LEIDY VANESSA ESPINOSA RUIZ

Analysis of bio-binders for paving as a total substitute for asphalt binder

São Paulo
2020

LEIDY VANESSA ESPINOSA RUIZ

Analysis of bio-binders for paving as a total substitute for asphalt binder

Original version

Thesis presented to the Escola Politécnica of the Universidade de São Paulo to obtain the degree of Master of Science.

Research area:
Transportation Engineering

Advisor:
Profa. Kamilla Vasconcelos

São Paulo
2020

Este exemplar foi revisado e corrigido em relação à versão original, sob responsabilidade única do autor e com a anuência de seu orientador.

São Paulo, 10 de setembro de 2020

Assinatura do autor: Leidy V. Espinosa Ruiz

Assinatura do orientador:

Catalogação-na-publicação

Espinosa Ruiz, Leidy Vanessa
Analysis of bio-binders for paving as a total substitute for asphalt binder / L. V. Espinosa Ruiz -- versão corr. -- São Paulo, 2014.
99 p.

Dissertação (Mestrado) - Escola Politécnica da Universidade de São Paulo. Departamento de Engenharia de Transportes.

1.PAVIMENTAÇÃO 2.REOLOGIA 3.SUSTENTABILIDADE 4.PAVIMENTOS FLEXÍVEIS 5.TERMOGRAVIMETRIA I.Universidade de São Paulo. Escola Politécnica. Departamento de Engenharia de Transportes II.t.

ESPINOSA RUIZ, L.V. Analysis of bio-binders for paving as a total substitute for asphalt binder. 2020. Thesis (Master of Science)- Escola Politécnica of the Universidade de São Paulo, São Paulo. 2020

Approved in

Examination commission

Profa. Dra. Kamilla Vasconcelos Savasini

Institution: Escola Politécnica da Universidade de São Paulo

Evaluation: Approved

Dra. Leni Figueiredo Mathias Leite

Institution: Universidade Federal do Rio de Janeiro

Evaluation: Approved

Profa. Dra. Lêda Christiane de Figueirêdo Lopes Lucena

Institution: Universidade Federal de Campina Grande

Evaluation: Approved

A mis padres y hermanas, por apoyar mis sueños, incluso
cuando eso nos llevó por caminos diferentes.

ACKNOWLEDGEMENTS

I would like to find enough words to thank my parents Aydee and Alejandro for the love and support that they have given me throughout my life, even when my decisions took me so far from home. They are my models of love, patience and integrity. A special thanks to my sisters, Lisney and Liany, who taught me that distance cannot break the ties of the heart. I feel so blessed because I am never alone, my family always celebrates each one of my little triumphs and suffers with me each difficult moment. My family love always reminds me that it does not matter if everything fails, I can always go back home. I would also thank Marcello, for always encouraging me to do my best, for his love, patience, support and for kindly enduring my mood swings during the making of this document and also feeding with wonderful food. I would also like to thanks Professor Allex Alvarez, that without his constant support and guidance, I would not have gotten to where I am today.

I would like to express my gratitude to Fernanda Gadler, who opened the doors of her heart, the doors of her home, and the doors of her family to me. Since the very first time I met her, she has been willing to give me a hand, teaching me how to speak ‘correct Portuguese’ and how to make brigadeiro. She was by my side during my most difficult moments in Brazil, she put me together when I felt the situation overwhelming me. *Senhora*, you deserve all the good things in life, God bless you forever. And it is thanks to her and to the undergraduate student and future engineer, Rafael Mota, that the extensive number of laboratory tests, material preparation and data analysis of this project was finished on time. Also thanks to Marcia and Iuri, for being willing to help, you always resolved every question about the tests procedures or every request for information, with a smile in your faces and with the words *vai dar certo*, when I needed.

I would like to thank my advisor, Professor Kamilla Vasconcelos, who is my model of how a professor should be, supportive, willing to listen, willing to teach. I thank her not only for the academic support but also for the human warmth that she shares with everyone around her. I would also to acknowledge Professor Liedi Bernucci for her constant encouragement, for the hard work that she does to keep the Laboratory of Pavement Technology-LTP running and for believing in my potential.

I would like to acknowledge to Greca Asfaltos and Quimigel, for supplying the materials tested in this thesis. Special thanks to Ingrid, for carrying out part of the tests, whose results are discussed here.

For the assistance with the material preparation, specimen compaction and laboratory test execution, a special thanks to Higor, Erasmo and Edson. I would also thank to Edson, Robson Iuri, and Marcia for their advice and constant guidance during tests execution and data analysis. For assistant with the monitoring of the experimental test site, special thanks to COPAVEL technical team, specially to Frederico.

I would like to thank to all my friends and colleagues from LTP that have contributed with this thesis: Diomária, Lucas Pereira, Edson, Robson, Erasmo, Higor, Fernanda Gadler, Laura, Frederico, Guilherme Castro, Julia, Talita, Zila, Marcia, Iuri, Lucas Andrade, André Rosa, Paulo, Marina, João Paulo Meneses, Beatriz, Gustavo, Raissa, Kamilla, Rosângela, and to those that are not more in the LTP but in some point were part of the team: Ingrid, José João, Rafael, Gabriel, Guilherme Pereira, Camila Christine, Fernanda Carvalho, Jõao Paulo Carvalho, Matheus, Kazuo.

For offering me a friendship full of joy and love and for making each day a new adventure, infinite thanks to *la muchacha,* Raissa, please, keep filling the world with your light.

Special thanks to Matheus for helping us to adjust the excel macro for the dynamic modulus calculation at the specific test conditions.

For the valuable discussion regarding thermo-gravimetric analysis and test execution, I would like also thank César, from PCC at PoliUsp.

Finally, I would like to thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) for the financial support.

RESUMO

Os bioligantes são ligantes ou óleos provenientes de biomassa de origem animal ou vegetal, que surgiram como materiais alternativos para reduzir a dependência da área da pavimentação no ligante asfáltico derivado de petróleo. As pesquisas em bioligantes têm focado na caracterização do material em termos de resposta mecânica em combinação com o ligante asfáltico. O caráter inovador dos bioligantes gera a necessidade de entender como seus componentes interagem e afetam o desempenho do material produzido para fins de pavimentação. Técnicas de caracterização aplicadas aos ligantes asfálticos, como a reologia e a avaliação de desempenho, têm sido utilizadas para avaliar o comportamento dos bioligantes e tem mostrado resultados benéficos para as misturas quando usados como extensores ou modificadores do ligante asfáltico convencional. Os bioligantes de origem vegetal, especialmente aqueles provenientes de madeira, tem apresentado um maior potencial para substituir totalmente o ligante asfáltico nas misturas para revestimento de pavimentos, quando comparados com aqueles provenientes de biomassa animal e óleos vegetais. Nesse sentido, esta dissertação apresenta a avaliação do potencial uso de dois bioligantes produzidos a partir de resíduos de madeira como substitutos totais do ligante asfáltico. Os materiais correspondem a duas gerações sucessivas do mesmo produto. O primeiro material foi avaliado em três escalas: comportamento do ligante, desempenho de misturas em laboratório e monitoramento em campo durante os primeiros três anos de vida de uma estrutura de pavimento com a camada de revestimento construída com esse material, comparando seus resultados com os de um ligante asfáltico convencional tomado como referência. Já o segundo bioligante foi avaliado na escala ligante, estudando seu comportamento reológico em comparação com um ligante asfáltico de referência e avaliou-se sua resposta quanto a resistência à deformação permanente e à fadiga, por meio dos ensaios MSCR e LAS, respetivamente. A análise termogravimétrica foi empregada para determinar a estabilidade térmica e os processos de deterioração dos ligantes envolvidos na pesquisa, e o efeito do envelhecimento foi avaliado por meio do acompanhamento de mudanças na reologia dos ligantes. A susceptibilidade ao dano por umidade desse bioligante foi avaliada com parâmetros baseados nas componentes da energia livre de superfície dos ligantes envolvidos na pesquisa com agregados de diferentes origens. Os resultados sugerem que os bioligantes estudados representam uma alternativa sustentável ao ligante asfáltico de petróleo, sem comprometer o desempenho mecânico das misturas para a construção de pavimentos flexíveis.

Palavras-chave: Bioligantes. Dano por umidade. Energia de superfície. Reologia. TGA. Monitoramento em campo.

ABSTRACT

The bio-binders are binders, or oils, made from animal or plant biomass, which have emerged as alternative materials to reduce the dependence of the paving area on the asphalt binder. Researches in bio-binders have been focused on characterizing the material in terms of its mechanical response when blending with asphalt binder. The innovative character of bio-binders generates the need to better understand how their components interact and how this affects their performance in pavement applications. The characterization techniques applied for asphalt binders, such as rheology and performance evaluation, are also used to evaluate the behavior of bio-binders and they have shown beneficial results for mixtures when used as extenders or modifiers of the conventional asphalt binder. The bio-binders from plant sources, especially the wood-based, have shown higher potential to total replacement of asphalt binder in mixtures, when compared with that binders from animal source or vegetal oils. In this context, this thesis presents the evaluation of the potential use of two wood-based bio-binders as total replacement of asphalt binders. The materials correspond to two successive generations of the same product. The first one was evaluated at three different scales: Binder behavior, mixtures performance in laboratory and field monitoring of a pavement structure build with that biomaterial, comparing their results with that of an asphalt binder taken as reference. The second bio-binder, on the other hand, was assessed on the binder scale, studying its rheological behavior in comparison with a reference asphalt binder. Its performance was evaluated in terms of resistance to permanent deformation and fatigue, using the MSCR and LAS tests, respectively. Thermogravimetric analysis was used to determine the thermal stability and the deterioration processes of the binders involved in the research. The aging effect was assessed by monitoring changes in the rheology of the binders. The moisture sensitivity of the binders was assessed through surface free energy (SFE) parameters, based on the SFE components of the binders and the aggregates from different origin. The results suggest that the studied bio-binders represent a sustainable alternative for the asphalt binder, for the construction of flexible pavements, without affecting the mechanical performance of the mixture.

Keywords: Biobinders. Moisture damage. Surface Free Energy. Rheology. TGA. Field monitoring

LIST OF FIGURES

LIST OF TABLES

TABLE OF CONTENT

1 INTRODUCTION AND BACKGROUND

1.1 INTRODUCTION

The 2030 Agenda for Sustainable Development, adopted by the United Nations (UN) members in 2015, is a universal and ambitious plan of action that seeks the equitable and sustainable human development, through goals that must be achieved by the year 2030 by all countries added to the plan. Economic development related to production capacity and raw materials availability, besides inherent social and political factors to human development, is also part of the proposed goals in the agenda. One of the targets of these goals is to ‘Improve progressively global resource efficiency in consumption and production and endeavor to decouple economic growth from environmental degradation’ (UN, 2015). In order to achieve that, it is necessary that all productive sectors of the country commit to the search for materials from renewable sources and the implementation of clean and environmentally friendly processing techniques.

The sector dedicated to the transformation and supply of energy stands out for its great social and environmental impacts. Currently, the world´s energy demand is mainly supplied by the petroleum and its derivatives. The processing of the crude results in the release of toxic substances and greenhouse gases emissions into the atmosphere, which, in addition to creating environmental imbalances, contribute to generates damage to the public health (CHEN et al., 2008). For this reason, Agenda goal 7 aims to increase the share of renewable energies in the global energy matrix, including concepts such as energy efficiency and advanced and cleaner fossil-fuel technology (UN, 2015).

In this context, research in generation of energy from alternative sources has gained interest worldwide, especially the production of fuels from biomass transformation processes (MACEDO; SEABRA; SILVA, 2008; RAGAUSKAS et al., 2014; SCHWAB et al., 1988). For this transformation, thermochemical processes are the main techniques (HOSSEINNEZHAD et al., 2016). This opened the door to the study of biomass processing in multidisciplinary fields, including the pavement area. As the case of the by-product of thermochemical processes of biomass studied by Dhasmana et al. (2015), which presented adhesive characteristics and chemical properties similar to those of a petroleum-based asphalt binder. This product, known as bio-binder or bio-oil, has potential use as partial or total substitute for asphalt binders in the construction of surface layers of flexible pavements.

Asphalt binder is the main pavement construction material in the world (AIREY; MOHAMMED, 2008), but it is also one of the most contaminants. Dorchies (2008) reported that extraction of the crude oil, its transportation and refining to produce 1 ton of asphalt, generates 285kg of greenhouse gases emissions, not to mention the energy consumption spent in the entire process. In addition, when heated to operating temperatures (165-175°C), asphalt binder releases vapors that contain toxic volatile components, affecting the health of workers.

With the purpose of reducing the environmental footprint of the paving activities, more sustainable technological solutions, with regard to construction systems, have been studied. Among the most explored techniques are the manufacture of warm mixes asphalt, the use of asphalt emulsion to cold mixes, foam asphalt for granular layers, rubber asphalt and the recycling of existent asphaltic layers. However, all the mentioned technologies make use of asphalt binder as the main product, even those that use recycled material as describe below.

