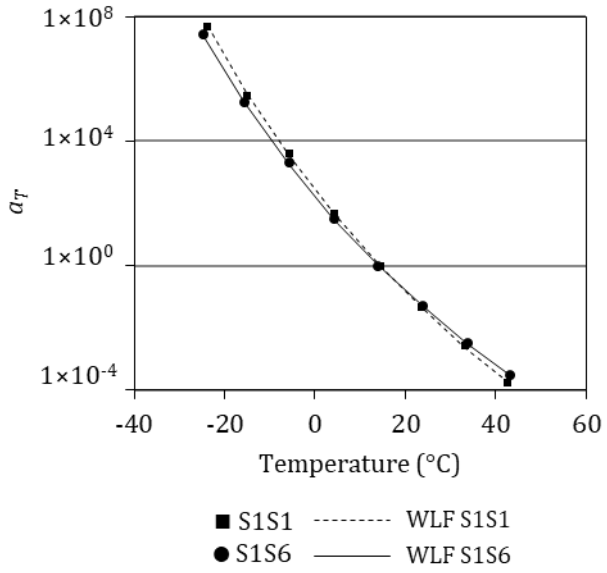


Figure 6-4 – Shift factors and WLF curves of specimen tested from Slab 1 (reference)

Table 6-1 - Constants C_1 and C_2 obtained from mixtures without plastic

Material	C_1 **(-)**	C_2 **(°C)**
MIX 1 - 0 % p. (S1S1)	25.40	163.98
MIX 1 - 0 % p. (S1S6)	22.37	155.84
Average Mix 1	23.26	155.72

From the analysis of shift factors, it was observed a dispersion in both extremities, relative to the temperatures of -25 and 45 °C. Since the disposition of the aggregate skeleton might vary due to the position of the specimen in the slab and the disposition of the aggregates, a small divergence between the two materials is already expected. However, it is not possible to say that the two specimens reflect the behavior of the same material.

The data from the two samples was plotted into the two master curves and presented in Figure 6-5. The graphs present curves of complex modulus and phase angle of each material plotted for T_{ref} = 15 °C, separately by temperature. In addition, 2S2P1D models of the curves are presented in the graphs. The parameters for elaboration of this model will be further discussed later in this chapter.

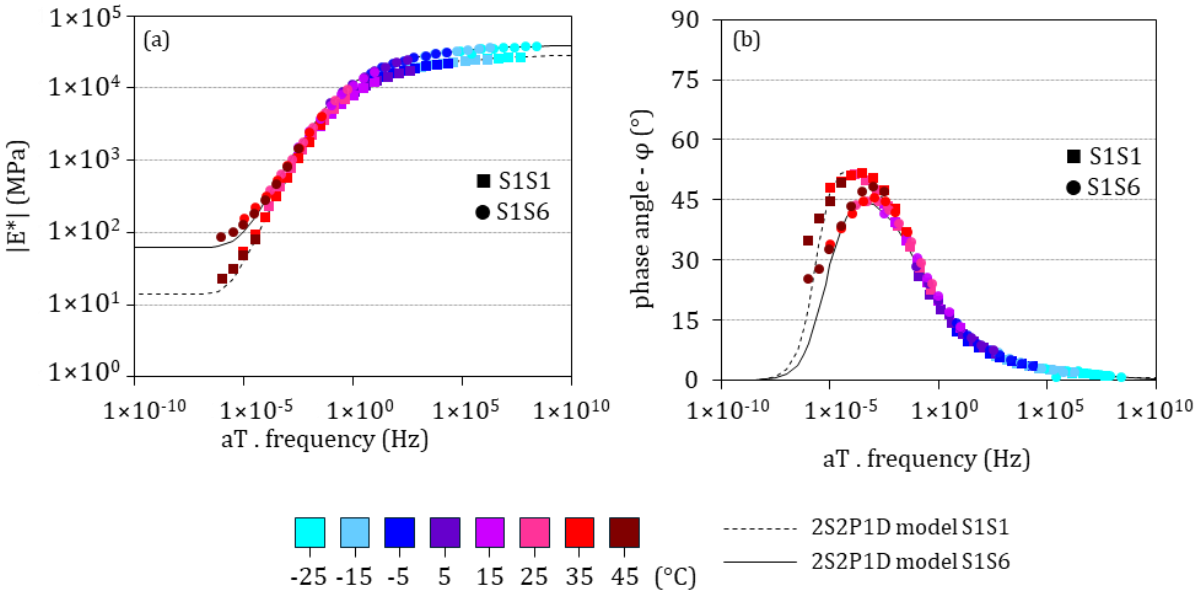


Figure 6-5 – Master curves of specimen tested from reference Mix (1) showing temperatures individually (T_{ref} = 15 °C)

The master curves of |E*| reflect in an increased stiffness of Specimen 6, noticeable in the two extremities of the graph. These areas refer to the lower and higher temperatures of the procedure. In the frequencies that refer to the temperature of 45 °C it was possible to observe a higher difference of |E*|. At this temperature, the Specimen 6 presented a clear stiffer behavior in comparison to Specimen 1.

Regarding the phase angle, it was also possible to note a deviation between the evolution of the two curves in lower frequencies. This indicates that at high temperatures the two specimens might perform differently in relation to the viscoelastic behavior.

Taking into account that the two samples passed through a control of oxidation and integrity of the specimen at 15 °C at the end of the test, it is possible to infer the two results reflect different internal organization of the aggregate skeleton of the same material. For effects of comparison, an average of the data obtained in each frequency and each isotherm was calculated and new master curves were plotted with intermediate shift factors. This average curve was then set as reference for the mix without plastic in the analysis of the mixes prepared with plastic in its composition.

6.3.2 Mix with 5% Plastic on top of Reference Mix (Mix 2)

For performing the mechanical tests with mix 2, specimen 4 and specimen 5 were selected for analysis. Figure 6-6 presents the distribution of the points separated by temperature in a Cole & Cole plot and in a Black Diagram.

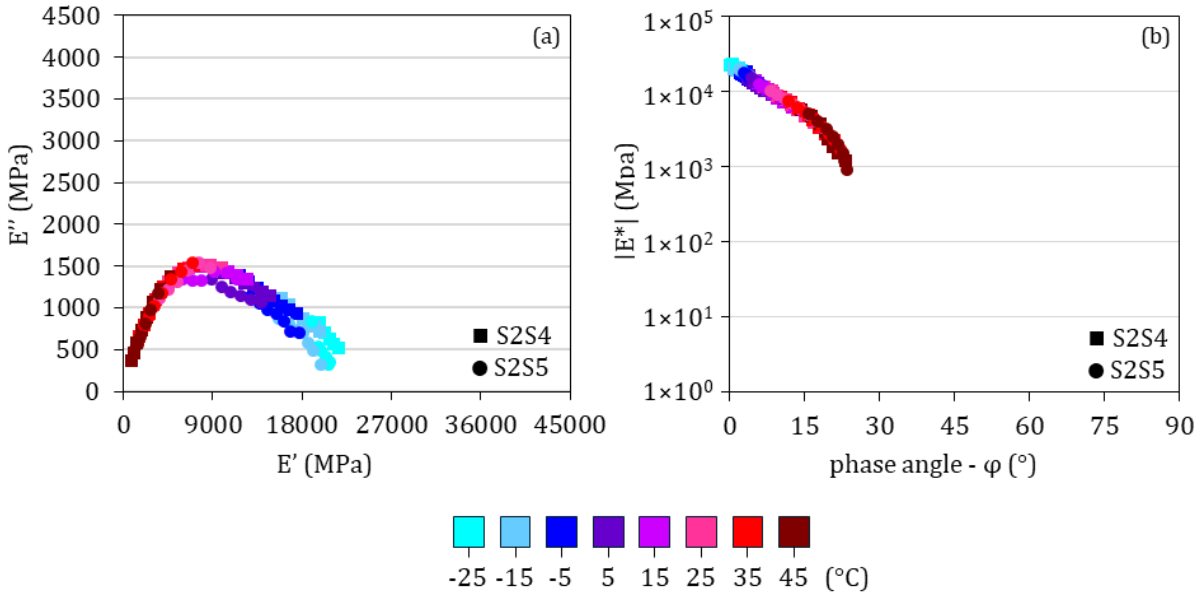


Figure 6-6 - Dispersion of the cleaned data of mechanical tests by specimen - Slab 2 (5% plastic on top). (a) Cole & Cole plot. (b) Black Diagram of Complex Modulus (|E*|)

The Cole & Cole plan (Figure 6-6a) presents the relation between the real and the imaginary part of the complex modulus (|E*|). In this graph, the scale was maintained the same as the one used in the analysis of the reference mix. It is possible to observe that the evolution of the asymptote was placed in a lower position in relation to mix 1. In mx 2 the maximum E'' in both graphs was closer to the level of 1500 MPa, compared to 4000 MPa observed in the reference mix.

Regarding the Black Diagram, it is possible to notice that the maximum phase angle of the curve did not surpass the level of 30-degree. Also, the elastic effect observed in mixtures at elevated temperatures was not reached under the interval of temperatures performed in the test.

Following the procedure of analysis arranged for the reference mix, Figure 6-7 shows the shift factors and the WLF curves calculated for the interval of temperatures of this test. The master curves were plotted in a reference temperature of 15 °C. The WLF curve of the average performance obtained from mix 1 is also presented. Since this material refers to a virtual

analysis and not from experimental data, the use of the model was limited for the reference in the evaluation of materials composed of plastic. The constants C_1 and C_2 from the WLF curve are presented in Table 6-2.

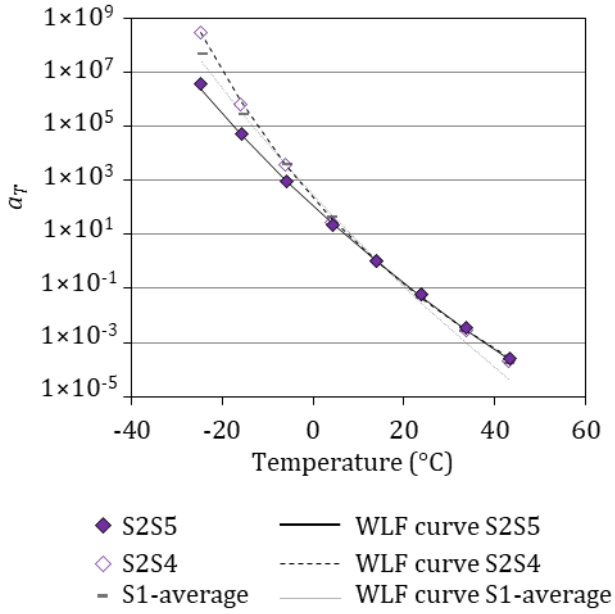


Figure 6-7 – Shift factors and WLF curves of specimen tested from Slab 2 (5% plastic on top)

Table 6-2 – Constants C_1 and C_2 obtained from mixtures with 5% plastic obtained from tests with slab 2

Material	***C_1 (-)***	***C_2 (°C)***
Average Mix 1	23.26	155.72
MIX 2 - 5 % p. (S2S5)	34.87	250.55
MIX 2 - 5 % p. (S2S4)	45.64	296.29

In general, a strong disparity was observed between the two specimens regarding their shift factors. In particular, in lower temperatures the WLF curves presented a trend of increases separation as they separate. From the constants C_1 and C_2, it is possible to infer a stronger temperature sensitivity in the samples with plastic, revealed by an average greater slope of the curve (C_1). At a preliminary analysis, it is possible to infer a lower reproducibility of behavior of the specimen extracted from the same slab, reflecting a stronger heterogeneity among the distribution of the aggregates.

Figure 6-8 shows the master curves of complex modulus (|E*|) and phase angle (φ) for each specimen plotted from the calculation of the shift factors. It is also presented the master curve of the average mechanical behavior of mix 1.

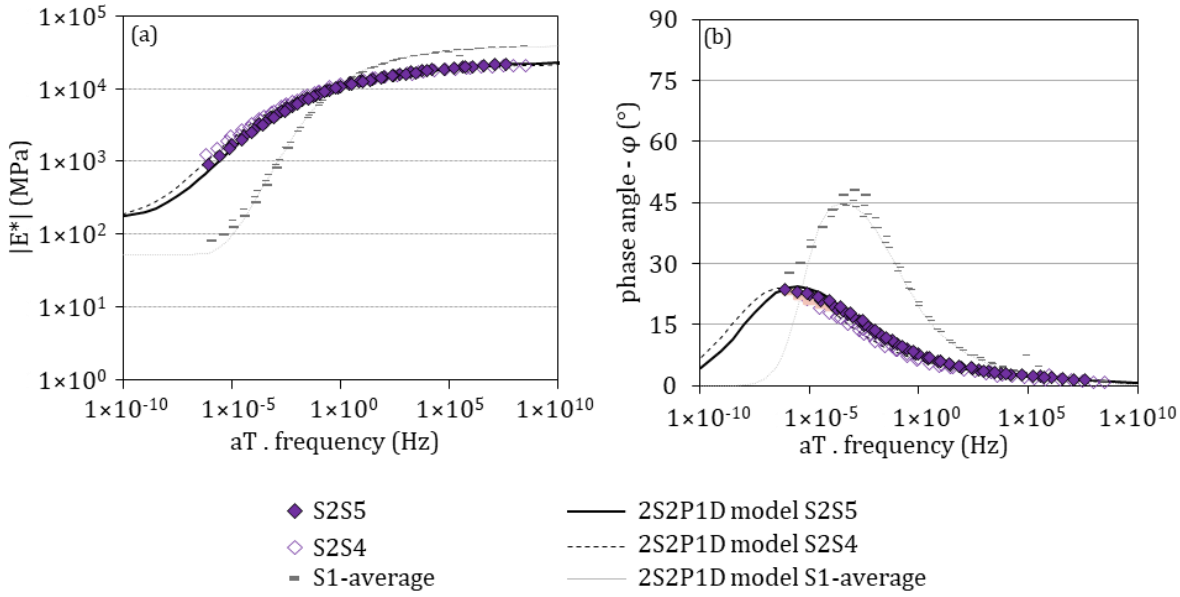


Figure 6-8 - Master curves of specimen tested from Slab 2 (5% plastic on top) and average of specimen tested from Slab 1 (reference) (T_{ref} = 15 °C)

In the first analysis, it was noticed a strong increment of the stiffness in the region of lower frequencies. This observation indicates that at higher temperatures, the mixture that incorporated the plastic reveals an increased stiffness and demonstrates an improvement of performances. In contrast, it can also be observed that, at lower temperatures (higher frequencies), the mix performs with a lower |E*|, consequently presenting a lower stiffness.

Regarding the phase angle, the specimens from mix 2 presented a different behavior, pending to a reduction of the phase angle in almost all frequencies. It can be inferred from this observation that the viscoelastic behavior of the material has shifted towards a more elastic response. This is consistent with the inherent properties of the polymers that compound the base plastic used for the production of the mixes.

However, it is relevant to highlight that in the idealization of the Dry Method, the plastic should perform like an aggregate without changing the chemical composition of the bituminous binder and/or its mechanical behavior. It is possible that these alterations observed in the curves refer to a partial mobilization of the plastic into the binder in the mixture process.

In terms of performance, it is possible to conclude that the insertion of 5% plastic in plant would be a possible alternative for improving the performance of mixtures at high temperatures without the necessity to resort to a PMB.

6.3.3 Mix with 5% plastic with compensated aggregate structure (Mix 3)

For performing the mechanical tests with mix 3, two specimens (located in the positions 1 and 4 of the coring plan) were selected for analysis. Figure 6-9 presents the distribution of the points separated by temperature in a Cole & Cole plot and in a Black Diagram.

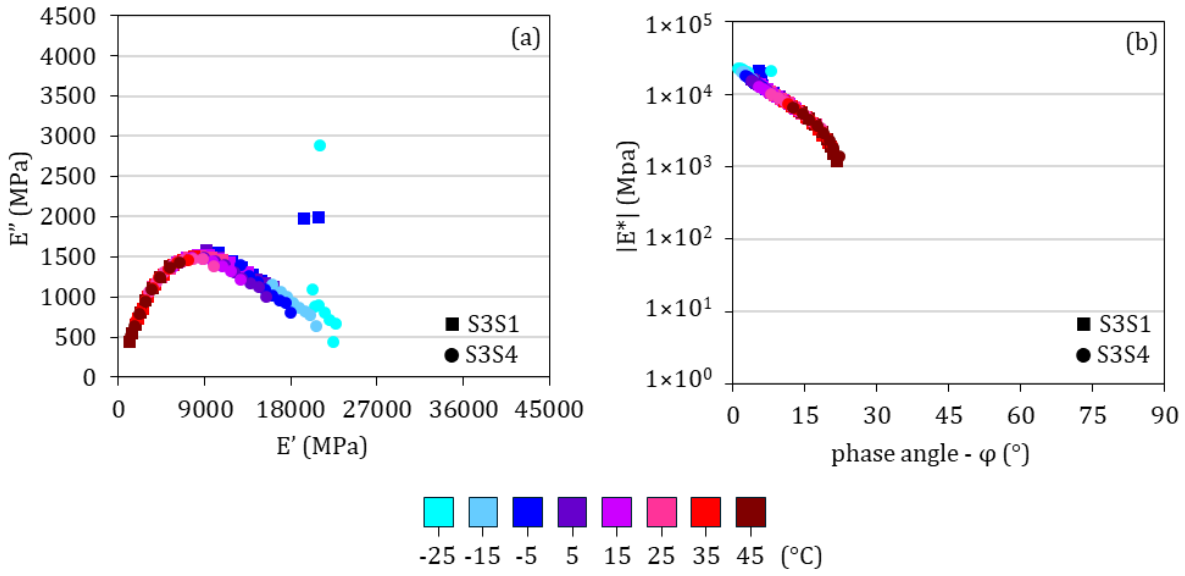


Figure 6-9 - Dispersion of the cleaned data of mechanical tests by specimen - Slab 3 (5% plastic in compensation of granulometry). (a) Cole & Cole plot. (b) Black Diagram of Complex Modulus (|E*|)

Similar to what was observed in mix 2, the analysis of mix 3 indicates an alteration of behavior in relation to the reference mix. In fact, although the two mixes were prepared with a different granulometry and different duration of heating of the plastic in the production, it was observed an approximate alteration of behavior. At very low temperatures (-15 °C and -25 °C), a few outliers remain visible above the general trend, even after the data cleaning procedure. These scattered points suggest a distortion in the loss modulus that could not be completely removed during processing. One possible explanation is the presence of ice on the extensometers during some tests, which may have influenced the measurements at these extreme conditions.

The Cole & Cole plot presented its peak in the same order of magnitude of the curve from mix 2. However, it is possible to observe that the two specimens tested from mix 3 presented more approximated curves. It is also important to remark that some points were dispersed in the plot out of the curve. For the calculation of the 2S2P1D model, these points will be considered as outliers.

Regarding the Black Diagram, the behavior was also similar to what was obtained in the analysis of mix 2. One point of attention that is possible to elaborate from the two samples is that the material seems to retard its peak of phase angle as one effect of the contact with the plastic.

It is normally expected that, when tested across different temperatures, unmodified mixtures exhibit a drop in phase angle after reaching a peak. This behavior is associated with increased relative participation of aggregates, which are less sensitive to thermal effects, to the overall behavior of the material, therefore making elastic behavior more prominent. However, no drop in the phase angle was observed in the Black Diagram for the mixture with plastic. The variations in void content make it difficult to clearly isolate and describe the effect of the addition of plastic on the behavior in the low-frequency range.

Understanding this effect would require a detailed experimental characterization of the plastic itself, considering its composition, the heterogeneity of polymers and the presence of non-polymeric components (aluminum and cellulose fibers), which was not possible in the time framework of this study.

Giving continuation to the analysis, Figure 6-10 shows the shift factors calculated for the two specimens in function of the temperature. The constants C_1 and C_2 from the WLF curve are presented in Table 6-3.

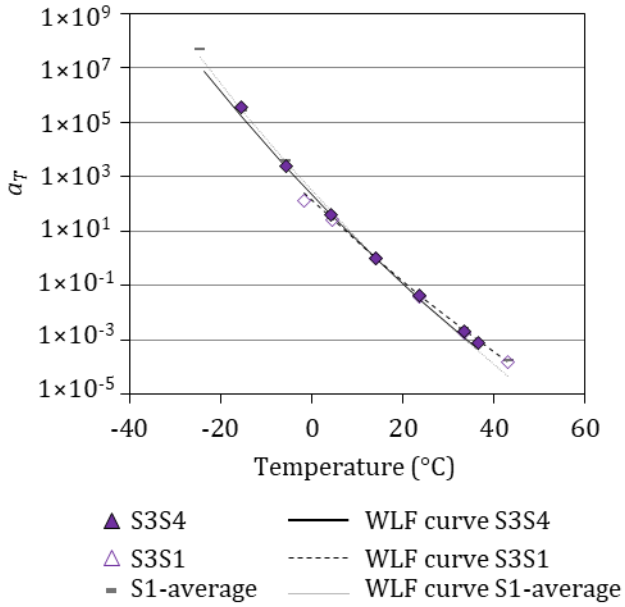


Figure 6-10 - Shift factors and WLF curves of specimen tested from Slab 3 (5% plastic with compensation of granulometry)

Table 6-3 – Constants C_1 and C_2 obtained from mixtures with 5% plastic obtained from tests with slab 3

Material	***C_1 (-)***	***C_2 (°C)***
Average Mix 1	23.26	155.72
MIX 3 - 5 % p. (S3S1)	43.40	299.59
MIX 3 - 5 % p. (S3S4)	48.34	304.52

In relation to the shift factors, it is possible to observe that the points and the WLF curves are almost superposed. In relation to mix 2, this indicates a better consistency of distribution of the material along the slab. It is important to note that the two curves were approximately similar to the virtual WLF curve calculated for the average behavior of mix 1. In a parallel analysis, it is possible to observe that the constants C_1 and C_2 vary in a similar magnitude when compared to samples from the Mix 2. As a consequence, this also suggests similar time sensitivity to this material. The master curves of complex modulus (|E*|) and phase angle (φ) for each specimen plotted from the calculation of the shift factors are presented in Figure 6-11.

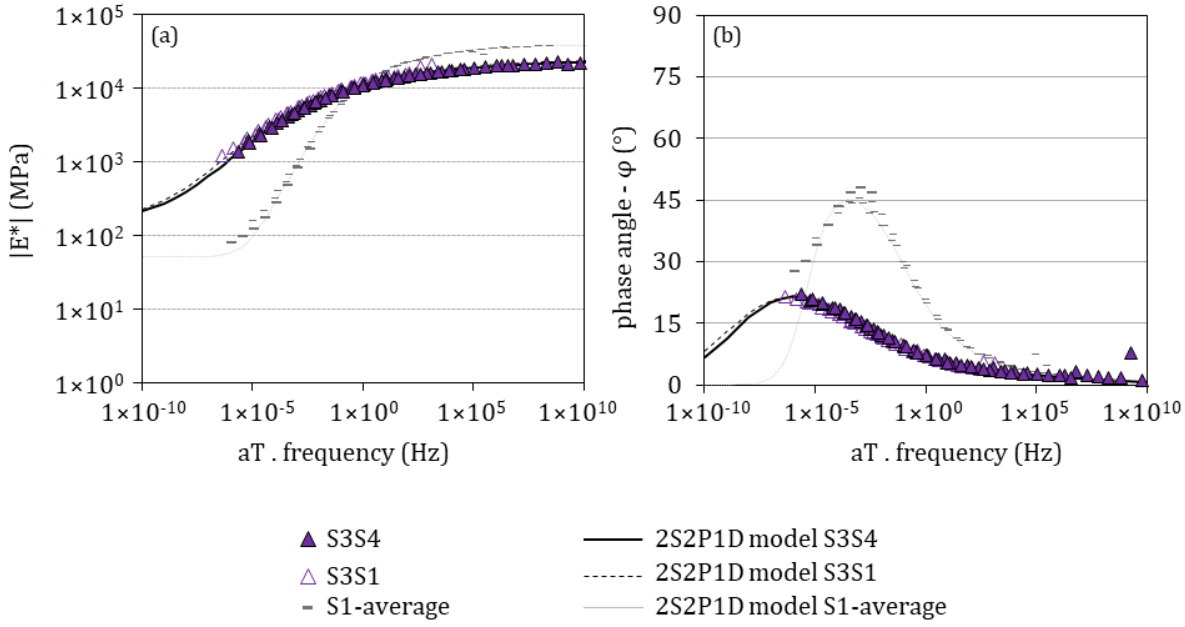


Figure 6-11 - Master curves of specimen tested from Slab 3 (5% plastic with compensation of granulometry) and average of specimen tested from Slab 1 (reference) (T_{ref} = 15 °C)

In both graphs, the two master curves presented very similar form, reinforcing the consistency of data between the two tested specimen. As it was observed in the samples from mix 2, the presence of the plastic changed the behavior of the plastic moving the curves towards a shape that reflects the improvement of the elastic portion of the material.

For this analysis, it is valuable to consider that mix 3 was projected to reproduce the same granular structure of the reference material (mix 1). Ignoring the eventual change of form and shape that the heating might cause in the plastic, it is possible to affirm that the two materials part from the same granulometry and the same binder content. Based on that, it is clear that the mechanical behavior of the plastic is partially incorporated into the mixture.

Another important factor to bring to the analysis is the fact that the plastic was inserted as last material in the mixer, leading to a heating time of only 5 minutes in contrast to the 15 minutes performed in mix 2. Therefore, even a short time of heating effort was enough to bring out the elastic behavior of the plastic to the performance of the samples.

This would be a relevant and relatively accessible solution for improving the performance of wearing courses at elevated temperatures with a low cost. Especially mentioning the regions that deal often with problems of rutting.

6.4 Discussion about how to implement the Dry Method

During Campaign 3, two different methods of Dry Process were investigated. Regarding the inclusion of the waste plastic, it is possible to say that the two methods are opposite among them.

In Mix 2, this material was inserted in the mix tank with the coarse aggregates in the beginning of the process. Considering the total time of handling the raw mixture and moving between the tank and the oven the accounted heating time for the plastic during this procedure is between 25 and 30 minutes. In contrast, during mix 3, the plastic was incorporated at the end of the process, accounting for only 5 minutes of heating.