In the recycling of surface asphalt layers, the damaged material - consisting of aggregates covered with asphalt and known as RAP - is recovered (milled) and used in new mixtures, adding virgin asphalt binder and aggregates. There are three approaches in the use of this material. In the first one, it is considered that there is no influence of the binder adhered to the recycled aggregate on the new mixture, being counted only as aggregate, known as 'Black rock'. In the second approach, ´partial blending´ part of the binder that cover the aggregate is blended with a new binder, which would reduce the virgin binder content to be added in the mixture. Finally, the 'full blending' approach considers that all asphalt binder from the RAP is mixed with the new asphalt binder, which further minimizes the consumption of virgin asphalt binder. It should be noted that the virgin binder, or recycling agent, to be incorporated is usually a higher penetration binder, which helps reduce the stiffness of the binder in the RAP that normally has advanced level of aging. In this sense, bio-oils may bring an attractive option in recycling due to the viscosity reduction of aged asphalt binders when used as modifiers (FINI; KALBERER; SHAHBAZI, 2011; MOGAWER et al., 2016).

From this perspective, the bio-binder and bio-oils production, besides of reducing the need for the area required for waste treatment (FINI et al., 2011), also reduces the consumption of asphalt binder, which represents an economic advantage, due to the high price of this material. The higher or lower reduction in the asphalt binder consumption is related to the approach of the bio-binder use. Researches in the area are focused in four perspectives: the first one is the total replacement of the asphalt binder in the mixtures. The second one is bio-oils as asphalt modifiers to improve binder workability and low temperature performance. Another focus is the partial replacement of the asphalt binder in the mixture to reduce the binder consumption, and finally, bio-binder as recycling agents in mixtures with high RAP content (DHASMANA et al., 2015; FINI; KHODAII; HAJIKARIMI, 2016; JIMENEZ et al., 2017a; RAOUF; WILLIAMS, 2010a).

The available literature shows that bio-modified asphalt and bio-binders generally have lower viscosity when compared with conventional asphalt binders. This reduced viscosity may increase the workability of the mixture at lower mixing and compaction temperatures than usual, which would reduce the aging of the binder and the greenhouse gases emissions.

It is worth to mention that the environmental gain of bio-binders is sustained by the fact that their raw material consists mainly of waste form other industries. This issue is fully aligned to the twelfth goal of the 2030 Agenda (UN, 2015), which includes sustainable production and focuses on substantially reducing the waste generation through prevention, reduction, recycling and reuse.

However, the fact that some bio-binders may have properties similar to conventional asphalt binders does not mean that they can be used as total substitute of asphalt binders. There are some restrictions such as the inherent variability in the type of biomass, the production method and the compatibility of the chemical components of the resulting bio-binder with the aggregates and modifiers (such as polymers) normally used in the construction of flexible pavements.

Czernik and Birgwater (2004) described bio-oils from plant origin as multicomponent mixtures of molecules of different sizes, derived mainly from depolymerization and fragmentation reactions of three essential components: cellulose, hemicellulose and lignin. Such chemical structure may interfere in the mixture with asphalt binder and aggregates. For example, Fini et al. (2017) compared the behavior of one bio-oil of plant origin, produced by pyrolysis, with a bio-oil product of the liquefaction of swine manure, both as asphalt modifiers. According to the authors, results showed that the bio-oil from animal source had more effect in the binder viscosity reduction than the bio-oil from plant origin.

Such behavior raises the problem of appropriate characterization methods for bio-oils and bio-binders to determine how it is possible to enhance their use. This would allow to determine whether certain bio-oils have greater advantage when used as asphalt modifiers, as partial substitutes of asphalt binder, as a total replacement or as a recycling agent.

This thesis is framed in the study of bio-binders and their use in road paving, within the scope of sustainability, with the objective of evaluating the performance of three wood-based bio-binders, two of them for total replacement for the asphalt binder and the last one as a recycling agent to interact with an aged asphalt binder.

1.2 BIO-BINDER PRODUCTION: METHODS AND PATENTS

The main thermochemical processes for the production of binders from biomass are liquefaction and pyrolysis. Nevertheless, there are research works using other methods to obtain bio-binders, for instance, Xu, Wang and Zhu (2017) added wood lignin powder to modified and unmodified asphalt binders, thus creating bio-modified asphalts. The choice of the production method to be used will depend on the type of biomass to be processed (DHASMANA et al., 2015; HOSSEINNEZHAD et al., 2016).

Pyrolysis consists of the thermal decomposition of a given biomass, in the absence of oxygen (BRIDGWATER, 2012; YANG; MILLS-BEALE; YOU, 2017). The fast pyrolysis, the most used for bio-binders from plant sources, occurs at moderate temperatures, with high rate of heat transfer to the biomass particles and a short time of hot vapor remaining in the reaction zone (CZERNIK; BRIDGWATER, 2004). The raw material to be used in this process must be free of moisture, requiring in many cases a pre-treatment of the sample to reduce its residual moisture.

Liquefaction consists of breaking bonds in the components of the biomass by subjecting it to pressures from 5 to 15MPa at high temperatures. This would induce the formation of new molecules, resulting in the formation of a gaseous fraction and a liquid fraction (DHASMANA et al., 2015; FINI; KALBERE; SHAHBAZI, 2011). This method allows the treatment of raw material with high moisture content, suitable for biomass such as swine manure, which have a large amount of water in its components.

There are few granted patents of bio-binder or bio-oils as partial or total substitute for asphalt binder. Around the world, there are commercial products with this purpose such as SYLVAROAD by Kraton Corporation, Vegecol® by Colas S.A, GEO320 by Ecopave Australia (LENNOX; MACKENZIE, 2008; NEWMAN et al., 2012), and Biophalt® by EIFFAGE Travaux Publics Research Center in France (POUGET; LOUP, 2013).

The existent patents and the current patents request are concentrated in products to be used as bio-modifier and partial substitute of asphalt binders, with the main purpose of improving the mechanical behavior and the durability of that material. For example, the product developed by White and Cooper (2001) is a thermoplastic bio-modifier that enhances the performance of the asphalt binder, mainly regarding the fatigue cracking resistance of the pavement surface layer. The bio-modifier is obtained from the liquefaction of the biomass and the patent defines the dosage to be incorporated in the asphalt concrete. The result of the combination is a homogeneous mixture with greater durability to weathering and higher fatigue cracking resistance. Another product patented by the same authors (WHITE; COOPER, 2008) is a bio-modifier with applications in pavements and cover materials and/or waterproofing system. According to the authors, production of the material has low cost, which allows the large-scale production.

The patent filed by Huang et al. (2015) presents a method to obtain a bio-modifier for the asphalt binder. The bio-modifier content is up to 20% by weight of asphalt binder. As advantages, that product generates an improvement in the asphalt binder thermal susceptibility and an increase in resistance to permanent deformation, moisture damage and cracking of the hot mix asphalt.

Owerhall (2016) patented a total substitute of asphalt binder. The bio-binder, that it is called in the patent as ´bio bitumen binder´, can vary in composition in order to achieve products with multiple penetration and hardness values, that present mechanical and rheological properties similar to the asphalt binder, when tested under Australian Standard AS 2008 and applicable specifications (OWERHALL, 2016).

In Brazil, a patent request was filed by Quimigel in 2016, referring to an invention of bio-binders with applications on paving. The material is from renewable sources, composed of at least one resin of plant origin and is used as partial or total replacement of asphalt binder, in the construction, maintenance and waterproofing system of any type of pavement surface (QUIMIGEL, 2016).

1.3 EFFECT OF THE BIOMASS SOURCE AND TYPE

As mention above, the type of biomass used in the production of bio-binders and bio-oils directly affects its behavior. The literature shows that bio-oils from the processing of swine manure tend to reduce the viscosity of the asphalt binder in a higher degree, when compared with bio-oils of plant origin (POURANIAN; SHISHEHBOR, 2019). However, a common aspect of bio-binders from different sources is the large amount of functional groups with oxygen among their components, which differentiates them from petroleum-based asphalt binders and may change the material´s stability (CZERNIK; BRIDGWATER, 2004; POURANIAN; SHISHEHBOR, 2019).

In the following sub items, different research developed to evaluate the bio-binders behavior are described. The studies are grouped according to the main sources of bio-binders: wood and plant materials, swine manure and waste cooking and vegetable oils.

1.3.1 Bio-binders produced from wood and plant materials

Wood and plant materials represent an attractive resource for the production of bio-binders due to the possibility of using waste or by-products from industries that already process these materials. Raouf and Williams (2009) used the pyrolysis product of oak flour, switchgrass, and corn stover as a total substitute of asphalt binder. The authors measure the viscosity of the bio-binders at different temperatures and time intervals. Results suggest that a pretreatment of the studied binders is necessary due to the increase in temperature and the consequent significant formation of vapors, which indicates the presence of water and volatile elements in those binders. In Raouf and

Williams (2010b), it was determined that, even after the pretreatment (which consisted of heating the material at 110°C for two hours), there is a higher susceptibility to the temperature variation in the bio-binders when compared with asphalt binders.

In Chailleux et al. (2012) a by-product of the microalgae production was chemically modified in order to be used as a total substitute of the asphalt binder. The binder test results showed the potential use of the bio-binder, presenting a rheological behavior similar to a neat asphalt binder. The processing of lignin and cellulose, natural tree and gum resins (ECOPAVE AUSTRALIA, 2009), sugarcane bagasse, corncobs, and rice husk (CARO et al., 2016) as asphalt modifiers, have also shown acceptable values of resistance to permanent deformation and fatigue in addition to increasing the asphalt binder stiffness.

Yang and Suciptan (2016) observed the behavior of a bio-oil from Japanese cedar as partial substitute for the asphalt binder. The bio-oil was added in 25% and 50% by weigh of binder and the viscosity and permanent deformation susceptibility of the bio-asphalt were evaluated. The authors conclude that the addition of bio-oil increased the viscosity of the asphalt binder, indicating that the bio-asphalt resulting would have higher mixing and compaction temperatures, when compared to unmodified asphalt binders. The results of permanent deformation test were more promising. The non-recoverable compliance (Jnr), which is the physical inverse of stiffness, decreased with the addition of bio-oil, while the elastic recovery increased. These outcomes indicates that the bio-oil decreased the susceptibility of the base asphalt to permanent deformation.

On the other side, the chemical analysis developed by Yang, You and Mills-Beale (2015) in a bio-asphalt made from the blend of a PG 58-28 asphalt binder and a bio-oil produced from waste wood, showed a significant loss of mass during the aging of the material. That points to the existence of light elements in bio-binders. In addition, the authors found that the bio-asphalt was more susceptible to aging when compared with the neat asphalt binder, which is consistent with the results found by Camargo, Bernucci and Vasconcelos (2019), Dalmazzo et al. (2020), Dong et al. (2018), Tang and Williams (2009) and Yang, Mills-Beale and You (2014).

The studies carried out by Peralta et al. (2012a) and Zhang et al. (2017) evaluated the behavior of bio-binders when combined with usual modifiers in road paving, such as polymers and tire rubber, finding good performance of the bio-binders with these additives.

Regarding to mixtures, Mohammad et al. (2013) and Yang et al. (2014) presented contradictory results of fatigue life. Mohammad et al. (2013) found that the addition of 50% by weight of asphalt of a bio-oil, obtained from pyrolysis of pine wood, in a PG 58-28 asphalt binder, increased the permanent deformation resistance of the mixture, but reduced the fatigue life, when compared with the reference asphalt mixture. In contrast, Yang et al. (2014) concluded that the addition of a bio-oil, also from pyrolysis of waste wood, in 5% by weight of asphalt, in a PG 58-28 asphalt binder, improved the fatigue life, but reduced the permanent deformation resistance of the mixture. Although the dosages of bio-oil in both studies were very different, the contradiction in the behavior of the mixtures raises the problem of standardizing methods of production of bio-binders and bio-oils.

Another use of bio-binders is as rejuvenator and extensor of the asphalt binder from the reclaimed asphalt pavement (RAP) in recycled asphalt mixtures (BLANC et al., 2019). The results presented by Jimenez et al. (2017b) and (2019) showed the potential of binders from biomass as a new binder to be incorporated into mixtures with high RAP content, although the authors are concerned about verifying the durability of the recycled mixtures with this material.

1.3.2 Bio-binders produced from swine manure

In 2010, Fini; Yang and Xiu presented results from the study on the implementation of a binder produced from the liquefaction of swine manure, as a partial or total substitute for asphalt binder in asphalt concrete. The use of this type of material would help to reduce the contamination of air and groundwater associated with the final disposal of this waste in treatment ponds. In 2011, Fini et al. present a chemical analysis of this material, highlighting the high amount of oxygen and nitrogen between its compounds when compared with neat asphalt binders. Fourier transform infrared spectroscopy (FTIR) and determination of saturates, aromatics, resins, and asphaltenes (SARA) fractions showed that the bio-binder studied had a low concentration of saturates and aromatic naphthene when compared with the asphalt binder. This indicates that bio-binder is mainly composed of resins, polar aromatics and asphaltenes, results that are in agreement with Miao and Wu (2004).

Regarding viscosity, Mills-Beale et al. (2012) and Onochie et al. (2013) found that the addition of bio-binder made from liquefaction of swine manure reduces the viscosity of the bio-modified asphalt binder. It was also found that the Superpave parameter for permanent deformation, $G^*/\sin\delta$, of the PG 64-22 asphalt binder used as the base binder, increased with the addition of the bio-binder (MILLS-BEALE et al., 2012). This suggests that this kind of binder would perform well at high temperatures. Onochie et al. (2013) evaluated the addition of nano-particles of clay to the bio-modified asphalt (PG 58-28 base binder) which also produced an improvement in the binder properties at high temperatures and reduced the effect of the bio-oil in the viscosity of the bio-modified asphalt.

According to Fini et al. (2017), in addition to the reduction in viscosity, the bio-binder from the liquefaction of swine manure also contributes to the reduction of the aging effect in asphalt binders, since the bio-modified asphalt presented lower stiffness after aging when compared with neat asphalt binders.

Recycled mixtures made with bio-modified asphalt and high RAP content (i.e., >30%), showed workability similar to the conventional asphalt binder mixtures (HILL et al. 2013; MOGAWER et al., 2012). Results indicate that the high stiffness of the binder from RAP is counterbalanced with the addition of the bio-binder, resulting in mixtures with good performance against fatigue and permanent deformation (MOGAWER et al., 2012).

From the mentioned above, bio-binders produced with swine manure are efficient in reducing the viscosity of asphalt binders and thus, reducing the mix and compaction temperatures of asphalt mixtures. In addition, they are good candidates as a new binder or modifier of virgin asphalt binder in recycled mixtures. In environment terms, this represent four advantages: (*i*) reduction of energy consumption for heating aggregates and binders in the production and compaction of asphalt concrete, (*ii*) reduction in the emission of greenhouse gases by reducing the mix and compaction temperatures, (*iii*) reuse of RAP material, and (*iv*) appropriate reuse of swine manure.

1.3.3 Bio-binders produced from waste cooking and vegetable oils

The preparation of some foods for human consumption requires the use of oils, mostly vegetables, which are discarded after use. In the quest to reduce the contamination of water sources with these residues, and with the success of incorporating alternative materials in the asphalt mixtures, the paving road researchers have applied techniques to produce bio-binders from these waste oils.

Wang et al. (2018) assessed the chemical and rheological properties of a neat asphalt binder (Pen 60/80) modified by bio-oil from waste cooking oil. Results of fatigue test showed an increase in the fatigue resistance of the bio-modified binder when compared with the neat asphalt binder. Similar to this study, Cao et al. (2018) evaluated the same properties for an asphalt binder rejuvenated with waste vegetable oil, where in addition to the exponential increase in the fatigue life of the rejuvenated material, it was found a rise in the workability of the binder due to the reduction in viscosity caused by the bio-oil.

Gong et al. (2016) compared the effect of adding bio-oil from waste cooking oil, also used for production of biodiesel, in a neat asphalt binder of Pen 50 and in an asphalt binder modified by polymer (SBS). The chemical analysis determined that the bio-oil may not favor resistance to moisture damage due to its solubility in water.

Wen, Bhusal and Wen (2013) evaluated the performance of hot mix asphalt bio-modified with a thermochemically processed cooking oil, using three base asphalt binders (PG 58-28, PG 76-2 and PG 82-16) and basaltic aggregates. The dynamic modulus master curves and the flow number indicated that by increasing the percentage of bio-oil in the mixture, it reduced its stiffness and increased the susceptibility to permanent deformation while improved resistance to low temperature thermal cracking.

1.4 TECHNIQUES USED TO CHARACTERIZE BIO-BINDERS

As innovative materials, there is not characterization methods specifically formulated to be applied on bio-binders. However, the similarity in some properties with asphalt binders encourage the use of characterization techniques commonly used with those materials. Along this thesis, tests of rheological, mechanical and thermal characterization were used in order to better understand the behavior of the bio-binders. This section will introduced those tests and mention others found in the literature, grouped by binder scale evaluation, mixture evaluation and finally, field evaluation.

1.4.1 Binder scale evaluation

Although conventional characterization tests, such as penetration and softening point, have been used to characterize bio-binder, the research is moving to more fundamental techniques, used to determine the rheological properties of the binders. The dynamic shear rheomoter (DSR) is one of the most used equipment that performs oscillatory tests to determine the linear viscoelastic properties of binders, mainly the dynamic shear modulus, $|G^*|$, and the phase angle, δ (AIREY; HUNTER; RAHIMZADEH, 2002), along with performance tests related to the most common distresses found in the asphalt pavements.

According to Airey, Hunter and Rahimzadeh (2002), $|G^*|$ could be defined as the total resistance of the sample to deformation when subjected to shear loading. The phase angle can be defined as the delay between the applied loading and the response to this load. When δ is equal to 0°, the material may behave similarly to a solid elastic, when δ is 90°, the material could present behavior of a viscous liquid (LAVIN, 2003). Asphalt binders and also the bio-binders previously tested phase angles vary between those magnitudes at standard field applications. The variation of the dynamic shear modulus (or phase angle) with the frequency are plotted for each temperature and then, master curves are constructed at the reference temperature, based on the time-temperature superposition principle (AKCELRUD, 2007).

Viscosity test also have been used to characterize and compare bio-binders with asphalt binders (FINI et al., 2017; XU; WANG; ZHU, 2017; YANG; SUCIPTAN, 2016). This test assesses the workability of the binder to determine the temperatures at which it has adequate consistency to be mixed with the aggregates and compacted (BERNUCCI et al., 2008; KIM, 2009).

The DSR can also be used to evaluate the resistance of the binder to permanent deformation and fatigue (KIM, 2009). The Multiple stress creep and recovery (MSCR) test was proposed as a test to determine the susceptibility to permanent deformation of binders. The procedure consists of the application of thirty cycles of loading, where in each cycle the sample is loaded at constant stress for 1s, then allowed to recover for 9s. Twenty creep and recovery cycles are run at 0.100 kPa creep stress followed by ten creep and recovery cycles at 3.200 kPa creep stress (ASTM 7405-15). From the test it is possible to determine the non-recoverable compliance (Jn_r) and the recovery (R) values. The higher the Jn_r, the higher the binder susceptibility to permanent deformation.

In regard to fatigue, the linear amplitude sweep (LAS) test have been commonly used due to its reduced testing time. LAS test was proposed by Johnson (2010), improved by Hintz et al. (2011) and have been modified since them. The procedure consists of the application of cycling loading, considering a progressive increase in the loading amplitude, which contributes to accelerate the fatigue degradation process of the material. The test is divided into two stages: the first one is a frequency sweep from 0.2Hz to 30Hz, keeping constant the deformation rate of 0,1%, to obtain linear viscoelastic properties of the undamaged binder. The second stage is an amplitude sweep test, where the frequency is kept constant at 10Hz, and for each loading cycle the deformation rate applied progressively increases by 1% until reaches 30%. The continuum damage approach is used to calculate the fatigue resistance from linear viscoelastic properties and amplitude sweep results (AASHTO TP 101-14).

Regarding to thermal cracking, the used of a bending beam rheometer (BBR) is very common. Fini et al. (2012), Mills-Beale et al. (2012) and Wen, Bhusal and Wen (2013) used BBR to determine the thermal cracking susceptibility of bio-asphalts and bio-modified asphalts, while Aflaki et al. (2014) used it to compare the effect of bio-oil with other asphalt modifiers on low-temperature characteristics of the asphalt binders. However, it was not found literature of thermal cracking evaluation of bio-binders as total replacement of asphalt binders.

The thermo-gravimetric analysis (TGA) have been recently applied to study the thermal stability of bio-modified asphalt (ALAMAWI et al., 2019; DA COSTA et al., 2020). The TGA is a technique in which the weight loss or gain is determined as a function of temperature at a given thermal procedure (CINCOTTO, 2014). From this procedure, it is possible to elaborate thermo-gravimetric (TG) curves, which allow the identification of the changes that heating can cause in the mass of substances. In TG curves it is possible to determine the temperature range of degradation, monitor the progress of reactions of dehydration, oxidation, among others (CANEVAROLO, 2003).

The first derivative of the TG curve is called the DTG curve. This type of curve allows the determination of the temperature where the rate of mass variation is maximum. In addition, in a DTG curve it is possible to separate reactions that appear overlapping in a TG curve, identifying the temperature where a reaction ends and the next starts.

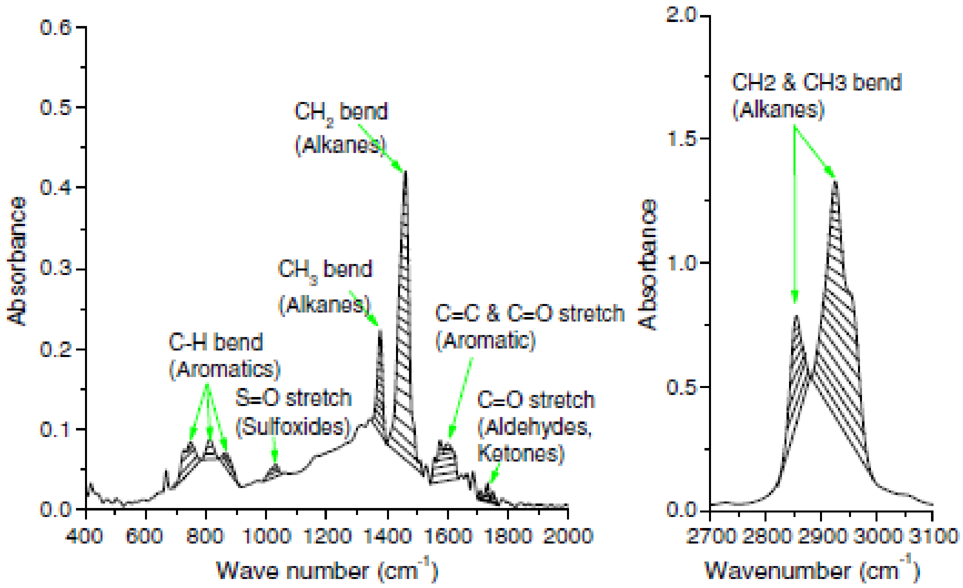
As a complementary analysis, the differential scanning calorimetry (DSC) provides information on the type of reaction that occurs in the material during the test. It determines the amount of heat required in the exothermic or endothermic transformations that take place in the sample during the test (CINCOTTO, 2014).

Probably, one of the most used chemical technique to evaluate bio-binders is the Fourier transform infrared spectroscopy (FTIR). The FTIR have been widely used to evaluate the effect of aging in asphalt binders (LAMONTAGNE et al., 2001; DE SÁ ARAUJO et al., 2013; SOARES et al., 2004) and now it is used to evaluate the effect of the addition of bio-oils and bio-binders in the aging characteristics of asphalt binders (FINI et al., 2017; QU et al., 2018; XU; WANG; ZHU, 2017; YANG; YOU; MILLS-BEALE, 2015).

The FTIR permits the identification of different molecular groups that are associated with well-defined wave amplitudes in an absorbance spectrum. In the test, infrared radiation is directed to a sample placed on a medium of high refractive index (optically dense crystal). Under these conditions, the incident radiation is fully reflected in the sample-crystal interface, producing a wave that penetrates a few microns beyond the surface of the sample in direct contact with the crystal. From de interaction between the wave and the sample, it is possible to obtain the infrared spectrum (KHOSHHESAB, 2012).

Based on the spectrum of an asphalt binder sample, the carbonyl and the sulfoxide indexes (related with the oxidation of functional groups present in the sample) can be computed (LAMONTAGNE et al., 2001; LU; ISACSSON, 2002). The change in sulfoxides is related to short-term aging (during mixing and compaction), while changes in carbonyls group are associated with long-term aging (during service life of the mixture) (MOUILLET et al., 2008; SIDDIQUI; ALI, 1999). Figure 1 presents a typical infrared spectrum of a neat asphalt binder, pointing out the bands or regions where the aging is analyzed.