In relation to the workability, it was observed that the inclusion of the plastic at the beginning of the mixture leads rapidly to a stiffer mix. This characteristic made it more difficult to properly mix the other base materials, including the filler, which was incorporated after the bituminous binder in the mixing procedure. In this perspective, thinking of the application of this technique in the field, an improvement of the mixing tank should be considered.

When it comes to the mechanism of incorporation, a longer heating period might melt the particles of plastic and can be favorable to a stronger interaction plastic-binder. If a compatibility is reached during this process, it would be possible to achieve increment of performance in high temperatures, as observed in mixtures designed with PMBs. Another point is the possibility of this material perform as a coat in the surface of the aggregates, increasing the adhesivity of the aggregates, such as in the methodologies that included a pre-heating of the polymers (Agha et al., 2023; Pasetto et al., 2022; Radeef et al., 2021). On the other hand, the aggregate structure is more easily preserved when including the plastic in the end of the process.

Considering that and in view of the mechanical behaviour, Figure 6-12 shows the master curves of the samples from mix 2 and 3 compared and in a detail. Although the two mixtures were designed with different methodologies, it was observed that both presented shape of curve very similar.

The previous section discussed as in high temperatures, both mixtures presented a more elevated complex modulus when compared to the reference mix. In fact, the two methodologies presented improvements in high temperature. The analysis in comparison showed that the improvement is similar in both conditions of mixture.

In the analysis of the master curves the most evidence of difference between the two materials was observed in the extremities of lower frequencies, which is linked to the higher temperatures. To observe these differences in detail, the isotherm curves of |G*| and φ were evaluated and presented in Figure 6-12 (c and d).

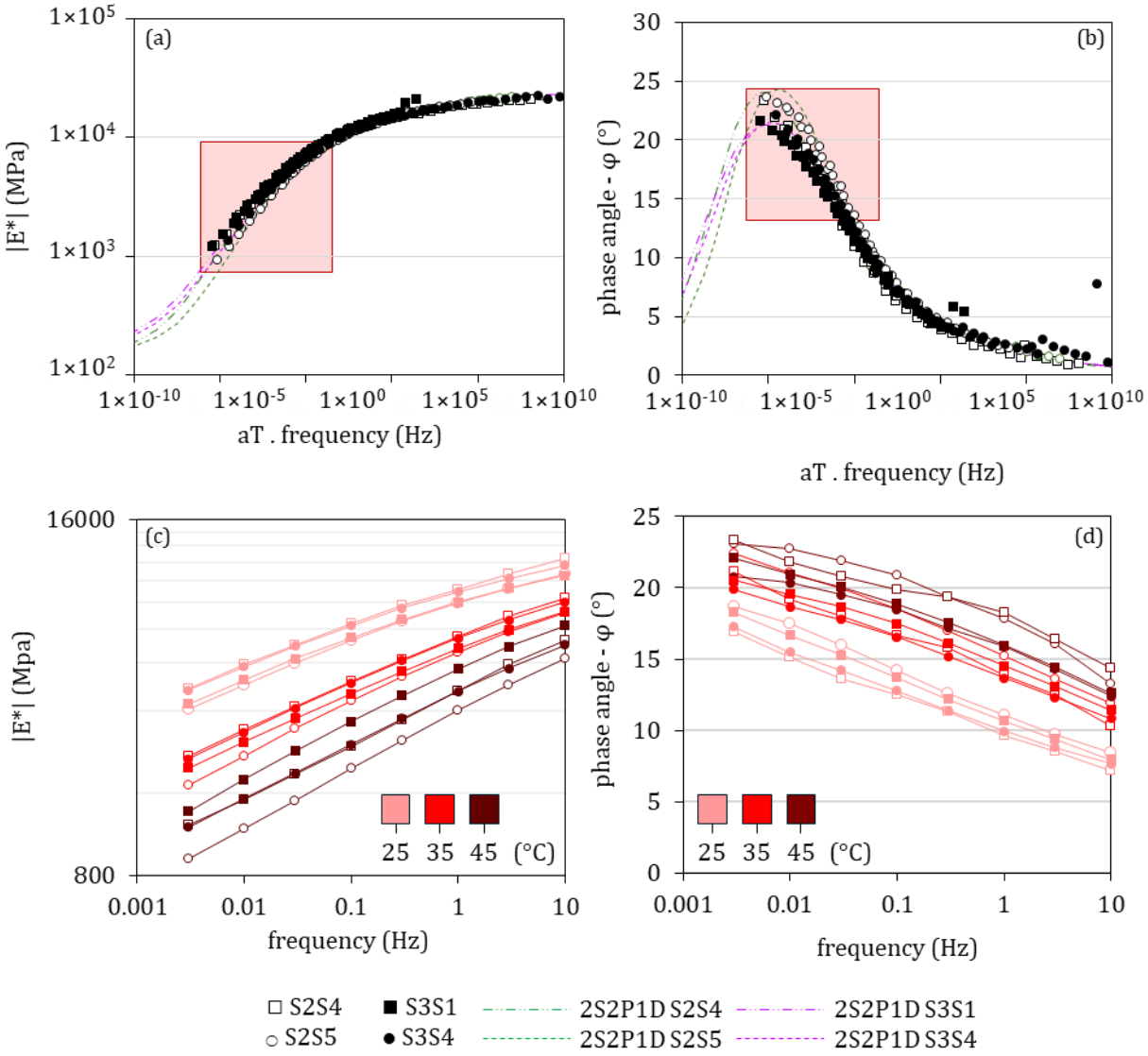


Figure 6-12 – Comparison of master curves and isotherms of mix 2 and 3. (a) master curves of |G*| (T_{ref} = 15 °C) with detail in high temperatures. (b) master curves of φ (T_{ref} = 15 °C) with detail in high temperatures. (c) Isotherm curves of |G*| at 25, 35 and 45 °C. (d) Isotherm curves of φ at 25, 35 and 45 °C.

The analysis of the isotherms does not allow to establish a strong divergence between the two mixes. However, it is possible to observe that in the highest temperature (45 °C) the samples from mix 3 tends to present a stiffer behavior, evidenced by the average higher complex moduli.

At the same temperature, the isotherms of φ indicate a more elastic aspect of mix 3. Although this does not confirm that the two mixtures are different materials, it is relevant to observe that it led to a difference on the prolongation of the 2s2p1d model curves. This indicates that following the model implicates as well consider a stiffer and more elastic behaviour of mix 3 in temperatures around 45 °C and higher.

Although mechanically there is a possibility that the two methodologies lead to the same type of mixture, a reflection can be made about the workability of the two methods. Incorporate the waste plastic in the end of the mixing process was a methodology easier to implement and lead consistently to a similar stiffness of incorporating in the beginning.

This methodology allowed achieving benefits expected from PMBs using a dry process and consequently employing more recycled material. Seemingly, this was confirmed when using a key proportion of 5% by weight of mixture. The workability of the mixture might also vary in function of the amount of plastic that is incorporated into it.

6.5 Mechanical Analysis – Campaign 4

This section discusses the outputs obtained in campaign 4. The results presented in this section are also linked to results obtained in Campaign 3. Based on that results from that part of the experimental plan will be mentioned when necessary to comment results.

The proportions of waste plastic studied in this campaign were different from what is most frequently observed in experimental plans that assumed dry process. In this campaign, a greater and a lower proportion of plastic (7.5 and 2.5 %) were submitted to test aiming to verify the influence of the plastic content on the mechanical behavior.

Taking that into perspective, some particularities of this composition must be highlighted. In first place, it is possible to mention the influence of the plastic in the composition of the gradation curve. In this campaign all granulometries were compensated in order to correspond to the same targeted curve. However, this compensation only works if the hypothesis of the dry process is confirmed.

The analysis of composition indicates that this waste plastic is composed mainly of derivates of LDPE and HDPE. As observed in the literature, these polymers could perform in both dry and wet processes, due to its melting point and glassy transition around the temperatures of production of the mixture (Cardoso et al., 2023; Duarte & Faxina, 2021; Xu et al., 2021). In fact, the characterization of the plastic has also shown that two reactions two endothermic reactions occur first around 103 °C and then around 124 °C.

During the preparation of these materials, the plastic was incorporated as the last material among the aggregates, aiming to decrease the possibility of loss of materials. However, a mixing time of 5 minutes was still included aiming to guarantee the distribution of the aggregates inside the mixture.

If the hypothesis of dry process is ignored, the resulting mixture would have an aggregate skeleton composed only by mineral aggregate and a higher binder content due to the mobilization of polymer. This assumption would impact directly the behavior of the mixtures knowing that they are linked to the gradation curve. Figure 6-13 presents the gradation curve of the samples studied in this campaign in two opposing scenarios, the first admitting dry process and the second admitting mobilization of all plastic content into the binder.

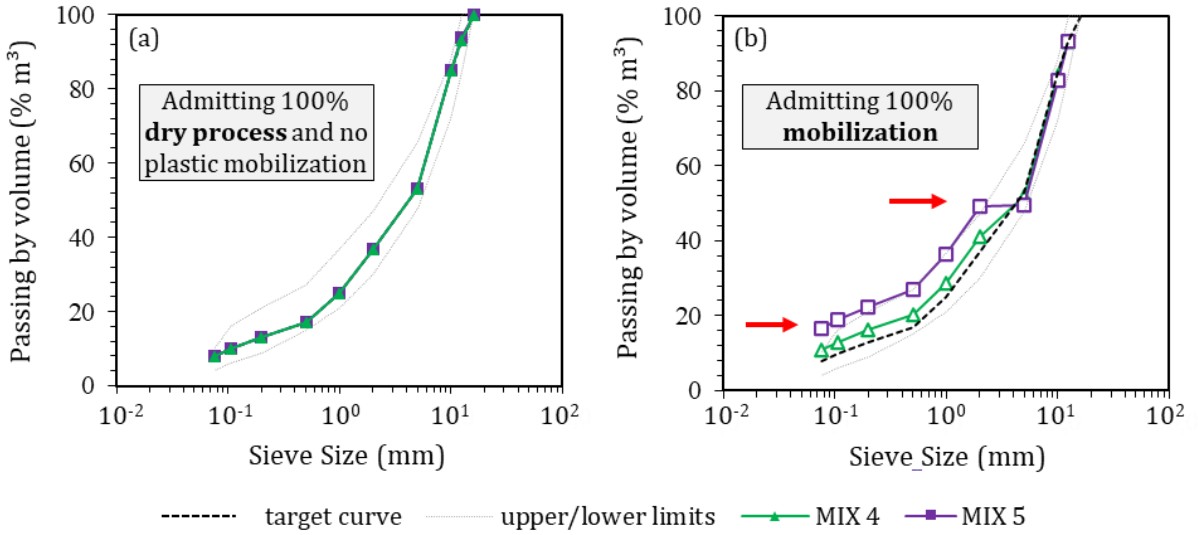


Figure 6-13 – effects of plastic melting in granulometry. (a) admitting dry process. (b) admitting mobilization

Taking as an example the gradation of Mix 5, produced with 7.5 % plastic, the second assumption would result in a granulometry curve placed out of the limits, which would correspond to a poor performance of the mixture. Observing from the other side, a total mobilization of the plastic would naturally result in increased stiffness in some temperatures, which would be beneficial to the pavement.

In campaign 3 it was observed that heating the plastic for longer periods would not affect negatively the mixture. In comparison, this would indeed result in similar mechanical behavior. However, it must be noted that these tests were performed with a plastic content of 5% by weight of mixture which was already demonstrated to be a safe content for this type of mixture.

Another factor that must be considered when working with greater proportions of plastic such as that used in Mix 5 is the workability. During the production of this group of samples it was observed that there was a greater resistance of the mixture to the compaction load, which was not observed in the other samples. It is possible that the presence of plastic resulted in an elastic behavior even under high temperature, resulting in some areas of the slab returning to the rest position after the application of load. Figure 6-14 illustrates the surface of the slab showing an asymmetrical compaction.



Figure 6-14 – Example of asymmetric compaction obtained in Mix 5

In parallel it was observed that the average volume of voids in this material was 12% when compared to the theoretical Gmm. This value stayed around 3% in all samples produced with 5% plastic. However, the slab designed with 2.5 % plastic also presented higher volume of voids. Considering as only variable the plastic content, this observation induces the assumption that the relation between this variable and workability does not follow a linear trend.

Since both materials presented discrepancy in the volume of voids, in this campaign the samples were selected for test targeting to find the lowest observation of this parameter among all specimens.

The next subsections detail the analysis of the mechanical tests. Firstly, the Black Diagram and the Cole & Cole plot are individually observed and discussed. In sequence, the isotherms are adjusted in a master curve relative to the reference temperature of 15 °C. Lastly, the mechanical characterization of the samples is compared focusing on their evolution of stiffness and viscoelastic behavior.

6.5.1 Black Diagram

Figure 6-15 presents the Black diagram of two samples selected for test, extracted from Mixes 4 and 5. In the graph it is also presented the diagram corresponding to the average of Mix 1

(produced without plastic) and Mix 3 (produced with 5% plastic following the same mixing procedure adopted for campaign 4.