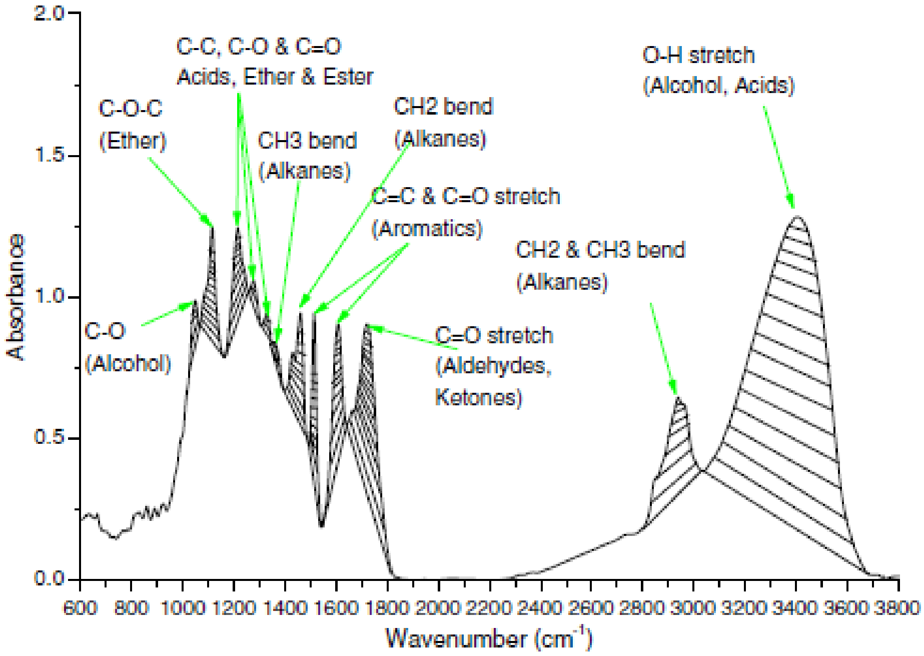
Figure 1– Infrared spectrum of an asphalt binder.



Source: Yang, You e Mills-Beale (2015)

However, Camargo, Bernucci and Vasconcelos (2019) and Dalmazzo et al. (2020) found that the carbonyl and sulfoxide indexes for bio-binders did not show the same tendencies observed for the asphalt binder as the aging increase, suggesting different aging mechanisms. According to some researches (CZERNIK; JOHNSON; BLACK, 1994; DIEBOLD, 2000; YANG; MILLS-BEALE; YOU, 2014), the oxidation in bio-binders is characterized by an increase in the concentration of carbonyls, ester and ether. Yang, You and Mills-Beale (2015) suggested the computation of the Aromaticity, C-O bond, CH_2 bond, and CH_3 bond indexes, bands presented in Figure 2.

Figure 2 – Infrared spectrum of a bio-asphalt binder.



Source: Yang, You and Mills-Beale (2015)

1.4.2 Mixture evaluation

The response of asphalt mixtures to stress and strain conditions simulated in laboratory test, provide parameters that can be used in pavement prediction models to determine the answer of the surface layer to fatigue and permanent deformation (ROMERO; MASAD, 2001). The viscoelastic properties of the binder are transmitted to the mixture, creating a dependency of their performance on the temperature and loading test conditions (KALOUSH; WITCZAK; SULLIVAN, 2003).

In viscoelastic materials, the lower the temperature, the less significant the viscous behavior will be and the mixture will behave more like an elastic solid. On the other hand, with the increase in temperature, the viscous portion becomes more dominant and the material acquires a viscoelastic or even viscoplastic behavior (SILVA; SILVA; FROTA, 2014). The loading time has also an important influence in this type of material. A short load (simulating a higher track speed, for example) is less significant than the same load applied for a longer time, and this will influence the determination of the material's response. From this, one can conclude that there is not a single value capable of completely characterizing the stiffness of viscoelastic materials. Thus, temperature and loading frequency must be taken into account in order to determine that parameter. Dynamic modulus (DM) test is one tool for this.

The DM test consists of the application of sinusoidal loading in a specimen, at different temperatures and load frequencies, in order to assess the material viscoelastic properties of modulus and phase angle. There are different specimen geometries for the test, but the most frequent DM test is conducted in cylindrical specimen, under cyclic uniaxial compression stress-controlled condition. Based on this, cylindrical specimen tests have been commonly used to determine the properties of bio-binder produced mixtures (MOGAWER et al., 2016; WEN; BHUSAL; WEN, 2013).

The evaluation of pavement distresses such as permanent deformation and moisture damage are also important to predict the performance of the mixture during the service life of the pavement structure. There are many procedures and equipment to determine the permanent deformation of asphalt mixtures, must of them simulate the traffic conditions in critical temperatures and test environments (such as presence of water), they are known as rutting tests. However, there are other kind of test, such as flow number, where repeated compressive axial load is applied at a specific test temperature, until the permanent axial strains reach the lowest minimum rate of the specimen (FHWA, 2013).

The rutting test using the Laboratoire Central des Ponts et Chaussés (LCPC) traffic simulator consists of the passage of a tire, applying a load into de surface of an asphalt mixture plate, at a temperature of 60°C and frequency of 1Hz. As the load passes over the plate, measurements of rut depth are taken at 100, 300, 1.000, 3.000, 10.000 and 30.000 cycles.

Rutting test are most common in mechanical characterization of mixtures containing bio-binders (BLANC et al., 2019; DONG et al., 2018; MOGAWER et al., 2016; ZHANG et al., 2017), while flow number is less popular, but also used (BLANC et al., 2019; WEN; BHUSAL; WEN, 2013)

Regarding to moisture susceptibility, most of the test consist of comparing the response of specimens exposed to the action of water with the response of unconditioned specimens, in order to determine the moisture effect in the parameter evaluated. One type of test used is the indirect tensile strength of the conditioned and unconditioned compacted samples (HICKS, 1991)

Jimenez et al. (2019) used Surface Free Energy and Pneumatic Adhesion Tensile Test Instrument (PATTI) to assess the moisture damage sensitivity of recycled mixtures rejuvenated with bio-binders from plant resource. Mogawer et al. (2016) carried out rutting test in the presence of water to determine the moisture susceptibility of mixture containing bio-binder. Dong et al. (2018) used the Immersion Marshall and freeze-thaw split test. Those studies focuses in the bio-modification of asphalt mixtures and there is a lack in the literature of studies characterizing this phenomenon in bio-binder as total replacement.

1.4.3 Field evaluation

There is no experience in field application of bio-binders as 100% replacement of asphalt binder reported in the literature. A full scale validation was made in bio-recycled asphalt mixtures (BLANC et al., 2019), where the structural health of the pavement sections was monitored through periodic falling weight deflectometer (FWD), as well as with strain gages and temperature sensors.

The FWD test consists of analyzing the recoverable vertical displacements (called deflections) at the pavement surface when subjected to a specific load. The purpose of this evaluation is to indirectly asses the load capacity of the pavement structure, and it also permits to infer properties, such as stiffness or resilient modulus and Poisson coefficient, of the structure layers.

On the other hand, the functional evaluation of pavement structures in the field is made with the International roughness index (IRI). Pavement roughness is defined as an expression of irregularities in the pavement surface that have a negative effect in the ride quality of a vehicle (and thus, the user). These monitoring techniques may offer interesting information about the behavior of the mixtures made with bio-binders during their service life.

1.5 OBJECTIVES

The main objective of this study is to evaluate the feasibility of using wood-based bio-binders in road paving projects, as a substitute for conventional asphalt binder, by characterizing their rheological and mechanical behavior.

In order to achieve the main objective, the following specific objectives were set:

- Verify the applicability of traditional asphalt binder Performance Grade (PG) specification to characterize the rheological behavior of wood-based binders (bio-binders).
- Determine the moisture susceptibility of the bio-binder based on energy parameters computed from the surface free energy of binders and aggregates.
- Compare the response of bio-binders with the response of petroleum-based asphalt binders in binder and mixture laboratory tests and field application and monitoring.

1.6 THESIS OUTLINE

This thesis is organized in five chapters:

Chapter 1 presents an introduction and a brief background of bio-binders, including a description of their behavior according to the source and production methods found in the literature available. This chapter also contains the general and specific objectives and the thesis outline.

Chapter 2 presents the assessment of one bio-binder (BioA) as an alternative for total replacement of the asphalt binder, including three levels of evaluation: binder and mixture laboratory tests and field application and monitoring of an experimental test site, with one section built with the bio-binder and another one constructed with a hot mix asphalt taken as reference. With some modifications, chapter 2 was submitted to evaluation in an indexed journal. The authors of the paper are Leidy V. Espinosa, Fernanda Gadler, Rafael V. Mota, Frederico V. Guatimosim, Ingrid Camargo, Kamilla Vasconcelos, Rodrigo M. de V. Barros, Liedi L. B. Bernucci.

Chapter 3 presents the analysis of a second bio-binder (BioB) compared with a neat asphalt binder. BioB is the optimized generation of BioA. The discussion focused in the binder laboratory test results. A version based on chapter 3 was accepted in the event ISBM Lyon 2020: International Symposium on Bituminous Materials to be held in Lyon, France at the end of 2020. The authors of the paper are Leidy V. Espinosa, Fernanda Gadler, Rafael V. Mota, Kamilla Vasconcelos, Liedi L. B. Bernucci. A summarized version of this chapter was submitted to the 9th European Asphalt Technology Association (EATA) Conference, to be held in Vienna, Austria in 2021.

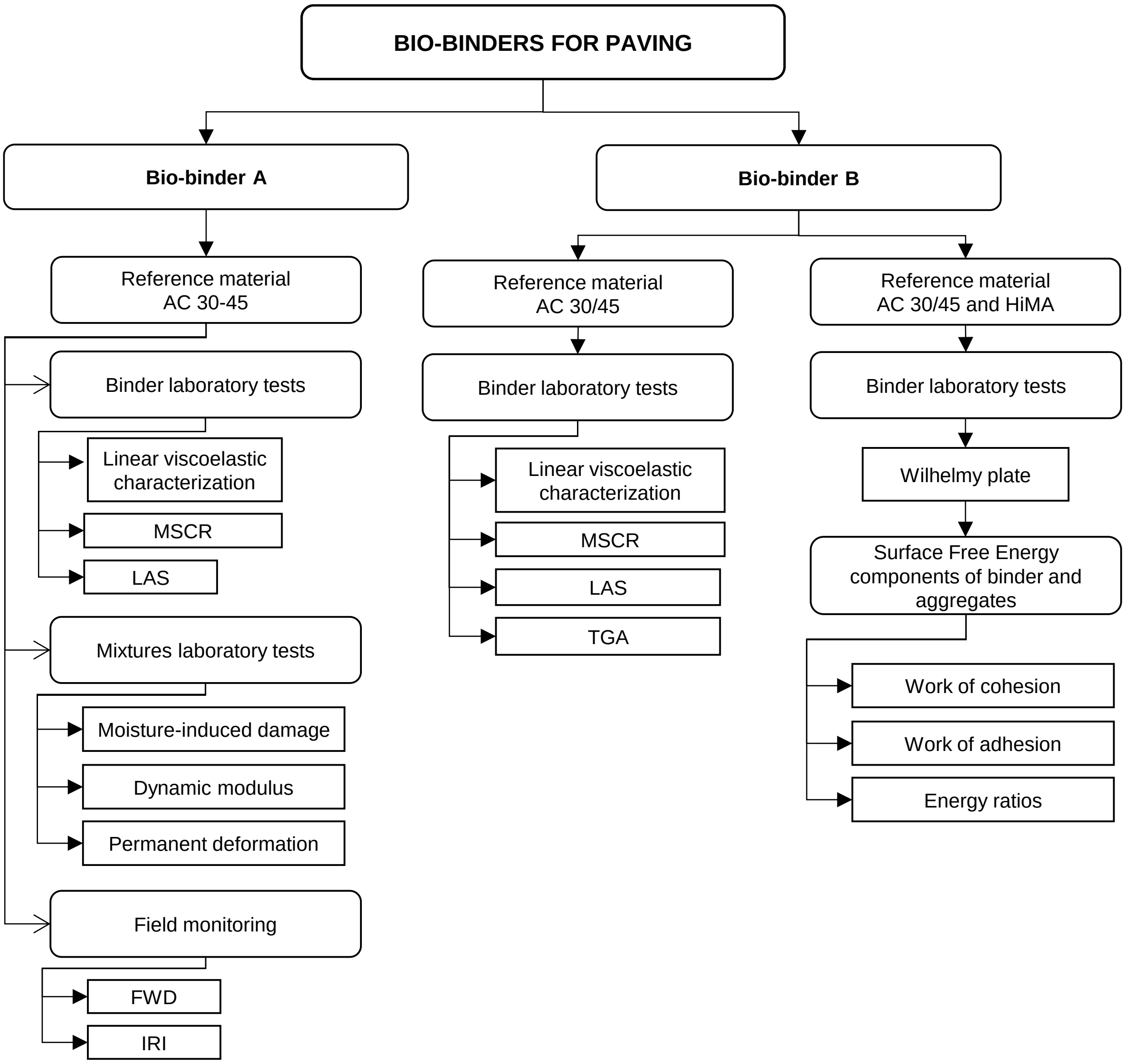
Chapter 4 presents the evaluation of the moisture damage susceptibility of the BioB when compared to a neat asphalt binder and a highly modified asphalt binder. The Surface Free Energy components of the three binders are combined with seven aggregates from different origins and several energy parameters are computed and compared to assess the moisture sensibility of the materials studied.

Finally, Chapter 5 presents the conclusions and recommendations for future work.

Some information may be repetitive from Chapter 2 to Chapter 4, especially for test section details and materials. This was necessary since the chapters were written in the technical paper format and used the same methods to assess the materials.

In order to better picture the thesis organization, Figure 3 shows the flowchart of the study, including materials and tests. The bio-binders involved in this study are from plant sources, a neat asphalt binders and a highly modified asphalt were used as reference materials.

Figure 3 ─ Flowchart of the thesis.



Source: Author (2020)

1.7 STUDIED MATERIALS

Literature review showed that wood-based bio-binders have a better potential to be used as total or partial substitute for asphalt binders (CAMARGO; BERNUCCI; VASCONCELOS, 2019; POUGET; LOUP, 2013; YANG; SUCIPTAN, 2016; YANG; MILLS-BEALE; YOU, 2017). Additionally, when used as fresh binder in mixture with high content of reclaimed asphalt pavement in recycled mixtures, bio-binders from pine resin have shown good performance in terms of permanent deformation, fatigue (JIMENEZ et al., 2017a) and moisture damage susceptibility (JIMENEZ et al., 2019).

For these reasons, in this study, two Brazilian produced wood-based bio-binders were evaluated and compared with an asphalt binder of penetration grade 30/45 (AC 30/45) and an asphalt binder highly modified by polymer (HiMA), taken as reference materials.

The bio-binders, named BioA and BioB, correspond to two generations of the same product. The Brazilian company Greca Asfaltos in partnership with the chemical industry Quimigel supplied both binders, developed from by-products of the treatment of pine wood resin. The final product is not yet commercial and the patent has been required. Therefore, the difference between both products remains unknown, however, the producers inform that they were combined with an elastomeric terpolymer (POLIMUL), and the reason of the modification is linked to the economic feasibility of the application of BioA and the search for improved properties. BioA was also studied in a previous thesis focused in their thermal susceptibility and the aging effect (CAMARGO, 2018).

Table 1 presents the conventional characterization of the binders involved in this study. The highly modified asphalt binder has thermoplastic elastomers (SBS) in its composition, however, the base asphalt is unknown.

Table 1. Conventional characterization of the binders studied.

Test/Standard		**BioA**	**BioB**	**AC 30/45**	**HiMA**
Penetration at 25°C (0.1mm)	ASTM D5 M - 13	21	29	25	45
Softening point (°C)	ASTM D36 M-14	57	55.2	55	84
Rotational viscosity at 135°C (cP)	ASTM D4402 M-15	638	572.2	361	2170

Source: Author (2020)

2 LABORATORY VALIDATION AND FIELD MONITORING OF BIO-BINDERS MIXTURES COMPARED WITH HOT MIX ASPHALT

2.1 INTRODUCTION

In this chapter, one bio-binder produced from vegetal biomass, by-product of the treatment of pine wood resin and used as 100% asphalt binder replacement was evaluated in terms of its rheological characteristics, as well as its mechanical behavior when combined with aggregates, and finally its performance in field application. The performance of the binder and mixture was assessed in laboratory and the behavior of the pavement structure was monitored in the experimental test site, located in a Brazilian Highway (BR-050/GO). The chapter compared the performance of the bio-binder with the performance of a neat asphalt binder used as the reference material. Hence, the contribution of this paper is to assess the feasibility of the bio-binder as an asphalt binder replacement, pointing the technical benefits when compared to the neat asphalt binder and presenting the potential limitations of its application.

2.2 BACKGROUND

Due to the innovative characteristics of bio-binders and the possibility of having different biomass sources, studies have focused on the rheological and chemical characterization of blending of asphalt binders with bio-binders. These studies aim to assess and predict their performance against the temperature and the traffic conditions imposed in the field during the material life cycle. Fini, Kalberer and Shahbazi (2011) studied a bio-oil produced from swine manure as a modifier of asphalt binder through its chemical and rheological characterization. The results showed that its use contributes in the binder's low temperature properties and the asphalt pavement construction costs.

Regarding to the performance of this type of materials, there is no consensus on the results. It depends on the type of biomass used and on the bio-binder or bio-oil proportions. Yang et al. (2014) studied mixtures manufactured with asphalt bio-modified with three bio-oils from waste wood resources at 5% and 10% by weight, the results showed that for all mixtures, the addition of bio-oil improved the fatigue performance. Nevertheless, the rutting performance could be negatively affected by the incorporation of the bio-oils (YANG et al., 2014). On the other side, He et al. (2019) also assessed and compared three different biomass sources (pine wood, willow wood and poplar wood) by means of their chemical composition. The authors found that the addition of the bio-binders to the neat asphalt can improve its high-temperature performance anti-rutting ability, whereas its low temperature anti-cracking ability is slightly harmed. This discordance on the results might be associated with the pre and post treatment of the bio-oil involved in each study.

The resistance to moisture damage of mixtures with bio-binders is another topic of concern. Some authors indicated that there are some compounds in bio-binders, especially those wood-based, that might have more affinity for water (MILLS-BEALE, 2013), or that there are soluble components in water (YANG et al., 2014). However, other authors found that the incorporation of bio-oils from waste wood could improve the moisture damage resistance of the mixture (HAJJ et al., 2013; MOHAMMAD et al., 2013). As mentioned before, the differences in the results are due to the various sources, different production methods and different dosages of bio-binder in the mixture.

In the literature available, there is no record of field performance of this type of materials. A full scale study related to the project Biorepavation by IFSTTAR in France with bio-binders as recycling agents (BLANC et al., 2019), shows the potential use of this type of material in the recycling of asphalt layers. There are also few studies about bio-binder as total replacement of asphalt binder. Chailleux et al. (2012) and Camargo, Bernucci and Vasconcelos (2019), presented an evaluation of bio-binder, at binder scale, and Pouget and Loup (2013) present results of mixtures with bio-binder. The results shown in those studies suggest that vegetable and wood sources might be more appropriate than animal and waste oil sources in order to produce bio-binder as 100% substitute of asphalt binder.

In this context, this chapter is aimed to present an evaluation of a wood-based bio-binder for total replacement of asphalt binder, presenting laboratory test results and field performance.

2.3 BINDERS EVALUATION

In this paper, two binders were studied. The first one is a neat asphalt binder, named AC 30-45 as a reference to its penetration specification. The second one is a bio-binder produced by a joint effort from Brazilian asphalt distributor Greca and chemical industry Quimigel. The bio-binder is produced from by-products of the treatment of pine wood resin combined with a terpolymer (POLIMUL), named BioA. Both binders were characterized by the standards for petroleum-based neat binders and the results are shown in Table 2.

Table 2 – Standard characterization of the binders studied

Test/Standard		AC 30-45	BioA
Penetration at 25°C (0.1mm)	ASTM D5 M - 13	25	29
Softening point (°C)	ASTM D36 M-14	55	52.5
Rotational viscosity at 135°C (cP)	ASTM D4402 M-15	361	572.2
Rotational viscosity at 155°C (cP)	ASTM D4402 M-15	127	262
Rotational viscosity at 177°C (cP)	ASTM D4402 M-15	53	86

Source: Author (2020)

2.3.1 Linear viscoelastic characterization

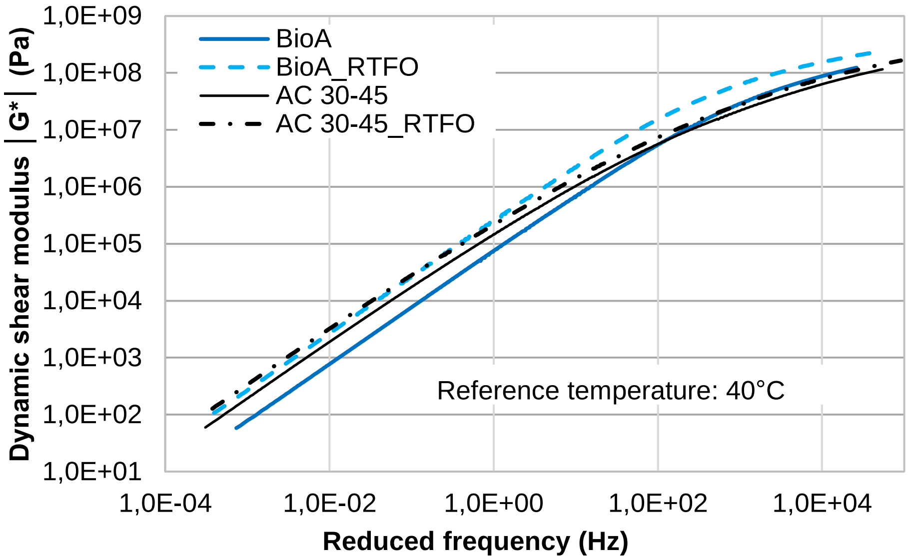
The AC 30-45 and the BioA were also characterized by their liner viscoelastic properties. In order to study and compare the effect of aging in both binders, the rheological behavior of the aged and unaged binders was assessed. The short-term aging process for both binders was simulated as described in the ASTM D 2872-2012, using the Rolling Thin Film Oven (RTFO) test.

Figure 4 shows the results of the Frequency Sweep test. The test was carried out with deformation rate of 0.01%, frequency between 1 and 100 rad/s, and test temperature from 10°C to 80°C. Three samples of each binder in each aging state were assessed. The master curves at the reference temperature of 40°C were constructed based on the time-temperature superposition principle.

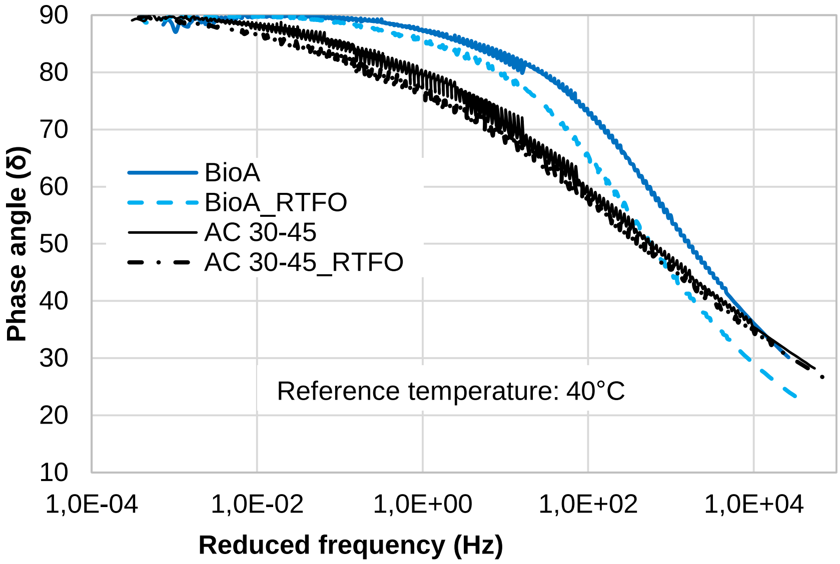
Results showed no considerable variation between samples of the same material and aging condition. Due to that, the Figure 4 presents the dynamic shear modulus-$|G^*|$ (Figure 4a) and the phase angle-δ (Figure 4b) master curves of one sample for each condition. The master curves of │G*│ suggest that the BioA presented similar behavior to that of the AC 30-45 in each aging condition. Nevertheless, the BioA exhibited a higher sensitive to the frequency/temperature changes. According to Da Silva et al. (2004), the difference in the slope on the │G*│ and the more abrupt decrease in the δ curve might be an indicative of the molecular weight distribution in the materials. The results in Figure 4 suggest that the BioA has a narrower molecular weight distribution than the AC 30-45 which might be an indicative that the bio-binder has a lower level of elasticity. That is also supported by the proximity of the phase angle curve of BioA to 90° (Figure 4b).

The short-term aging seems to have similar effect on both binders, the │G*│ increased and the δ decreased in the aged state. However, the modulus increase for the AC 30-45 was from 70% to 80% in low frequencies and from 20% to 40% in high frequencies, whereas for BioA the modulus increased by more than 150% in all frequencies. On the other hand, Yang, Mills-Beale and You (2017) found that wood-base bio-modified asphalt binders also exhibited more aging susceptibility than the neat asphalt binder. Different aging mechanisms might happen between a non-petroleum-based binder and an asphalt binder.