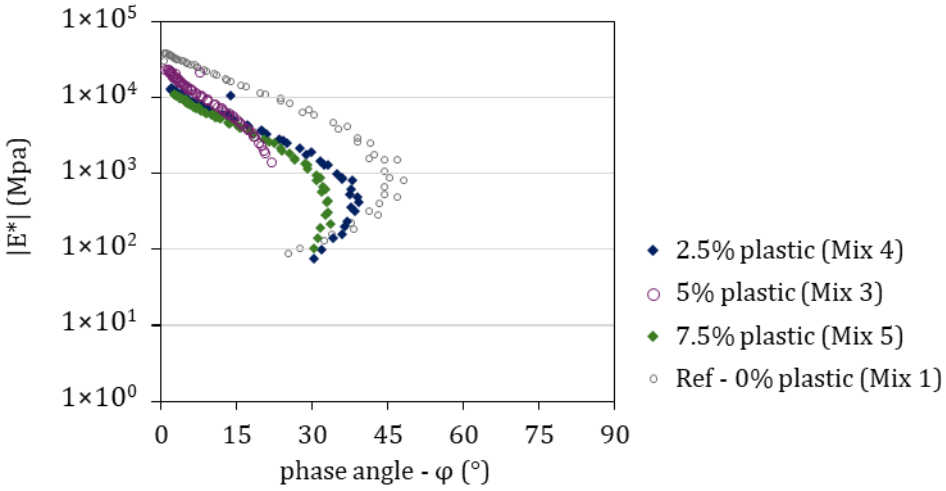


Figure 6-15 – Black Diagram of samples from Campaign 4

Considering the maximum phase angle reached by the four curves, the materials composed of 2.5% and 7.5% of plastic stayed below the curve of reference. This result reflects the improvement of the elasticity of the mixture in the two cases. In the reference mixture, the phase angle decreases after reaching a maximum around 48 degrees. This same aspect is also observed in the curve of Mix 4, after reaching 38 degrees, and in the curve of Mix 5, after reaching 32 degrees. Under the conditions tested, Mix 3 did not reach an elastic recovery. However, all the curves remained below 22 degrees.

Separating the data from the graphs by a divisor line set in the phase angle of 45 degrees it is possible to observe that all samples designed with plastic are placed below that, indicating that during all the tests the behavior was mostly elastic not reaching a zone of predominance of viscous behavior even when submitted to high temperatures.

Even though the samples presented different volumes of voids, it was still possible to observe a trend of increase of the elastic behavior of the mixture. Having that in perspective, it would be possible to infer that the incorporation of plastic by this method reflects directly in the elasticity. One hypothesis for this trend would be the mobilization of content of polymer from plastic into the binder. However, these results do not suggest that this trend follows a linear

relation. This gives support to a parallel assumption that the elastic increment depends on an optimum concentration of plastic in the mixture.

6.5.2 Cole & Cole plot

As observed in the previous subsection, the three samples designed with incorporation of plastic are placed in a zone of mostly elastic behavior. This indicates that these samples must present Storage Modulus (E') greater than the Loss Modulus (E''). This can be observed in a Cole & Cole plan. Figure 6-16 shows the Cole & Cole plot of the same samples.

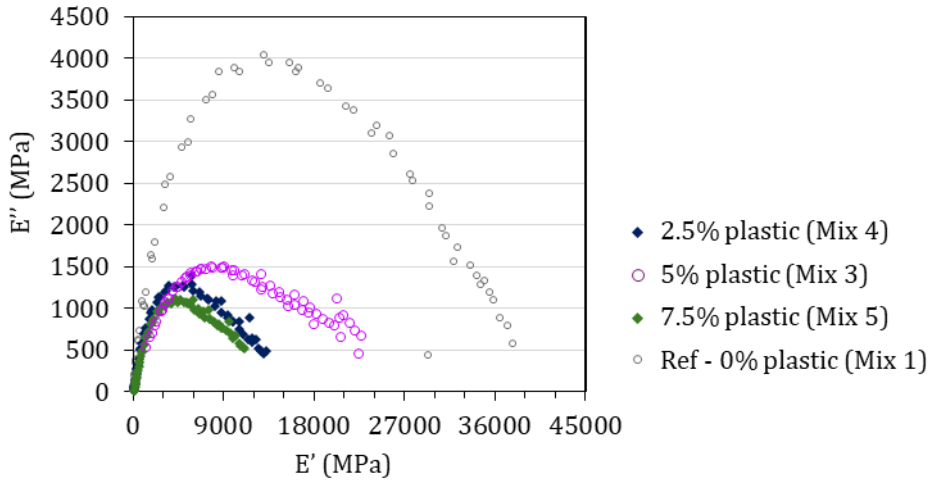


Figure 6-16 – Cole & Cole plot of samples from Campaign 4

The maximum value of E'' for both mixes 4 and 5 is set around 1200 and 1100 MPa, respectively. When this value of E'' is reached in the curves, E' is approximately 4000 MPa. In contrast, the curve of the reference sample without plastic reaches a maximum in a peak where E'' is 4000 MPa and E'' 13000 MPa. The notorious difference obtained from the two samples in comparison to the reference is probably linked to the lower compaction reached by samples with plastic. In fact, while the reference mix reached the targeted voids, this was not achieved in the samples that incorporated 2.5 and 7.5 % plastic. The following section discusses with details this effect.

Besides this particular side effect of the incorporation of plastic, it is possible to estimate that the proportion of E' compared to E'' can be approximated in the two samples. In addition, this reason is maintained proportionally the same along the curve, which leads to a similar shape. Further insights can be obtained when comparing these mixes with mix 3. In contrast to the

other mixes, the curve of this material when plotted in a Cole & Cole plan present a flatter shape.

This characteristic reinforces the elastic aspect of this material over the viscous aspect. As mentioned in the previous sections, the three materials were produced following the same procedure. In the analysis of the mechanical improvements brought by the method applied for producing mix 3 it was possible to observe an incorporation of elastic aspects even considering it was applied a minimized heating time. This factor put in perspective the efficiency of the method on incorporating the elastic aspects of the polymers into the mixtures.

6.5.3 Master curves of mixes with 2,5 % (Mix 4) and 7.5% (Mix 5) plastic

Similarly to the other samples, the mechanical behavior of mixes 4 and 5 was also evaluated through a master curve. In view of this analysis, Figure 6-17 shows the shift factors calculated for the two specimens in function of the temperature. In parallel, Table 6-4 presents the constants C_1 and C_2 calculated from the WLF curve.

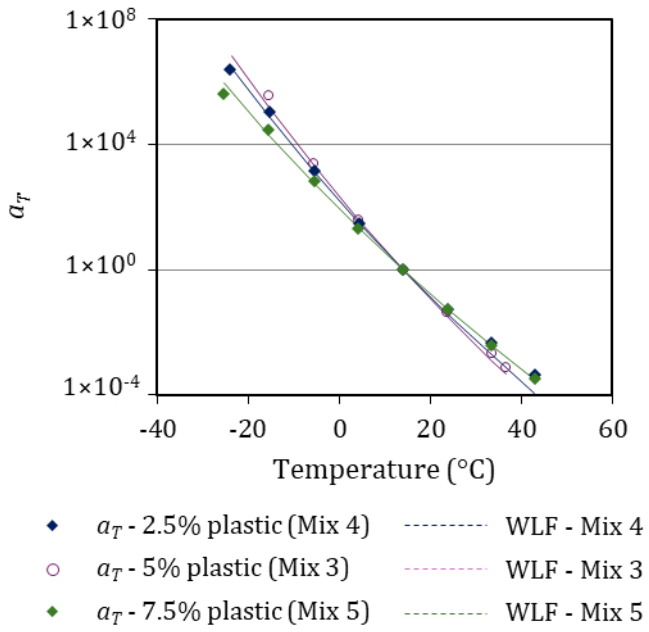


Figure 6-17 - Shift factors and WLF curves of specimen tested from Slab 4 and 5 (respectively 2.5% and 7.5% plastic with compensation of granulometry)

Table 6-4 - Constants C_1 and C_2 obtained from mixtures with 2.5% and 7.5% plastic obtained from Slabs 4 and 5

Material	C_1 **(-)**	C_2 **(°C)**
Average Mix 1	23.26	155.72
MIX 3 - 5 % p. (S3S4)	48.34	304.52
MIX 4 - 2.5 % p. (S4S4)	44.28	295.25
MIX 5 - 7.5 % p. (S5S3)	42.30	319.41

In the previous analysis it was observed that there is evidence that the three materials do not correspond in terms of mobilization of polymer and aggregate structure. Although it was expected that this difference would be reflected in the master curves, the calculation of the a_T does not follow a pattern when observing only the plastic content as variable.

The graph of a_T presents the three plastic contents (2.5, 5, and 7.5 %). Among those, the sample designed with 5% plastic presented the greater slope, which also means a stronger gradient of shift factor between each temperature. Since the same T_{ref} was used for the master curves (15 °C), in this temperature all values of a_T aligns to 1. Taking this point and the slope defined by the values from the 5% plastic curve as a reference, lower slopes were observed in the 2.5% curve, followed by the 7.5% curve.

Comparing the constants from the WLF model (C_1 and C_2), it is possible to observe that all samples showed increased values. However, these values do not follow a trend in function of the plastic content. Based on that, a first comparison of the mechanical behavior of these three materials indicates that the temperature sensitivity is stronger when analyzing the sample with 5%.

The master curves of |G*| and φ for these samples is presented in Figure 6-18 for the temperature (T_{ref}) of 15 °C. In addition, the curve of the average of the samples of reference, produced without plastic are also presented for comparison of magnitude.

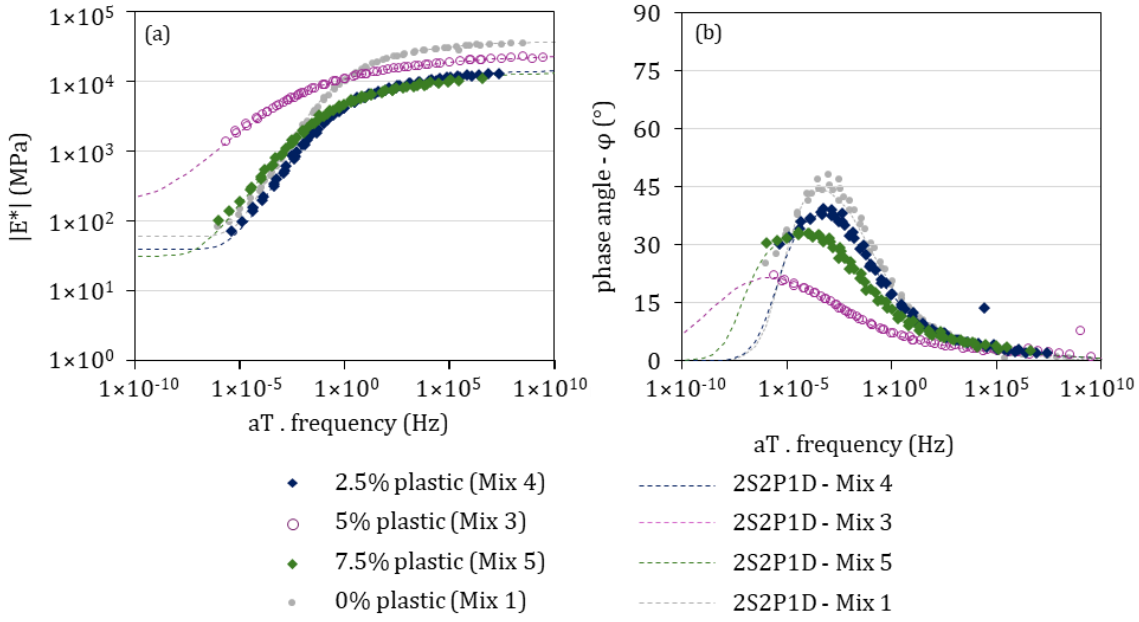


Figure 6-18 - Master curves of specimen tested from Slab 4 and 5 (2.5 and 7.5% plastic respectively) (T_{ref} = 15 °C)

Concerning the differences of φ, it was observed that all samples designed with incorporation of plastic presented stronger elastic aspect then the reference, evidenced by the decrease of this parameter in higher temperatures. Reflecting what was observed in previous analysis, the decrease was more evident in the curve of the 5% plastic. However, between 2.5% and 7.5% plastic, a lower φ was observed at 7.5%, reflecting a similar trend to what was observed in the analysis of samples from this campaign 4.

When it comes to |G*|, it was observed that the shape of the curves diverged, which induced different stiffness in different temperatures. In general, the curves designed with plastic presented a flatter shape when compared to the reference, indicating a lower discrepancy under different temperatures, which can also be related to mobilization of content from the plastic. Concentrating on the analysis of the lower frequencies it is possible to understand the performance of this parameter at high temperatures. Under these conditions, the performance of the samples with 2.5 and 7.5% plastic were approximately similar to the reference without plastic. Among these two materials, the second presented a slight greater stiffness.

At lower temperatures there is a notorious difference between all samples designed with incorporation of plastic and the reference. Between 2.5 and 7.5% there was no evidence of different behaviour, at the same time as these two curves presented lowest |G*| in lower

temperatures. Considering these two curves do not cross the reference curve in an intermediate temperature, as it was expected, it would be possible to estimate that besides the effect of the plastic there is another parameter in the constitution of these two mixtures that affect their performance. However, the flatter shape and the fact that these curves still match in high temperatures indicates that there is still a portion of the plastic that is mobilized into the bituminous binder.