Figure 4 — Master curves of (a) Dynamic shear modulus and (b) Phase angle of BioA and AC 30-45



(a)



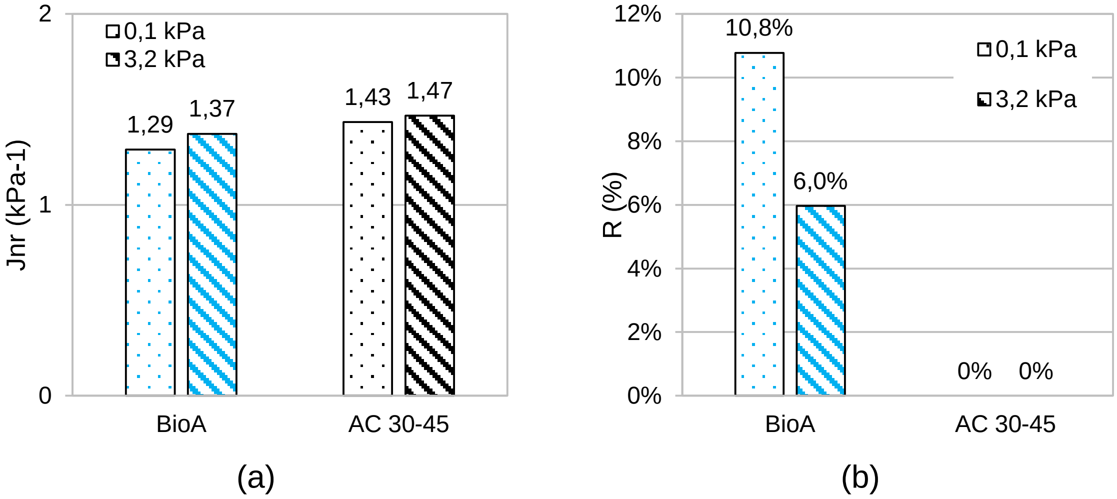
(b)

Source: Author (2020)

2.3.2 Permanent deformation susceptibility

In terms of permanent deformation, the Multiple Stress Creep and Recovery (MSCR) test (ASTM D 7405, 2015) was applied to three short-term aged samples for both binders. Three samples for each binder were tested at 64°C, since it was the high PG temperature (AASHTO M320-09) for the AC 30-45 used in this study. Figure 5 shows the average values of non-recoverable compliance (Jnr) and the recovery (R) for both binders, obtained from the MSCR tests. The coefficient of variation (COV) of Jnr for BioA samples was 23% and for the AC 30-45 samples was 3%. Results showed no significant difference in the permanent deformation behavior of both binders, despite a small difference on the recovery. The literature report that wood-based bio-binders might improve the elastic recovery and reduce the non-recoverable deformation when used as modifiers and extensor (XU; WANG; ZHU, 2017; YANG; SUCIPTAN, 2016). However, no reference was found on permanent deformation susceptibility of bio-binder for total replacement of asphalt binders.

Figure 5 ─ Non-recoverable compliance (Jnr) and the recovery (R) of the bio-binder and the asphalt binder



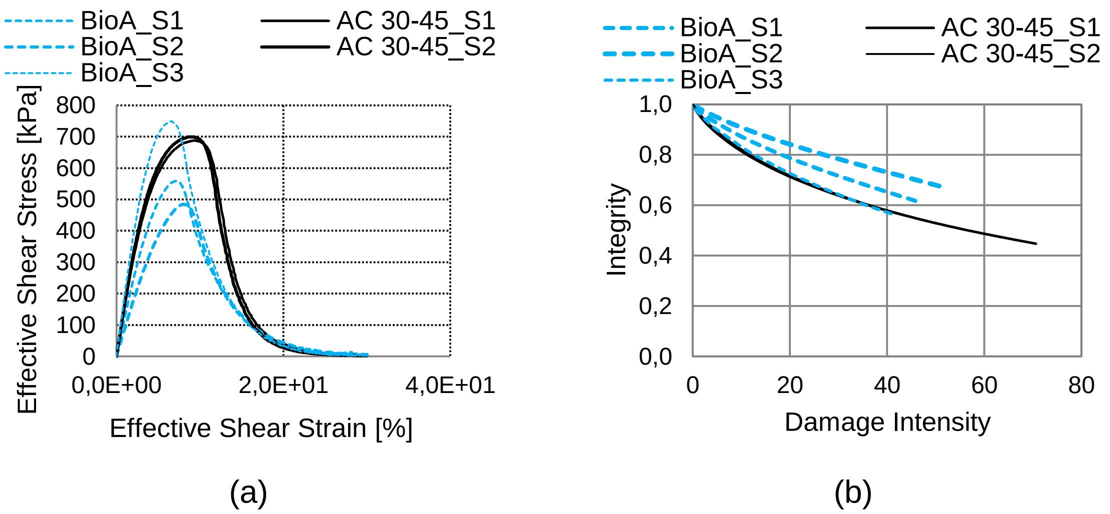
Source: Author

2.3.3 Fatigue evaluation

The fatigue response of both binders was assessed with the Linear Amplitude Sweep (LAS) test. The standard AASHTO TP 101-14 was applied to three samples of bio-binder and two samples of the neat asphalt binder. The criterion for cohesive fatigue proposed by Safaei and Castorena (2016) was adopted to choose the test temperature, which was 25°C for both binders. The maximum value of the shear stress was assumed as the failure criterion for this study, and the results were analyzed with the Viscoelastic Continuous Damage (VECD) approach (Figure 6).

As can be seen in Figure 6a, the BioA samples presented damage at lower values of strain, when compared with the AC 30-45, thus, the bio-binder behavior was more brittle than the AC 30-45 at the temperature set. The damage characteristic curves from the VECD analyses are shown in Figure 6b. It can be seen that the AC 30-45 presented higher damage resistance than BioA. Similar results were obtained by Xu, Wang and Zhu (2017) when adding lignin powder as modifier for asphalt binders, as it reduced the fatigue resistance of the asphalt binder.

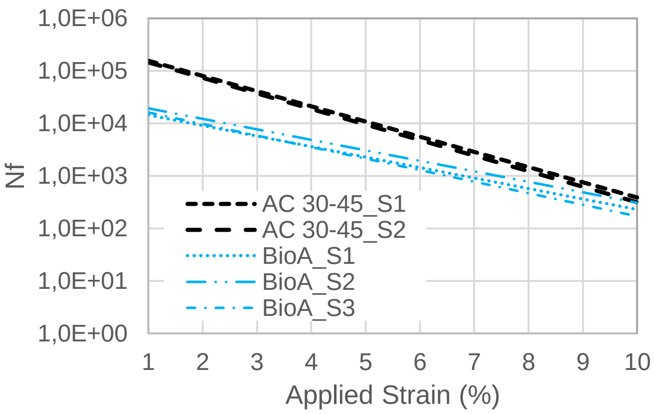
Figure 6 — LAS results in terms of (a) Effective shear stress and (b) Integrity curves



Source: Author (2020)

The number of cycles to fracture (Nf) for both binders studied are shown in Figure 7. The parameters A and B need to be calculated based on the results of the LAS test. The COV of A for BioA samples was 8% and for AC 30-45 was 5%. The parameter B had COV of 7% for BioA and 2% for AC 30-45. The AC 30-45 presented longer fatigue life than the BioA at different strain rates. These results and those showed in Figure 6b suggest that in terms of fatigue, the asphalt binder had better response compared with the bio-binder tested. However, the angular coefficient of the AC 30-45 curves allows to infer that the asphalt binder has more susceptibility to the variation of the applied strain than the bio-binder.

Figure 7 — Fatigue life (Nf) of the neat asphalt binder and the bio-binder



Source: Author (2020)

2.4 MIXTURE EVALUATION

In order to evaluate the mixtures performance, the binders described in the section above were combined with granitic aggregates, which characteristics are listed in Table 3.

Table 3 – Characterization of aggregates used in this study

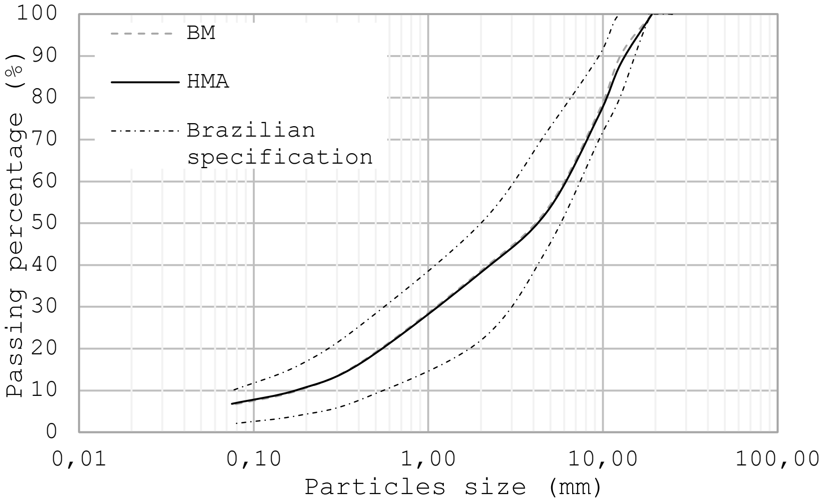
Test/Standard		Specification	Resuslt
Sand Equivalent Value (%)	ASTM D2419-02	≥55	71
Bulk density (g/cm^3)	ASTM C29M - 17a	Indicative	2,663
Shape index (%)	DNER-ME 086/64	≥0,5	0,76
Adhesion with BioA	DNER-ME 078/64	Satisfactory	Satisfactory
Adhesion with AC30-45	DNER-ME 078/64	Satisfactory	Satisfactory

Source: Author (2020)

2.4.1 Mixture design

A dense graded gradation was chosen to prepare mixes with both BioA and AC 30-45 binders, named BM and HMA, respectively. The gradation and the Brazilian specifications are shown in Figure 8. For HMA, 1,5% of hydrated lime (HL) was added in order to improve adhesion between aggregates and binder. For the BM, the HL was not added, as it was verified in laboratory that the HL reacted with the BioA, and it compromised the mixture workability (fast increase of binder viscosity), probably due to some endothermic reaction. Mixtures were designed using Marshall methodology with 4% of air voids, which is summarized in Table 4.

Figure 8 ─ Mix gradation



Source: Author (2020)

Table 4 ─ Marshall mix design for the BM and HMA

Test/Standard		Specification	HMA	BM
Asphalt content, %	DNER-ME 053/94	4.5 - 6.5	4.8	5.1
Specific Gravity	AASHTO T166-16	-	2.335	2.317
Stability, kgf	ASTM D 1559/92	>770	1100	884
VFA, %	ASTM D 1559/92	65 - 75	73	73.8
Air voids, %	ASTM D 1559/92	3.0 - 5.0	4.5	4.0
VMA, %	ASTM D 1559/92	>15	17	15.1

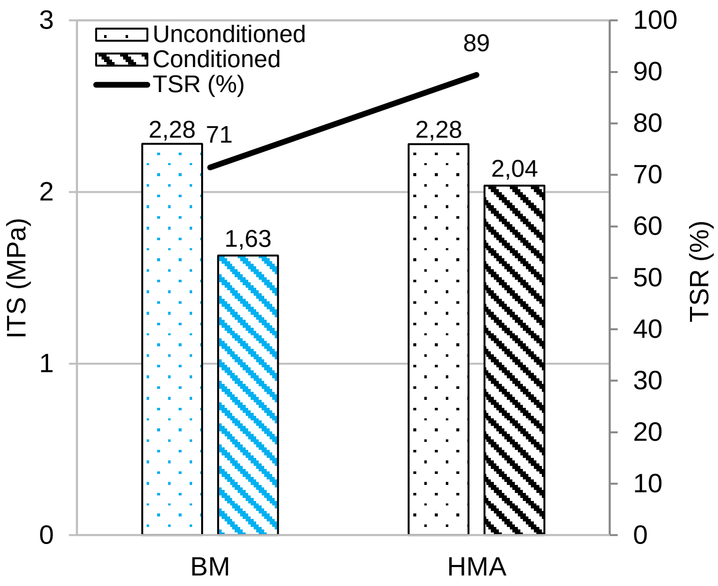
Source: Author (2020)

2.4.2 Moisture-induced damage

ASTM D4867-14 standard was used to investigate moisture susceptibility of both mixtures. Six specimens per mixture (three unconditioned and three conditioned) compacted with 7±1% air voids was fabricated following the standard recommendations. The conditioning process consisted in water saturation (55-80%) under vacuum, followed by freezing (16h at -18°C), heating (24h in a 60°C water bath) and cooling (2h in a 25°C water bath) in sequence. Both conditioned and unconditioned samples were tested in order to obtain the indirect tensile strength (ITS). The average ITS for the conditioned specimens is compared to the average ITS for the unconditioned ones, to determine the Tensile Strength Ratio (TSR), as shown in Figure

9. The COV for the conditioned samples of BM was 24%, while the unconditioned ones had a COV of 14%. For HMA those values were 5% for unconditioned and conditioned samples.