All the parameters discussed in this section contributed to similar inferences, as evidenced by the stiffness analysis. Firstly, when comparing the incorporation of 2.5 and 7.5% it is evident a better performance of the mixture designed with higher plastic content. However, when comparing these two materials with the one with 5%, it is evident that the better performance rests in the intermediate plastic content. This analysis allows to conjecture that there might be an optimum plastic content when designing mixtures through a dry process. However, it is important to consider if this efficiency is reached due to a particularity of the materials or due to the differences in workability when working with different plastic contents.

6.6 2S2P1D modelling

In Chapter 5, the 2S2P1D model was employed to describe the mechanical behavior of the binders produced in this study. The advantage of using a mechanical model usually relies in the possibility of describing the materials' performance in all different conditions of temperature and traffic load. Complementary to that, the discussion of the use of the 2S2P1D model with those binders had two additional goals: finding in the variation of the constant the shape of the curve evidence of the presence of the plastic and validating the model for the materials that interacted with plastic without following a protocol of modification. This discussion was described in section 5.6 - 2S2P1D modeling (Campaign 2).

Giving continuation to that analysis, the mechanical performance of the mixtures developed in this study was submitted to similar analysis aiming to adjust their behavior in a model. Similarly to bituminous binders and mastics, the application of the 2S2P1D model is already valid and verified (Di Benedetto et al., 2004; Olard & Di Benedetto, 2003). Based on that, the methodology of fitting point-by-point was also applied into the materials in order to shape the curves presented in the previous discussions of this chapter.

The analysis of these materials enables inferring that the influence of this type of recycled plastic was multidirectional, since at the same time the plastic takes part in the aggregate skeleton, it seems that there is partial mobilization of content to the binder eventually modifying the viscoelastic character of the mixture. In fact, this model is broadly efficient in reproducing the behavior of PMBs, which would be comparable to the second assumption (Cai et al., 2019; Olard, 2003; A. Singh & Gupta, 2024). However, considering the effects of dry and wet processes seem to run simultaneously and knowing that recycled plastics are composed of a mixed composition of polymers that affect the behavior on high and cold temperatures differently it is still pertinent to verify the efficacy of this model when describing these effects on modified mixtures.

This section focuses on the parameters found to develop this model. Considering that plastic incorporation influenced the mixture at both macro and micro scales, affecting workability and production, the analysis was conducted by comparing it to the reference material (Mix 1). In addition, an analysis of adherence of the model using the calculated parameters is made.

6.6.1 Calculation of parameters

The analysis of the parameters obtained from the bituminous binders showed that the most evident effects of the incorporation of the plastic would be noted in the constants G_0 and β. The first one increased, even knowing that 0 was the value expected for unmodified binders, and the second one decreased. Both parameters are linked to the Newtonian flow at high temperatures. Although conventional mixtures do not reach this behavior under the same conditions, it is expected that an increase of stiffness at very low frequencies is still experienced due to the participation of the binder.

Table 6-5 presents the parameters calculated for the mixtures studied in this experimental plan. Samples that deformed or did not pass through the data processing phase for another reason are not shown. In addition, a virtual analysis considering the average |G*| and φ in each frequency was made for Mixes 1, 2 and 3. This analysis was made aiming to establish a standard behavior between samples tested from similar materials.

Table 6-5 - Optimized 2S2P1D constants calculated for bituminous mixtures tested during Campaigns 3 and 4

Material	E_{00} ***(MPa)***	E_0 ***(MPa)***	***k (-)***	***h (-)***	***δ (-)***	$\tau_{\varepsilon 15}$ ***(s)***	***β (-)***
MIX 1 - 0 % p. (S1S1)	52	38400	0.195	0.565	1.9	2.6×10^{-1}	350
MIX 1 - 0 % p. (S1S6)	76	39000	0.190	0.565	1.75	2.6×10^{-1}	180
Average Mix 1	52	39000	0.195	0.565	1.9	2.6×10^{-1}	350
MIX 2 - 5 % p. (S2S5)	155	24500	0.118	0.38	2.1	1.9×10^{1}	*
MIX 2 - 5 % p. (S2S4)	155	22800	0.118	0.38	2.1	9.0×10^{1}	*
Average Mix 2	155	24000	0.118	0.38	2.1	3.8×10^{1}	*
MIX 3 - 5 % p. (S3S1)	170	25450	0.110	0.33	1.8	2.8×10^{1}	*
MIX 3 - 5 % p. (S3S4)	170	24500	0.110	0.335	1.8	1.9×10^{1}	*
Average Mix 3	175	24500	0.110	0.335	1.7	1.9×10^{1}	*
MIX 4 - 2.5 % p. (S4S4)	40	15000	0.150	0.5	1.76	2.0×10^{-1}	1000
MIX 5 - 7.5 % p. (S5S3)	32	14200	0.130	0.44	1.72	6.0×10^{-1}	7000

It was adopted a value close to the maximum β *

In the 2S2P1D model, the elastic aspect of the material is regulated by the two springs mathematically represented by E_{00} and E_0 - E_{00}. Concerning E_0, an increase was observed when comparing the reference (*Average Mix 1*) and all the samples produced with 5% plastic. The sharpest increase was observed in Mix 3, which reached 170 MPa from the experimental data. In parallel, Mix 2 reached an approximate value, reaching 155 MPa.

Considering the two materials similar in terms of plastic content, this difference can be associated with the granulometric approach. While in Mix 2 the plastic was introduced as an extra material to the aggregate projected in Mix 1, in Mix 3 the two materials were equally accounted during the calculation of the gradation of project, repeating the same used in the reference and avoiding have increase of particles between 2 and 5 mm.

In the second spring of the model, the stiffness is represented by the difference between the two first constants of the model (E_0 - E_{00}). In view of that, it was observed that there was a decrease in modulus between the Mix 1 and all other samples with plastic. The reference value of 38948 MPa (*Average Mix 1*) dropped to around 24000 MPa in the samples with incorporation of 5% plastic. As observed from the literature review, one of the effects of the introduction of polymers in PMBs that compose mixtures is the decrease of the stiffness on the highest frequencies, due to the lower sensitivity of the elasticity of these materials to the temperature. Based on that, it would be possible to expect a flatter shape of the master curve of |E*|, and consequently a lower difference between the two constants.

When it comes to the samples from Mix 4 and 5 it was possible to observe some divergencies from the other three. In first place, there was no difference in magnitude on E_{00}. In fact, this parameter was slightly below the reference, reaching the lower value in the material produced with 7.5% plastic (32 MPa). It is possible that the lower workability and the resistance to compaction represent partially this result.

When it comes to the parabolic elements, their behavior can be evaluated through the constants *k* and *h* that describe the creep of the material. Considering *k* as the parameter representative of the first parabolic element, while this constant was approximately 0.19 for the reference mix, it decreased to around 0.11 in the samples from mix 2 and 3. This decrease reveals a less pronounced inclination of the master curve in lower temperatures, and lower variation in the complex modulus. At the same time, the same tendency was observed in *h*. For this constant, the value decreased from 0.57 (*Average Mix 1*) to 0.38 (*Average Mix 2*) and 0.33 (*Average Mix 3*).

Together, the decrease of these two constants is associated with a lower variation of the imaginary part in relation to the real part of |G*|. Creating a relation between that and the presence of the plastic inside the bitumen, it would signify a lower variation of the viscous part in relation to the elastic part of the modulus, which is increased with the association with

polymers. In fact, the decrease in the two constants was also observed in the other samples produced with plastic, but less expressive.

The Newtonian flow seems also to be affected, based on the analysis of the constant β and the dashpot. In all the models that incorporated 5% plastic the better fitting was achieved when this constant was maximized. This would also mean that the part representing the effects of this element in the equation is ignored. In the analysis of the bitumens it was observed that this parameter was also sensitive to the incorporation of the plastic.

In all samples, the incorporation of the plastic seems to be linked to two aspects: first, a lower variation of the loss modulus in comparison to the storage modulus; and secondly, an impact on the Newtonian flow. When using 5% plastic this flow was already minimum, which indicates that a higher concentration of plastic would not impact this particular element of the model.

6.6.2 Adherence of the model

Similarly to the formulation of models for the bituminous binders, the validation of the 2S2P1D models for the mixtures included an analysis of adherence for asserting reliability. The same protocol was used in this analysis, parting from the extraction of values of |E*| and φ from the experimental data and from the calculations of the model in similar frequencies. As proceeded in the analysis of binders, in this phase the quadratic variation in each point was calculated followed by a measure of the coefficient of determination (R^2) of this error.

Figure 6-19 presents the plot of the comparison between the experimental data and the calculation on the model for all mixtures. The coefficients of determination are presented in Table 6-6.

Table 6-6 - coefficient of determination of adherence test (mixtures)

	R^2	
	$\|G^*\|$	φ
MIX 1 - 0 % p. (S1S1)	0.999	0.960
MIX 1 - 0 % p. (S1S6)	0.996	0.948
MIX 2 - 5 % p. (S2S5)	0.999	0.994
MIX 2 - 5 % p. (S2S4)	0.999	0.989
MIX 3 - 5 % p. (S3S1)	0.999	0.997
MIX 3 - 5 % p. (S3S4)	0.999	0.977
MIX 4 - 2.5 % p. (S4S4)	0.999	0.980
MIX 5 - 7.5 % p. (S5S3)	0.990	0.993

The analysis of the residues indicates that in general the phase angle presents more discrepancies than the complex modulus. This is perceived from the cloud of points, where some points are distant from the targeted curve. Most of the discrepancies were observed in the reference mixture.

In all samples the distribution of the residues follows a normal shape and the R^2 was generally above 0.95. This observation suggests that the experimental data is well represented by the 2S2P1D model with more than 95% of reliability. In addition, it is possible to observe that the model was well adapted to all samples, including those with plastic in their constitution.

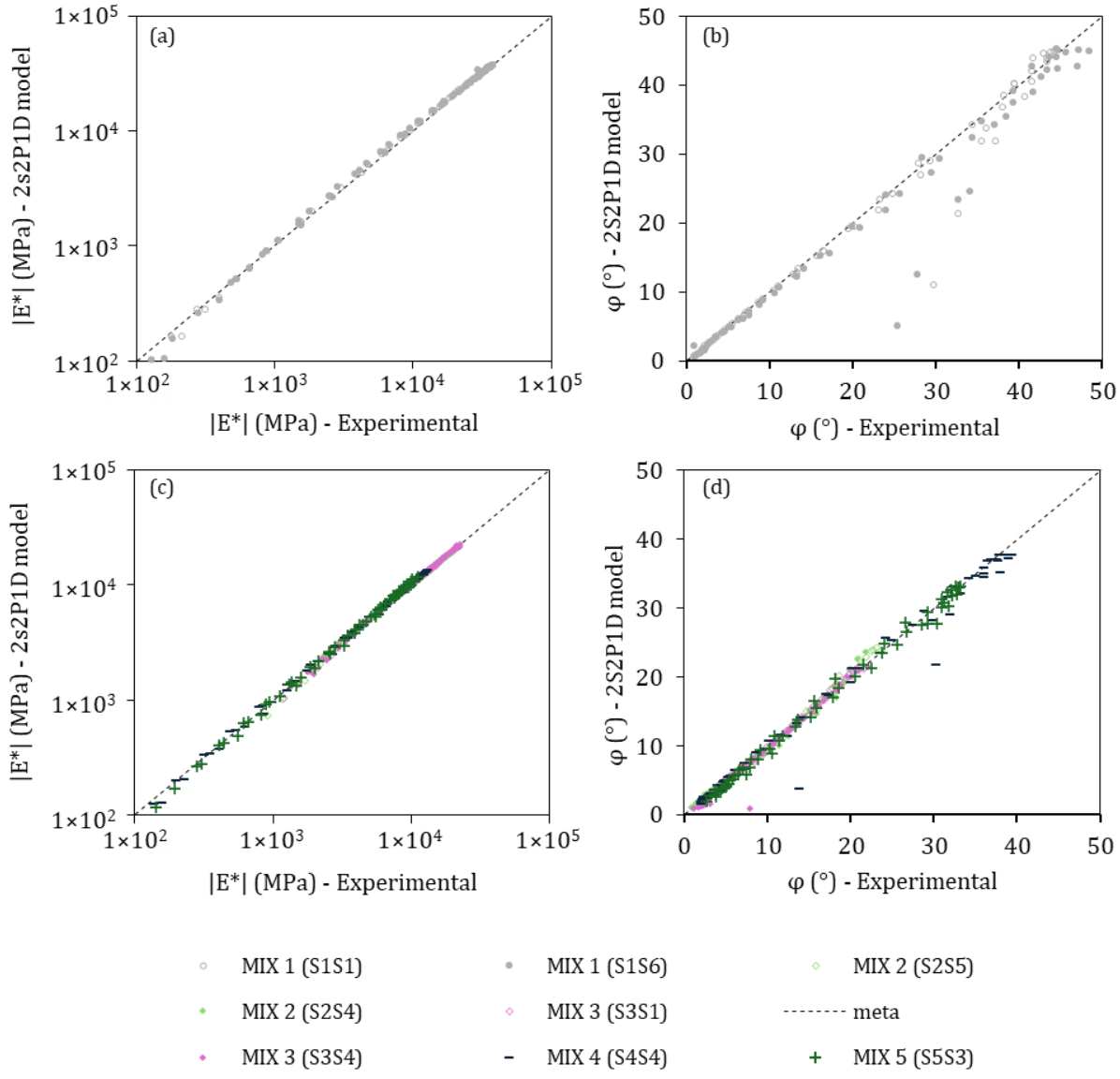


Figure 6-19 - Analysis of adherence of 2S2P1D model to experimental data of |E*| and φ. (a) analysis of reference mixture - |G*|. (b) analysis of reference mixture – φ. (c) analysis of mixtures with plastic incorporated - |G*|. (d) analysis of mixtures with plastic incorporated – φ

6.7 Discussion about the progression of the effects of plastic in mixtures

As outlined in the previous section, the compaction was found to be the factor that predominantly influenced the production of mixtures with varying contents of recycled plastic. This issue must be considered when implementing methods of construction that include this alternative material, since it might offer a resistance to compression when not designed in a specific proportion.

At the same time, the inclusion of waste plastic in the mixtures can be a means for improving their stiffness at higher temperatures, which is favourable to avoid failure of pavements. Although there is no evidence that the level compaction and the plastic content follow a linear trend, these two parameters influence simultaneously the stiffness of the mixtures.

This section presents a complementary analysis on the progression of the effects of the percentage of plastic in the complex modulus (|G*|) of mixtures considering the side effects that the plastic brings into the compactability of these mixtures. For the purpose of this evaluation, five mixes were selected from the samples presented in this chapter. Samples from mix 2 were ignored from this analysis. As a result, only samples produced following the same method of dry process were included and the variability in the method of production was eliminated from the analysis. In addition, one of the samples produced without plastic was also included. This allows the analysis to also count with a perspective from a mixture that was designed without plastic.

In view of the effects of the presence of plastic occurring predominantly at higher and lower temperatures, these effects were approached when choosing the temperatures for this evaluation. The temperature of 15 ℃ was set as intermediate temperature, understanding that at this condition the effects of the plastic are minimized. In sequency, the effects of the variation of temperature were observed within temperatures placed at ± 30 ℃. Thus, this evaluation set in this section considered three temperatures: -15, 15 and 45 ℃.

At 15 ℃, the effect of the plastic incorporation presents in theory a minimum magnitude. Based on that, if this variable is ignored, |G*| would vary in function of other variables, such as materials, granulometry and volume of voids (*Vv*). Since the last was the only parameter that did not remain constant during the preparation of the samples, it would be possible to expect a correlation between |G*| and *Vv*.

Considering the isotherms of the materials at this temperature, this assumption would suggest that the curve would be placed in parallel, with those materials with higher *Vv* below. The experimental isotherms of each sample are presented in Figure 6-20. Generally, it is possible to observe that the only isotherm that crosses the others is the one referring to the sample designed with 0% plastic, which crosses the curves of the samples with 5% around the frequency of 1 Hz. This behavior seems to be linked to the effect of plastic on changing the inclination of isotherm curves.

Among the frequencies tested in 15 °C, the frequencies of 0.3 Hz and 1 Hz should represent better the neutrality of the plastic effect due to be around the area where the intersection between the curves is traced.

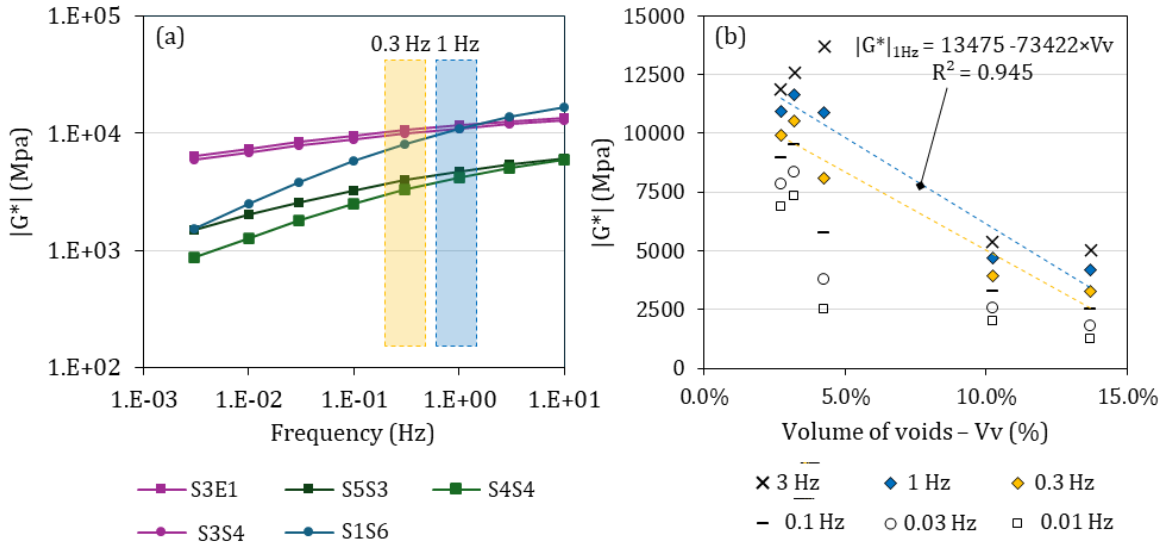


Figure 6-20 – Evaluation of relation between complex modulus (|G*|) and volume of voids (*Vv*) at 15 °C. (a) Isotherms at 15 °C. (b) Linear regression between |G*| and *Vv* by frequency

Having that in perspective, the values of |G*| were plotted in a cloud of individual frequencies to observe the evolution of this parameter in function of *Vv*. A linear regression of the values of |G*| was traced for each frequency and their R^2 are presented in Table 6-7. The extremities of the isotherms were eliminated from this analysis since they are far from the intersection of curves.

Table 6-7 – R^2 of the evolution of |G*| in function of *Vv* for different frequencies

	0.01 Hz	*0.03 Hz*	*0.1 Hz*	*0.3 Hz*	*1 Hz*	*3 Hz*
R²	0.660	0.740	0.852	0.935	0.945	0.881

The highest correlation among the frequencies was observed in the point of intersection (1 Hz). In this frequency, the R^2 was 0.945, indicating that at this frequency the |G*| can be approximately 95% explained by the volume of voids in the mixture. In other frequencies, the R^2 stayed above 0.75 indicating that there is good correlation between these two variables within this temperature. It is relevant to remark that this coefficient reinforces the assumption that the variation of the granulometry is minimum under the conditions of dry method established.

Considering the two frequencies of higher R^2, 1 Hz and 0.3 Hz respectively, it is possible to estimate that that the |G*| in each frequency could be estimated by a linear model. This model is composed by a maximum value for |G*|, that is achieved when *Vv* = 0, and a constant that indicates the quantity that is lost by unity of *Vv* (%).

At extreme temperatures, however, the amount of plastic takes place as a second variable that influence |G*|. Assuming that the correlation at the central frequencies 1 Hz and 0.3 Hz is preserved in other temperatures, these frequencies could be used as a mean to estimate the magnitude of the effect of the plastic at -15 and 45 °C. In this scenario, this estimation consists of a correlation described by Equation (5):

$$|G^*|_{T\,°C;frequency} = c_0 + c_1 \times Vv + c_2 \times \%\,P \qquad (5)$$

From which

c_0 = the intersection of the curve, that corresponds to |G*| of a mixture with 0% voids and 0% plastic;

c_1 = the constant linked to the volume of voids;

c_2 = the constant linked to the percentage of plastic;

Vv = the volume of voids; and

% P = the percentage of plastic (by weight)

In order to verify if this hypothesis is valid a multiple regression with two independent variables was carried out. The results obtained from this regression are presented in Table 6-8.

Table 6-8 – Results of multiple regression carried out with *Vv* and % plastic as two independent variables

y	*Intercept*	c_1 (x_1 = *Vv*)	c_2 (x_2 = *%P*)	R^2
$\|G^*\|_{45\,°C;\,1\,Hz}$	2957.83	-31815.34	28880.25	0.699
$\|G^*\|_{45\,°C;\,0.3\,Hz}$	2314.02	-25808.47	23734.42	0.689
$\|G^*\|_{-15\,°C;\,1\,Hz}$	40281.36	-171692.66	-182285.02	0.817
$\|G^*\|_{-15\,°C;\,0.3\,Hz}$	38587.47	-162502.91	-179662.26	0.839

At 45 °C, the values of R^2 obtained for 1 Hz and 0.3 Hz were respectively 0.699 and 0.689. This means to say that, at this temperature, the plastic content and *Vv* can explain 70% of the variation of |G*|. Although this is not a low coefficient, this means that there is around 30% of the variation of stiffness that is not explained by the plastic content and by the volume of voids. It is possible to observe that both c_2 were positive, indicating the tendency of the |G*| to increase with the increment of plastic content.

On the other hand, at -15 °C the values of R^2 were 0.817 and 0.839. The same analysis indicates that around 82% of the variation of |G*| in low temperatures can be explained by these variables. This difference brings a necessity to further investigate the effects of this waste plastic and their compounds in relation to other polymers. Understanding whether the polymers present stronger effects at lower or higher temperatures would be important to extract the better potential of these materials in different projects.

CHAPTER 7
CONCLUSIONS AND PERSPECTIVES

This chapter presents the main findings obtained from this experimental plan and the perspectives for future work. Firstly, a recapitulation of the research objectives is made presenting the insights from the tested methods that have contributed to them. In sequence, this chapter presents the main gaps that were opened in relation to these objectives and the research problem approached in this dissertation.

7.1 Summary

The main objective of this research was to identify the effects that interactions and incorporation of three-layer recycled plastic could bring into the mechanical behavior of bituminous asphalts and mixtures. In this context, an experimental plan was proposed targeting study these effects in the scales of binder and mixture separately. For this purpose, specific objectives were outlined addressing each part of the experimental plan.

7.1.1 Conclusions

In the study of the binders a two-part specific objective was formulated: (a) identify the conditions and parameters that affect the interaction plastic-binder, considering the unknown nature of the recycled plastic; and (b) investigate the impacts of this interaction in the mechanical behavior once it is achieved. In view of these objectives and the experimental plan proposed in this research, the following conclusions were established:

i. The recycled plastic used in this research was mainly originated from sources of food packaging waste and three-layer packaging of drinks. In its base constitution, this material is mainly composed of PE, HDPE, and LDPE. This composition was further investigated by means of FTIR, DSC and TGA tests. The results of the chemical characterization indicated a predominance of these polymers. However, some signs suggested the presence of PET, PP, residual traces of cellulose and aluminum. The presence of other polymers suggests a contamination of this material with other sources of recycled plastic. The presence of aluminum and fibers of cellulose demonstrates the difficulties of extracting the full content of polymer from its three-layer form.

ii. From the DSC data, it was observed four distinct endothermic reactions occurring below the temperature of 175 °C. These reactions must be located around the temperatures of glass transition and melting point of the polymers that constitute the material. Three peaks were located in temperatures lower than 150°C, which was the same temperature targeted in the production of the mixtures and consequently used for inducing the interaction with the binder.

iii. FTIR absorbance spectra obtained on the binder after interaction with plastic at 20% dosage suggest potential mobilization of components from plastic to binder. In this sample, bands located between 700 and 1500 cm^{-1} presented an alteration of intensity, which reflects the presence of polymers such as PET, LDPE, or HDPE. Besides that, a

band around 3400 cm^{-1} was identified, which is most likely related to the influence of the fibers of cellulose in the binder.

iv. In the literature review, it was observed that most of the studies refer to the Compatibility as the phenomenon to explain the interaction between polymers and binders. This property does not follow a linear trend, which means that the content of plastic above or below the optimum content leads to poor performance. In addition, there is no mathematical model to explain this phenomenon. The content of plastic estimated in Campaign 1 and Campaign 2 was made targeting an optimum content for wet process, however an optimum mobilization was not verified.

v. Although the same plastic was used for both experimental campaigns, two different bitumens (both with 50/70 penetration grade) and two electrical mixers with different spindles were used for the two campaigns. The presence of absorption bands associated to cellulose in the FTIR spectrum of binder after exposure suggests the possibility that potential residues of plastics due to particle breaking during mixing (using the mixer at UFC) remain in the sieved binder after separation. This point suggests that besides the effect of mobilization and compatibility, a filler effect could influence the mechanical results during these campaigns.

vi. The results of the rheological characterization tests confirm the potential interaction between binder and plastic. In particular, the results of Campaign 1 (tests performed from 46°C to 82°C) showed that while the exposure to 5% of plastic (by weight of binder) had a limited effect on LVE properties of the binders, substantial variations could be observed for G* curves of binders after interaction with 20% plastic.

vii. In general, it was observed that as higher it is the surface of contact between a plastic and bituminous binder also is the interaction between these two materials. Although this surface depends on the size of the shreds or pellets of polymer/recycled plastic, this can be controlled in the production of the samples by modifying the heating time and the rotation speed. Among those, it was observed that changing the rotation speed from 200 RPM to 1000 RPM would reflect stronger interaction than changing the heating time from 30 to 60 minutes.

viii. The results of Campaign 2 at ENTPE (tests performed from -20°C to 70°C) highlighted variations of the asymptotic moduli of the binder after exposition to 20% plastic, with lower values of the glassy modulus G_0 at high frequency/low temperature and the

appearance of a static modulus G_{00} at low frequency/high temperature (instead of classical Newtonian flow with null G_{00}).