Figure 9 – Results of moisture-induced damage test



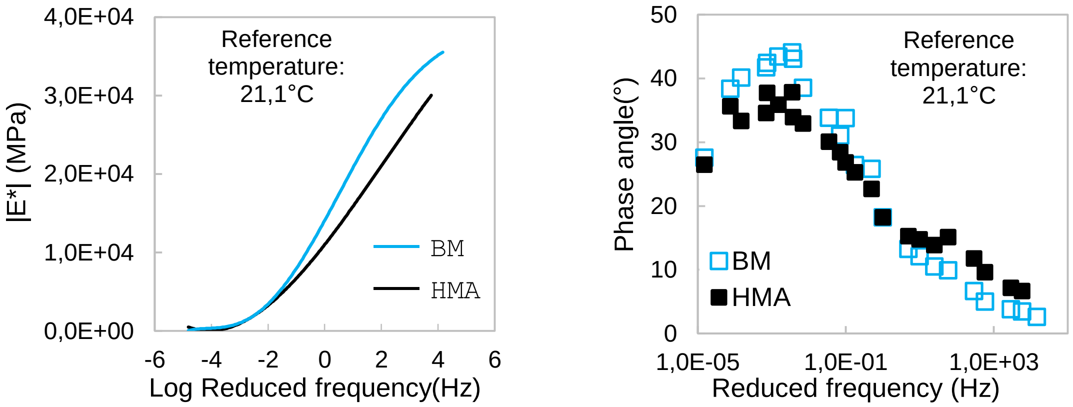
Source: Author (2020)

Considering a minimum limit for TSR of 70%, defined by ASTM D4867-14 both mixtures could be classified as resistant to moisture damage. However, HMA was less susceptible to degradation due to the action of moisture than BM. The moisture susceptibility of BM may be due to some components in wood-based binders that might have more affinity for water (MILLS-BEALE, 2013) or even some of its compounds could be soluble in water (YANG; MILLS-BEALE; YOU, 2017).

2.4.3 Dynamic Modulus

Complex modulus tests were conducted based on the standard AASHTO T 342-2011. The specimens with diameter of 100 mm and 150 mm height were prepared. The average air void was 6,4% for BM and 7,2% for HMA. Based on the time-temperature superposition principle, six frequencies (25 Hz, 10 Hz, 5 Hz, 1 Hz, 0.5 Hz, 0.1 Hz) and four testing temperatures (4,4°C, 21,1 °C, 37,8 °C, 54 °C) combinations were selected to construct the dynamic modulus (|E*|) and the phase angle (δ) master curves (Figure 10) at the reference temperature of 21,1°C.

Figure 10 – Master curves of (a) dynamic modulus and (b) phase angle of the bio-binder and asphalt mixtures



(a) (b)

Source: Author (2020)

As can be seen in Figure 10a, at higher frequencies/low temperatures BM showed higher |E*| values than HMA. However, at low frequencies/high temperatures, both binders presented similar behavior. As the aggregate matrix is the same for both mixtures and the air void is quite similar, the author believe that the difference between the materials tested is mostly due to the binders used. The trends showed in Figure 10a are in agreement with the master curves of the binder presented in Figure 4, where after RTFO aging, the stiffness of bio-binder was higher than the asphalt binder. In Figure 10b, it is possible to observe that BM exhibited a more viscous behavior at high temperatures and more elastic behavior at low temperatures when compared with the HMA.

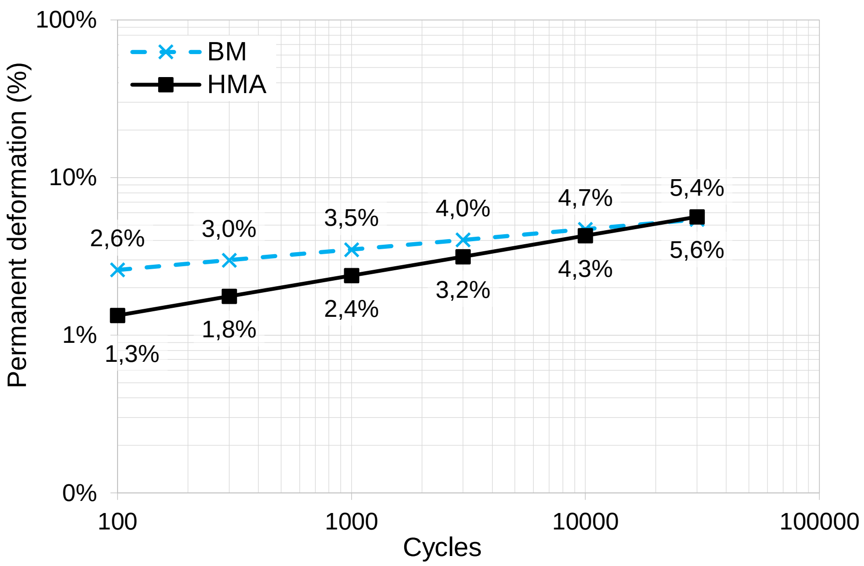
Pouget and Loup (2013) found similar results in BBSG mixtures (Béton Bitumineux Semi-Grenu) made with wood-based bio-binders. Although that bio-binder was highly modified by elastomeric polymers, there was no significant differences in the stiffness of the bio-mixtures and the asphalt mixture taken as reference.

These findings are positive considering the fact that this curve is often adopted in models for predicting the mixture performance (low frequencies/high temperatures related to rutting and intermediate frequencies/temperatures related to fatigue life) (EL-BADAWY; BAYOMY; AWED, 2012; WITCZAK; FONSECA, 1996; YU; SHEN, 2012).

2.4.4 Permanent deformation

The permanent deformation was accessed using the French laboratory traffic simulator, developed by Laboratoires des Ponts et Chaussées. The equipment simultaneously test two slabs molded with 500 mm length 180mm width and 50 mm height. The procedure is described in EN 12697-22-2003. The specimens were conditioned at test temperature (60°C) for 12 h before testing. Deformation measurements were carried out after 0, 100, 300, 1,000, 3,000, 10,000 e 30,000 cycles. The permanent deformation was reported as a percentage of the slab thickness as shown in Figure 11. The percentage was calculated as the average of 15 measurements divided by the original thickness of the slab.

Figure 11 – Results of permanent deformation test in mixtures



Source: Author (2020)

In view of the results presented in Figure 11, it is possible to observe that there was no difference on the permanent deformation of both mixtures at the end of the loading cycles. However, the initial values showed that BM had higher deformation than HMA, what might be associate with a higher air void content in the BM that caused a consolidation in the sample at the beginning of the test. These results are in agreement with the exposed in section 2.3.2 of this chapter, where evaluation in binder scale shows that the bio-binder and the asphalt binder have similar permanent deformation susceptibility. There is no reference in the literature to direct compare the results found in this study, since most of the research in mixture with bio-binder are focused in modification of the asphalt binder. However, some extensors and modifiers made from waste wood (ZHANG et al., 2017) and waste cooking oil (WEN; BHUSAL; WEN, 2013) have proven to reduce the permanent deformation resistance of the asphalt mixtures.

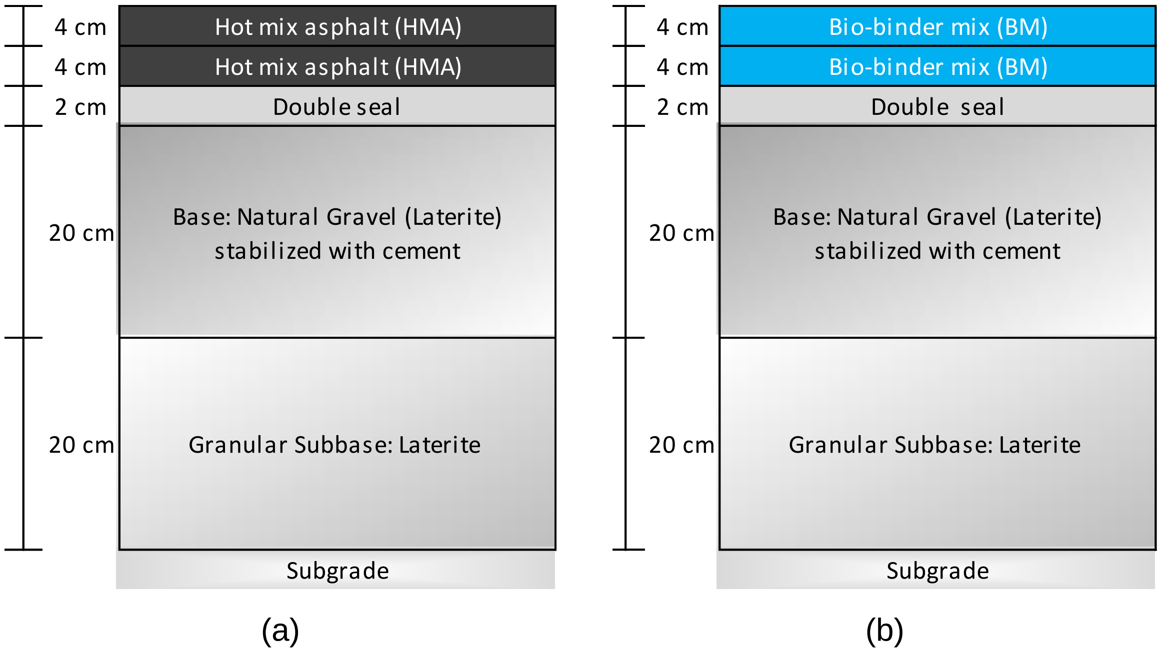
2.5 EXPERIMENTAL TEST SITE

The experimental test site is located in the highway BR-050/GO, at Minas Gerais, Brazil. This region is characterized for two well defined seasons, the rainy and the dry periods, with the temperature ranging between 40°C and 51°C during rainy peridos and between 31°C and 34°C in the dry period. Although there is no information on the volume of traffic on that highway, it is known that it is not heavy traffic. Two test sections were constructed, one of 630 meters with the hot mix asphalt surface layer and the other segment of 480 meters with bio-binder mix as the surface layer (following the mix design of the section 2.4.1).

2.5.1 Construction

Figure 12 presents the pavement structures of the test site. In order to study the mix behavior in the field without the influence of any other layer, the structure below the surface layer was the same for both segments. Due to equipment limitations in Brazil, the upper layer was applied and compacted in two lifts, with an emulsion tack coat between them.

Figure 12 — Field structure for a)hot mix asphalt and b)bio-binder mix segments



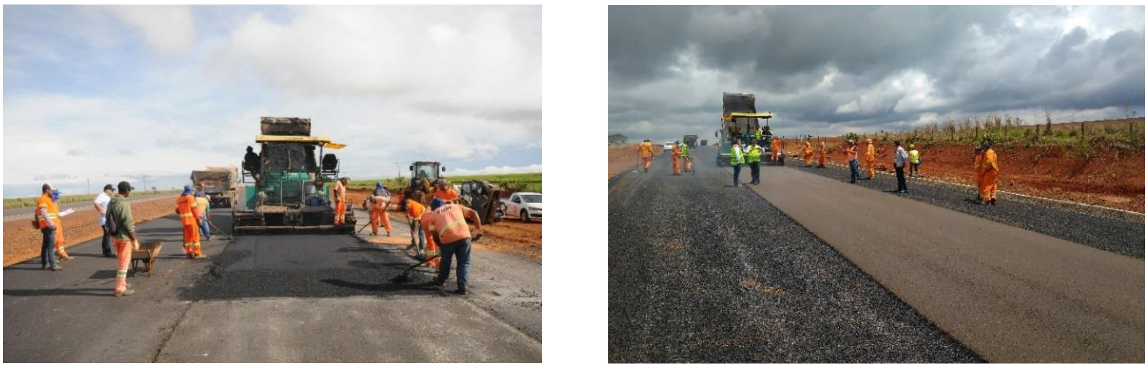
Source: Author (2020)

Both sections were constructed using the same equipment and executive procedures. The same paver and compaction rollers used for the execution of the HMA lifts were used for the application of the bio-binder mixture. Both compaction procedures consisted of 1 pass of a tandem roller (9 ton) for compaction breakdown, then two passes of a pneumatic tire roller (tire pressure of 100 lb, 27 ton of ballast), followed by two passes of a pneumatic tire roller (tire pressure of 110 lb, 27 ton of ballast) and 1 pass of the tandem roller (9 ton) for finishing.

Although there was no need to adjust the number of passes of the rollers to achieve the design density of the bio-binder mixture layer, the mixture temperature decreased rapidly during compaction, requiring attention and agility to perform the compaction adequately.

Figure 13 presents the construction of the experimental test site for both mixtures studied. It can be seen that the surface of the mixture with bio-binder has lighter color, similar to brown, different from the traditional black of conventional asphalt mixtures.