Giving continuation, the studies developed in the mixture scale targeted the second specific objective, characterizing the mechanical behavior of mixtures produced with incorporation of the same recycled plastic via a dry process. Taking that into perspective, the following conclusions were formulated:

ix. In general, the insertion of plastic into the mixture by the Dry Process resulted in the similar mechanical changes observed in mixtures designed with PMBs. In the analysis of high temperatures, it was observed an improvement of stiffness, while it decreased in lower temperatures. Simultaneously, the constitution of the mixture moved to a more elastic aspect.

x. In the literature review it was observed that there is a tendency for the Dry Processes to be less standardized than Wet Processes. In this part of the research two opposite methods for incorporating this material were evaluated, in the beginning and in the end of the mixing process. When the plastic content was 5% by weight of the mixture, the comparison of the two methods allowed infer that the two performed similarly. This suggests that, for this specific content, the moment of incorporation of the plastic does not result in strong mechanical differences.

xi. When comparing the mixes with 5% plastic with mixtures with the same granulometry without plastic there was strong improvement of the complex modulus (|E*|) in higher temperatures. In intermediate temperatures (around 15 °C) the complex modulus was equal and in colder temperatures slightly lower. This result implies that the compensation of granulometry allows the aggregate structure to perform similarly. In addition, the increment of performance regarding the reference mixture allows conclude that effects of wet method can were achieved even considering the mixtures were produced following a dry process.

xii. The workability of the mixtures was notoriously impacted by the presence of the plastic. In the mixing procedure, it was observed that there was a greater resistance of the mixer after the inclusion of the plastic. Considering some contents of the plastic tend to melt or reach the glassy transition in the temperature used for mixing the samples, this is

related to the elastic aspect of the melted polymers. In parallel, the compaction was also affected by the presence of the plastic. It was observed that the elastic resistance dissipated part of the load applied for compacting the samples.

xiii. It was not possible to verify a linear tendency of evolution on the mechanical effects in function of the plastic content. Among the three contents tested in this study, incorporating 5% of plastic resulted in a higher improvement of the elastic aspects when compared to 2.5% and 7.5%.

xiv. Regarding the stiffness of the mixtures with plastic, it was also noted that the compaction represented a factor as significant as the plastic content to explain the complex modulus obtained in extreme temperatures. Considering the plastic is the material that decreases the workability of the mixtures, the inclusion of this material in the construction of pavements must also include the improvement of techniques of compaction.

7.2 Perspectives

This research was organized to address the problem of poor comprehension of the mechanical effects of recycled plastics from food packaging when applied in the construction of bituminous mixtures. This was inserted into a macro problematic of the increase of disposals of this material without destination.

The four campaigns described in this report presented conclusions that can also guide the formulation of future research questions on this topic. With this focus in mind, this section outlines recommendations for the continuation of the research and future studies. The suggestions are organized by topic, with a brief discussion of their scientific and technical relevance provided for each:

i. Propose an index for quantifying the Compatibility

In the study of bituminous binders, it was observed that there are still some gaps in the understanding of the compatibility. It was not observed that an already validated mathematical model to explain and measure this phenomenon. Taking into perspective wet processes or partial wet processes, the definition of this index would represent a good benefit on the determination of a targeted polymeric content that leads to an optimum performance. A proposition for achieving that is elaborating an experimental matrix including bitumens from different origins and isolating the main type of polymers present in neat and recycled plastics. Evidence of interaction can be identified through FTIR spectroscopy and mechanical evaluation using DSR, both of which can be employed to develop the index.

ii. Investigate how the interaction plastic-bitumen occurs inside mixtures

Within this research, it was observed that the exposure of the plastic changed as a result of the blending mechanism, rotation speed, and heating time. Based on that, there were some uncertainties when achieving the configuration of the High Speed Mixer (HSM) that represents the conditions of mixture. Regarding the interaction between plastic and binder under these conditions, it is fundamental to explore how this interaction is proceeded inside mixtures. Based on that, a recommendation for future work is to perform the same chemical and mechanical characterization with binders extracted and filtered from mixtures. Following that procedure, it would be possible to compare the two methodologies and to determine the conditions of configuration of HSM method that leads to similar structural behavior.

iii. Verify the workability of RAP derived from mixtures produced with recycled plastic

Regarding the application of recycled plastics on modified mixtures in a long term perspective, it is fundamental to explore the applicability of Reclaimed Asphalts (RAPs) derived from mixtures produced with plastic. Identifying one use for this material is one step for achieving a desirable level of circularity. For this purpose, one suggestion is the use of induced-aging protocols for producing RAPs in laboratory comparing the aging effects on samples of unmodified and modified mixtures. Assessing the applicability of RAP derived from plastic-modified mixtures in new asphalt blends or other pavement layers is a key strategy to promote the use of this alternative material.

iv. Evaluate the environmental performance of modified mixtures

The introduction of a recycled material in the industry must be equally followed by an evaluation of the environmental cost of changing the standard methodologies of construction. In that perspective, it is relevant to verify the performance of the mixtures designed with this procedure in a Life-Cycle Assessment (LCA). For that purpose, the methodology proposed by the standard ISO 14040 must be followed. Some particularities of the construction of plastic-modified mixtures that might be included in a future derived study are the amount of energy required for accomplishing the mixing and compaction steps. Alternatively, the service life of these materials must be assessed. The use of a similar functional unity in a LCA compared with a reference unmodified mixture might reveal the effective environmental gains of the use of this technique.

v. Describe the relation between plastic content (%) and compaction energy dissipation (%)

During the production of mixtures with incorporation of plastic developed in this research it was observed that the presence of the plastic decreases workability, making the mixture more resistant to the mixing and compaction efforts. It was equally observed that even when the plastic improves the mechanical behavior of the bitumens and mixtures after prolonged contact, this improvement can be impacted by a decrease in the global behavior due to lower compactability. This issue is relevant to be addressed particularly when it comes to compaction, because, as one of its effects, the plastic can dissipate part of the compaction energy, increasing the volume of voids (*Vv*) from the targeted one. Based on that one important addition to a practice of Dry process would be to identify the amount of energy that is dissipated by plastic

content and the amount of plastic and compaction energy that make this problem can be minorized.

CHAPTER 8
EXPANDED ABSTRACT (FRANÇAIS)

Le chapitre 8 constitue une synthèse approfondie du contenu de la thèse. Il est organisé en sections reflétant la structure des chapitres précédents, permettant ainsi une mise en perspective cohérente des différentes étapes de l'analyse. Tout en préservant la rigueur des discussions menées, ce chapitre propose une reformulation condensée des résultats et des arguments développés. Ce résumé facilite ainsi la compréhension globale des contributions de la recherche.

8.1 Considérations initiales (CHAPITRES 1 et 2)

Les coûts environnementaux liés aux infrastructures constituent un nouvel aspect d'étude d'impact, incitant le secteur de la construction à prendre en compte la disponibilité des ressources et les coûts à long terme des projets. Pour y remédier, le recyclage et la réintégration des ressources sont essentiels. Le plastique, largement utilisé dans les emballages, représente un défi majeur. En Europe, le Green Deal encourage l'économie circulaire, réduisant l'enfouissement et augmentant le recyclage. Dans d'autres pays à économie émergente, la consommation de plastique croît rapidement, posant des problèmes de gestion. L'industrie de la construction pourrait intégrer ces déchets recyclés, soutenue par la science des matériaux pour optimiser leur utilisation durable.

L'incorporation de ces éléments dans les chaussées constitue une alternative intéressante pour réduire les coûts de production et d'entretien des infrastructures. Les plastiques, présentant un comportement élastique similaire à certains polymères industriels, peuvent être intégrés dans les enrobés bitumineux. Toutefois, des défis demeurent, notamment la maniabilité des matériaux et la résistance structurelle. La conception des nouvelles chaussées doit prendre en compte la durabilité, la charge de trafic et la facilité de mise en œuvre. Une longue durée de vie est essentielle pour limiter les réparations fréquentes et l'impact environnemental, garantissant ainsi que ces solutions recyclées soient à la fois économiques et respectueuses de l'environnement.

8.1.1 Pertinence de la recherche

Malgré l'utilisation généralisée des plastiques dans de nombreuses applications, la gestion de leurs résidus post-consommation reste inadéquate, conduisant souvent à l'enfouissement, à l'incinération ou à la pollution environnementale. Chaque type de déchet provient de sources différentes, impliquant des structures et propriétés polymériques variées. L'absence de stratégies efficaces pour réutiliser ces matériaux souligne à la fois les défis environnementaux et les occasions manquées d'employer les plastiques comme ressources précieuses dans la construction. Des approches innovantes, telles que la modification des liants bitumineux avec des plastiques recyclés, permettent d'améliorer les performances des matériaux tout en réduisant les impacts environnementaux. La construction routière constitue particulièrement une solution pratique pour réintégrer des quantités significatives de plastique dans l'industrie. Toutefois, des défis techniques subsistent, notamment l'incertitude quant au comportement

mécanique des enrobés modifiés avec des plastiques d'emballages alimentaires. L'intégration de plastiques dans les matériaux bitumineux représente ainsi une stratégie prometteuse pour améliorer la durabilité, soutenir la circularité et traiter simultanément le problème des déchets plastiques.

8.1.2 Objectifs

Une fois le problème de recherche identifié, les objectifs ont été formulés. Un objectif général a d'abord été établi, puis décliné en trois objectifs spécifiques. À partir de cela, il a été déterminé que l'objectif principal de cette thèse est d'identifier les effets de l'interaction et de l'incorporation de plastiques recyclés provenant d'emballages alimentaires à trois couches (polymère, aluminium et carton) sur le comportement des matériaux bitumineux.

Les objectifs spécifiques étaient les suivants :

I.A. Identifier les conditions et paramètres qui influencent l'interaction entre les déchets plastiques et les liants conventionnels ;

I.B. Étudier les impacts de l'interaction entre le plastique et le bitume sur le comportement mécanique du liant ;

II. Caractériser le comportement mécanique des mélanges incorporant du plastique recyclé selon la méthode à sec.

8.1.3 Littérature

Le chapitre de revue de littérature est structuré autour de quatre questions de recherche, comme présenté dans les sections suivantes :

i. Quels types de polymères sont les plus efficaces pour les mélanges bitumineux ?

ii. Quels sont les phénomènes impliqués dans le mélange entre polymères et liants ?

iii. Comment identifier la présence de plastique dans la composition d'un bitume ?

iv. Quelles différences mécaniques peut-on attendre lors du mélange d'agrégats minéraux et polymériques ?

La Figure 8-1 montre un schéma de quatre points clés discutés dans le chapitre de revue de littérature. Dans cette section, une version résumée du chapitre est présentée en se concentrant sur ces quatre points.

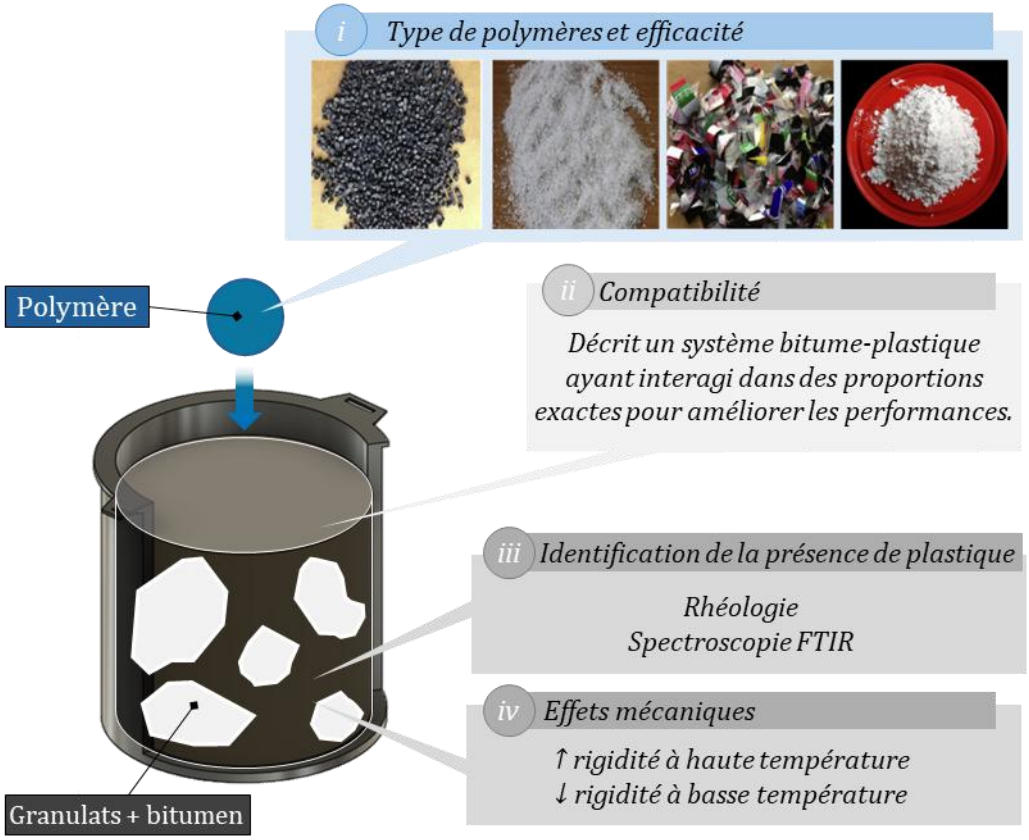


Figure 8-1 - Résumé des points clés étudiés dans la revue de littérature

Une revue des publications ayant étudié l'incorporation de plastiques purs et recyclés dans les mélanges a été réalisée, et les polymères les plus fréquemment rencontrés dans ces études ainsi que leurs effets lorsqu'ils sont appliqués dans des mélanges modifiés ont été compilés. Parmi ceux-ci, une forte présence de polymères tels que le polyéthylène (PE) et ses dérivés, notamment les formes basses (LDPE) et haute densité (HDPE), ainsi que le polyéthylène téréphtalate (PET), a été constatée. Des enregistrements de polystyrène (PS) et de polypropylène (PP) ont également été relevés. La Table 2-2 fournit un résumé des effets de chaque polymère.

Deux principes de modification peuvent être considérés pour la production de mélanges contenant du plastique : (1) procédé à sec (dry) : le plastique est incorporé directement dans le

mélange, en tant qu'agrégat ; (2) procédé à chaud (wet) : le plastique est utilisé comme modifiant et est préalablement mélangé au liant.

L'interaction entre le plastique et le bitume a été reconnue comme un point central dans les modifications du comportement mécanique des liants polymérisés. La compatibilité est comprise comme le phénomène qui régit cette relation. Elle constitue une propriété qualitative indiquant si la matrice polymérique en suspension dans le liant parvient à modifier la structure moléculaire de celui-ci et à rester stable ; en d'autres termes, si elle est compatible. Au contact des fractions SARA du bitume, les polymères ont tendance à se gonfler en raison des composants aromatiques légers présents dans la phase dispersée de la structure SARA, formant ainsi une phase riche en polymères également dispersée dans le liant.

Les effets mécaniques sont observés principalement à des températures plus élevées. La majorité des études recensées dans la littérature indiquent que les mélanges qui atteignent des conditions de compatibilité tendent à devenir plus rigides. En général, à de faibles fréquences — correspondant, sur les graphiques, aux performances à hautes températures — le bitume présente un module plus élevé. Par ailleurs, dans le diagramme Black, un changement de comportement se manifeste par une diminution de l'angle de phase.

Sur le plan expérimental, il est possible d'observer la modification du bitume en laboratoire selon deux approches : chimique et mécanique. Du point de vue chimique, l'objectif est de détecter des preuves moléculaires de la présence de plastique, par exemple au moyen de la spectroscopie FTIR. Du point de vue mécanique, les essais rhéologiques permettent d'observer les modifications de comportement à différentes températures.

8.2 Matériaux et Méthodes (CHAPITRES 3 et 4)

Le plan expérimental a été divisé en deux parties, chacune composée de deux campagnes expérimentales. La première partie concerne les objectifs I.A et II.B et fait référence aux essais réalisés sur les bitumes. La seconde correspond aux essais sur les enrobés et se concentre sur l'objectif II. Dans ce rapport de thèse, ces discussions correspondent aux chapitres 3 et 4.

Chaque campagne s'est focalisée sur un aspect spécifique de la procédure de mise en œuvre, comme synthétisé dans la Figure 8-2. Les détails des essais relatifs à chaque partie seront présentés séparément dans cette section.

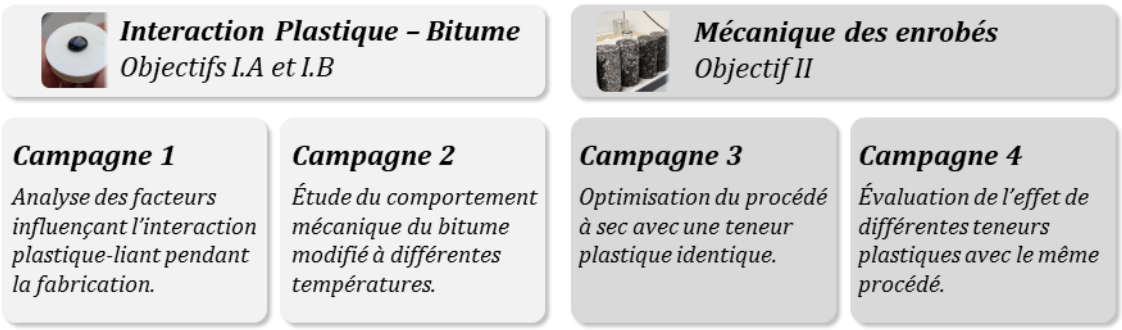


Figure 8-2 - Synthèse des quatre campagnes

Les campagnes 1 et 2 ont été réalisées à l'échelle du bitume. Un bitume non modifié 50/70 et du plastique broyé ont été utilisés lors de cette phase du plan expérimental. Dans cette phase, une méthode permettant de mélanger les deux matériaux, tout en observant et contrôlant l'ensemble des conditions, a été proposée. Tout d'abord, les deux matériaux ont été mélangés avec un mixeur (High Shear Mixer) en contrôlant la vitesse de rotation, puis séparés par tamisage du contenu solide. Le bitume séparé a été destiné aux essais, tandis que le contenu solide n'a pas été pris en compte pour l'analyse. Ce processus garantit que seul le bitume ayant potentiellement interagi avec les composants du plastique est considéré pour les analyses ultérieures.

La caractérisation rhéologique des liants bitumineux a été réalisée par des essais de module complexe à différentes fréquences et températures à l'aide d'un rhéomètre de type DSR. Lors de la première campagne sur le liant (campagne 1), les effets de l'interaction entre le plastique et le liant bitumineux à haute température ont été étudiés. Les paramètres testés comprenaient la durée de l'interaction avec le plastique (30 et 60 minutes), la teneur en plastique (5 % et 20 %) et la vitesse de rotation (200 et 1000 RPM). Lors de la seconde campagne sur le liant

(campagne 2), une plage complète de températures a été analysée (10 à 70 °C), avec une teneur en plastique fixée à 20 %.

Les essais ont été réalisés séparément. Pour la campagne 1, les tests ont été effectués à l'Universidade Federal do Ceará en Brésil, tandis que pour la campagne 2, ils ont été menés à l'ENTPE en France.

Les essais ont été effectués avec une configuration plan-plan, en contrôlant la déformation de cisaillement, et trois diamètres : 4 mm (basses températures), 8 mm (températures intermédiaires) et 25 mm (hautes températures). Au cours de cette phase, une caractérisation chimique des échantillons a également été réalisée par spectroscopie FTIR, portant sur le plastique, le bitume et les mélanges obtenus.

Les campagnes 3 et 4 ont été réalisées à l'échelle de l'enrobé. La courbe granulométrique visée pour fabriquer les enrobés est présentée dans la Figure 3-8. Les deux campagnes ont été réalisées en partenariat entre l'Università di Parma, Italie, où les enrobés ont été conçus et préparés, et l'ENTPE, où les matériaux ont été testés.

Pour la campagne 3, trois enrobés ont été conçus. Le Mix 1 correspond à l'enrobé de référence, sans plastique. Les Mix 2 et Mix 3 ont été élaborés avec 5 % de plastique en pourcentage du poids total de l'enrobé. La différence entre Mix 2 et Mix 3 réside dans la méthode d'incorporation. Dans le Mix 2, le plastique a été incorporé avec les granulats en supplément de la composition de référence (Mix 1). Dans le Mix 3, le plastique a été ajouté en fin de processus, tout en maintenant la même distribution granulométrique que celle de la référence.

Pour la campagne 4, la même méthode appliquée pour le Mix 3 a été utilisée pour produire un matériau contenant 2,5 % de plastique (Mix 4) et un second contenant 7,5 % de plastique (Mix 5). Pour les deux campagnes, les enrobés ont été préparés sous forme de plaques de 50 × 50 × 20 cm, et des échantillons cylindriques de 150 mm de hauteur et 75 mm de diamètre ont été extraits par carottage. Les essais ont été réalisés en traction-compression et en contrôle de déformation de -25 °C à 45 °C.

Le modèle 2S2P1D a été utilisé pour représenter le comportement des matériaux testés. L'utilisation d'un modèle mécanique pour simuler les résultats expérimentaux obtenus sur les matériaux permet d'obtenir des informations pertinentes sur leur comportement mécanique dans différentes conditions. De plus, l'application du même modèle aux liants bitumineux correspondants et aux enrobés aide à vérifier les relations entre le comportement de ces

matériaux à différentes échelles. Le modèle est une représentation bien établie des matériaux bitumineux (Di Benedetto et al., 2004). Il s'agit d'un modèle analogique viscoélastique linéaire (LVE) constitué d'un assemblage de deux ressorts (2S), de deux éléments paraboliques non linéaires (2P) et d'un amortisseur linéaire (1D).

8.3 Résultats

8.3.1 Résultats sur les liants bitumineux (CHAPITRE 5)

Dans le chapitre 5 sont présentés l'ensemble des résultats de la première partie du plan expérimental (campagnes 1 et 2). Les résultats ont été discutés séparément, puis les observations de chaque campagne ont été utilisés pour déduire des conclusions partielles.

La spectroscopie FTIR du bitume a montré des indications de la présence de certains composants des plastiques dans le bitume tamisé. Compte tenu de la possibilité de mobilisation et de mélange entre le plastique pur et le liant pur, il n'a pas été possible de déterminer précisément quels polymères ont migré vers le liant.

En relation avec les essais mécaniques de la campagne 1, il est possible d'observer que, indépendamment de la vitesse de mélange, une augmentation de la teneur en plastique entraîne une augmentation de |G*| à haute température/basse fréquence, sans différences significatives entre les courbes maîtresses des liants exposés à 5 % de plastique mélangé pendant 30 ou 60 minutes. De plus, des variations négligeables des courbes maîtresses de l'angle de phase φ ont été observées pour tous les liants exposés à 5 % de plastique par rapport au liant témoin.

Seuls les liants exposés à 20 % de plastique présentent des différences considérables par rapport au liant témoin, tant pour |G*| que pour φ. En effet, comme déjà remarqué lors de l'analyse du diagramme de Black, l'angle de phase du liant exposé à 20 % de plastique présente un comportement inattendu à haute température, ne montrant pas de tendance constante vers 90° avec l'augmentation de la température. Ce résultat indique un effet net de l'interaction entre le bitume et le plastique. Toutefois, il n'est pas possible d'exclure que l'impact observé sur les propriétés viscoélastiques linéaires du liant après exposition au plastique soit dû à la présence de particules de plastique dispersées qui ne s'intègrent pas à la structure du liant.

En passant à la campagne 2, il a été possible d'observer l'impact de l'interaction avec le plastique dans les différentes plages de température. De manière générale, une légère augmentation du module complexe a été constatée aux températures les plus élevées.

En comparant l'analyse du module complexe des bitume mélangés pendant 30 et 60 minutes, il est possible de supposer que le temps prolongé de mélange a favorisé une interaction plus forte entre le plastique et le liant, suffisante pour modifier sa rigidité à haute température, tandis qu'un mélange limité à 30 minutes n'a pas produit le même effet.

La courbe maîtresse de l'angle de phase du liant bitumineux exposé au plastique présente des valeurs de phi inférieures à celles du matériau témoin sur l'ensemble de la plage de fréquences considérée. À haute température, cette différence est apparue de manière encore plus marquée.

8.3.2 Résultats sur les enrobés bitumineux (CHAPITRE 6)

Au chapitre 6, les résultats obtenus à partir des essais sur les enrobés sont présentés. Chaque campagne est discutée séparément, et des analyses comparatives entre enrobés ont été réalisées lorsque cela était possible, en tenant compte des paramètres variables et de leur impact sur le comportement mécanique, tels que le pourcentage de plastique et le volume de vides.

Pour ce qui concerne la campagne 3, il a été possible d'observer que, indépendamment de la méthode d'incorporation, l'ajout de 5 % de plastique a entraîné une augmentation significative du la norme du module complexe et une diminution de l'angle de phase aux températures élevées. Cela constitue une indication de la possibilité d'un certain niveau de modification du liant dans les deux méthodologies. De plus, aux températures plus basses, la norme du module complexe a présenté une légère diminution.

En ce qui concerne la campagne 4, la variabilité de la compacité des enrobés testés s'est révélée être le facteur qui a le plus influencé les résultats obtenus. Cet aspect doit être pris en considération lors de la mise en œuvre de méthodes de construction incluant ce matériau alternatif.

8.4 Conclusions et Recommandations (CHAPITRE 7)

En se basant sur les objectifs établis au début de la recherche, plusieurs conclusions et recommandations ont été obtenues. Le chapitre des conclusions présente les observations et résultats correspondant à chaque objectif spécifique. Au total, la discussion a été organisée en quatorze points clés. Dans cette section de résumé, les conclusions ont été regroupées en deux points principaux :

i. L'interaction entre le bitume et le plastique était affectée par la vitesse et la durée de mélange mais surtout par la teneur en plastique ajouté. Le principal effet observé a consisté en une augmentation de la norme du module complexe du liant à haute température/basse fréquence.

ii. Les enrobés produits avec ajout de plastique ont montré une augmentation de la norme du module complexe à haute température et une légère diminution à basse température, en accord avec les observations faites pour les liants.

De plus, des recommandations pour les recherches futures ont également été discutées et présentées. Parmi elles, les trois principales sont :

i. Étudier comment l'interaction plastique-bitume se produit à l'intérieur des mélanges.

ii. Vérifier la maniabilité du RAP dérivé des mélanges produits avec du plastique recyclé.

iii. Évaluer la performance environnementale des mélanges modifiés.

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