Figure 13 – Construction of experimental test site for a) hot mix asphalt and b)bio-binder mix segments



(a) (b)

Source: RDT project (2018)

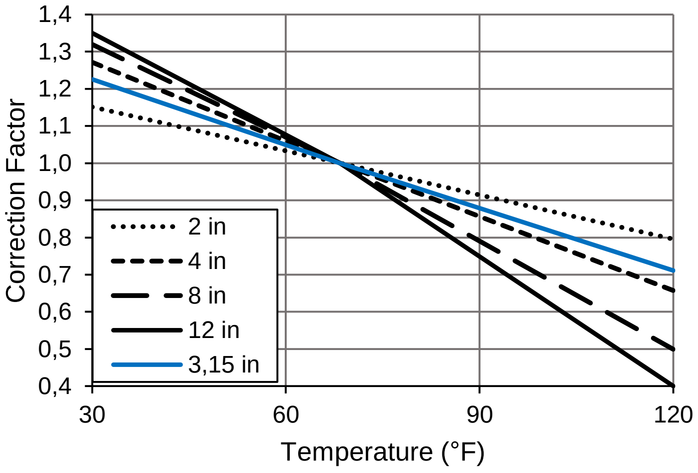
2.5.2 Monitoring

The evolution of both segments was monitored throughout three years since 2017. The tests applied for monitoring were the Falling Weight Deflectometer (FWD) and the International Roughness Index (IRI).

2.5.2.1 Falling Weight Deflectometer (FWD)

FWD measurements were performed at every 40 meters. The load was 40.2kN and the plate diameter was 30cm. An adaptation to the abacus of temperature correction, suggested in the 1993 AASHTO Guide for Design of Pavement Structures, was used to correct the maximum deflection values as a function of temperature. The adaptation consisted in the interpolation of the factor curves to attend a thickness of 8cm (3,15in). Figure 14 presents the abacus used. It is worth to mention that the correlations expressed in that abacus were calibrated for asphalt mixtures and may not be proper to non-petroleum based binders. However, it was applied in this case due to the lack of references for bio-binders mixtures in field applications. Besides, the bio-binder exhibited a similar rheological behavior of the asphalt binder studied. Additionally, maximum deflection values were also corrected based on the applied load.

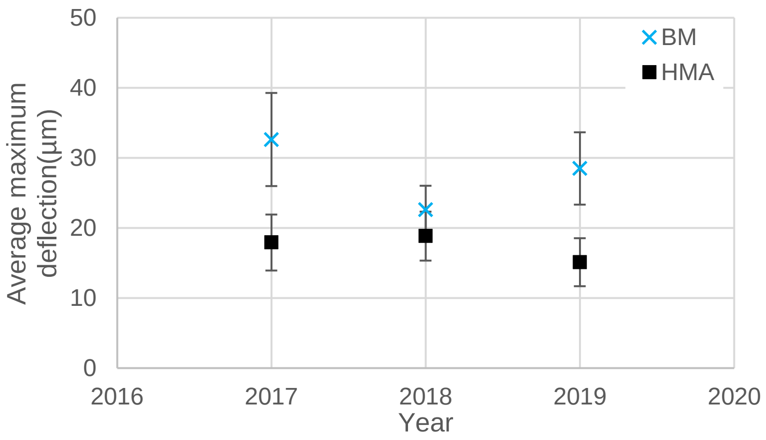
Figure 14 ─ Maximum deflection correction factor as a function of temperature - adapted from AASHTO, 1993



Source: Adapted from 1993 AASHTO Guide for Design of Pavement Structures

Figure 15 presents the corrected average maximum deflection per year for both segments. Monitoring was made in the same period of the year (from June to November), in order to observe the behavior of the structures without the direct influence of the climate variation (specially the moisture influence in the lower layers). It can be seen that, although the bio-binder mix structure (BM) presented the higher values, there was no significant variation in the maximum deflection for both segments along the monitoring years. It suggests that the behavior of both pavement structures is considered similar in the first three years of service life.

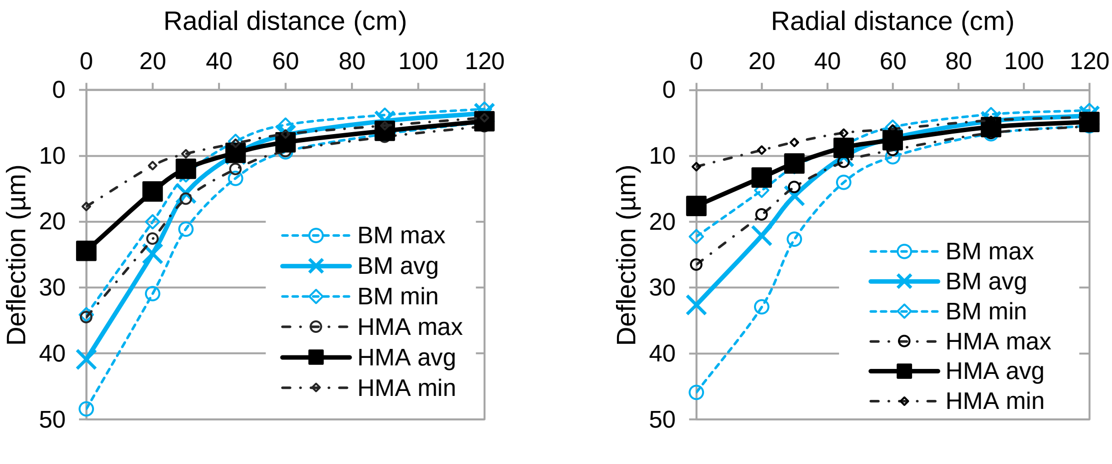
Figure 15 ─ Evolution of average maximum deflections for both segments



Source: Author (2020)

On the other hand, with the purpose of determining the effect of climate conditions in the structure response, a second monitoring was performed in 2019. Figure 16 shows results of tests completed in (a) January 2019 (Rainy period) and (b) July 2019 (Dry period). According to the data shown in Figure 16, during the rainy period both structures showed higher maximum deflection values than the values obtained in the dry period (July). This is related to the increase in the water content into the pavement structure during the rainy periods, which reduces the matric suction of the granular layers, affects layers´ stiffness, and the response of the entire structure.

Figure 16 ─ Deflection basins of both segments during 2019 in (a) January with temperature range of 40°C-51°C, and (b) July with temperature range of 31°C-34°C



(a) (b)

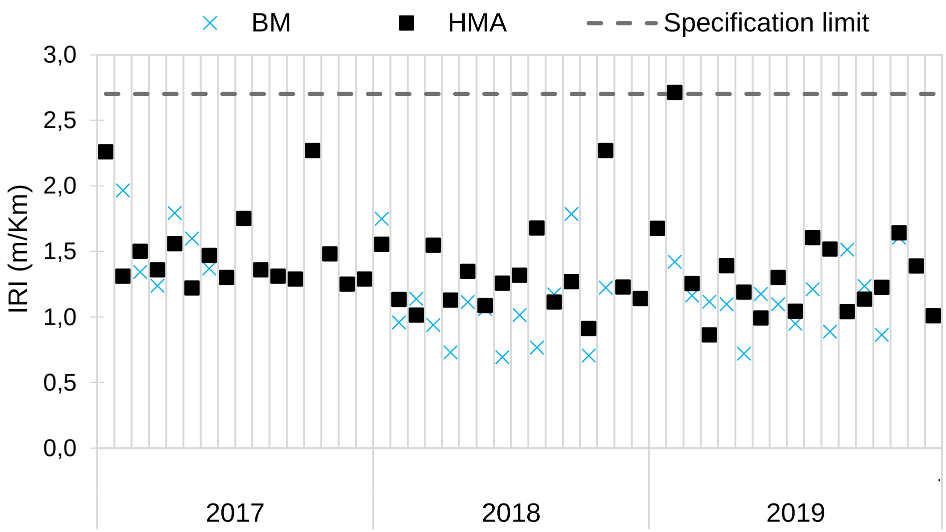
Source: Author (2020)

Additionally, it is possible to point out that the increase in maximum deflection is very similar for both sections, which can indicate that the increase in deformability is not related to the nature of the surface mixture. Also, the base and sub-base of both trial section structures are composed of Laterite which is a natural gravel. These materials are not as homogeneous as graded crushed stones, and could be the reason for some of the deformability differences between the two sections.

2.5.2.2 International Roughness Index (IRI)

A high-speed profiling system was used for monitoring the roughness of both segments. IRI was used for monitoring the roughness, according to ASTM-E-950/98, throughout the three years of monitoring for both segments. The results are shown in Figure 17. It can be seen that the mixtures made with bio-binder and neat binder had no significant variation during the monitoring period, which suggests that the surface characteristics of both pavements are similar and satisfy the specification limit (2.7 m/km).

Figure 17 – Monitoring of IRI for both segments



Source: Author (2020)

The results of field monitoring match with those findings in the laboratory evaluation of the mixtures, described in the section above, where mixture made from both types of binders showed a similar performance up to the third year of monitoring. However, those results are validated for highways with the same traffic conditions of the experimental test site that is considered standard traffic. More research is recommended about the application of the bio-binder studied in roads with heavy traffic to determine if it performance as well as asphalt binders.

2.6 SUMMARY AND CONCLUSIONS

In this study, laboratory tests and field monitoring of mixtures made with one bio-binder (BioA) derived from pine wood residues were carried out, in order to evaluate the potential of bio-binders as substitutes for asphalt binders. Results were compared with the performance showed for a mixture made with a neat asphalt binder (AC 30-45). Findings suggest that:

- At the binder scale, BioA showed similar rheological behavior than that displayed for the AC 30-45, despite of a lower performance in terms of fatigue in the LAS test;
- Mixture made with bio-binder showed lower moisture damage resistance than that made with asphalt binder, what might be related to the biomass source of the bio-binder;
- There were no significant differences in the performance showed for mixtures BM (made with BioA) and HMA (made with AC 30-45), in terms of stiffness and permanent deformation. The above was evidenced in laboratory and field test;
- The field performance of the BM was found to be comparable to that of a HMA surface layer, based on the FWD and IRI results gathered through three years of pavement monitoring.

According to the above, the bio-binder studied could be used as binder in mixtures of surface layers since it has a similar response, even in field, of that of the hot asphalt mixes. However, the durability of that type of mixtures, the environmental impact of the production process (from the production of the bio-binder until the compaction of the surface layer), and its response under different traffic conditions need to be studied in order to complement the evaluation of feasibility in terms of sustainability.

3 COMPARISON OF THE RHEOLOGICAL AND THERMAL BEHAVIOR OF A NEAT ASPHALT BINDER AND A BIO-BINDER FROM RENEWABLE SOURCE

3.1 INTRODUCTION

Swine manure, wood residues, microalgae and vegetable oil are some of the most commonly used raw materials to produce biomass and hence bio-binder. As mentioned in the chapter 1, depending on the source and on the manufacturing process, bio-binders present different rheological and physical properties (AZIZ et al., 2015). Liquefaction and fast pyrolysis are the most frequently used thermochemical techniques for the production of bio-binders from swine manure and plant biomass, respectively (BRIDGWATER, 2012; FINI; KALBERER; SHAHBAZI, 2011; AZIZ et al., 2015). However, depending on the type of biomass, there are others methods to obtain bio-binders or bio-modified asphalts (AZIZ et al., 2015). Chailleux et al. (2012) studied a by-product of the industry known as “algo-refinery”, chemically modified to achieve rheological properties of the asphalt binder. Da Costa et al. (2020) added fibers from banana plant to asphalt binders, whereas Xu, Wang and Zhu (2017) used lignin powder to create a bio-modified asphalt binder. The choice of the proper bio-binder production technique depends on the properties and applications aimed.

As long as there is such variety of biomass source, processing technique and binder application, there is no consensus in the literature about the performance of the bio-binders, whether used as substitute, extender or modifier. In order to characterize this kind of materials, techniques commonly applied to asphalt binders have been used in bio-binders as well. Rheology and performance evaluation with a dynamic shear rheometer (DSR) have been the most used: Peralta et al. (2012a) used it to assess a product of fast pyrolysis of red oak wood in comparison with a PG 64-16 asphalt binder, the author also added rubber as modifier to the bio-binder and to the asphalt binder. Camargo, Bernucci and Vasconcelos (2019) used it to study a wood-base binder that showed higher thermal susceptibility when compared with an asphalt binder. Dalmazzo et al. (2020) assessed the viscoelastic behavior from a bio-binder made of pitch (obtained as a by-product of the papermaking industry). Yang and Suciptan (2016) studied the rheological behavior of Japanese cedar-based biobinder for partial replacement of asphalt binder. Fini et al. (2017) used rheology to assess the difference on behavior of bio-binders from different sources, used as asphalt modifiers, including products from the thermochemical conversion of swine manure to bio-oil and from pyrolysis of three different biomass: miscanthus pellet, corn stover, and wood pellet. Jimenez et al. (2017b) evaluated the biomaterials rejuvenating effect on binder from RAP also using rheology.

The chemical and thermal analysis have been also applied to better understand the results on rheology, the most commonly used are the Fourier transform infrared spectroscopy (FTIR) (PERALTA et al., 2012a; YANG; YOU; MILLS-BEALE, 2015), the thermogravimetric analysis (TGA) (DA COSTA et al., 2020), elemental analysis, fraction analysis of SARA, Gas Chromatography-Mass Spectrometer (GC-MS) (DONG et al., 2019).

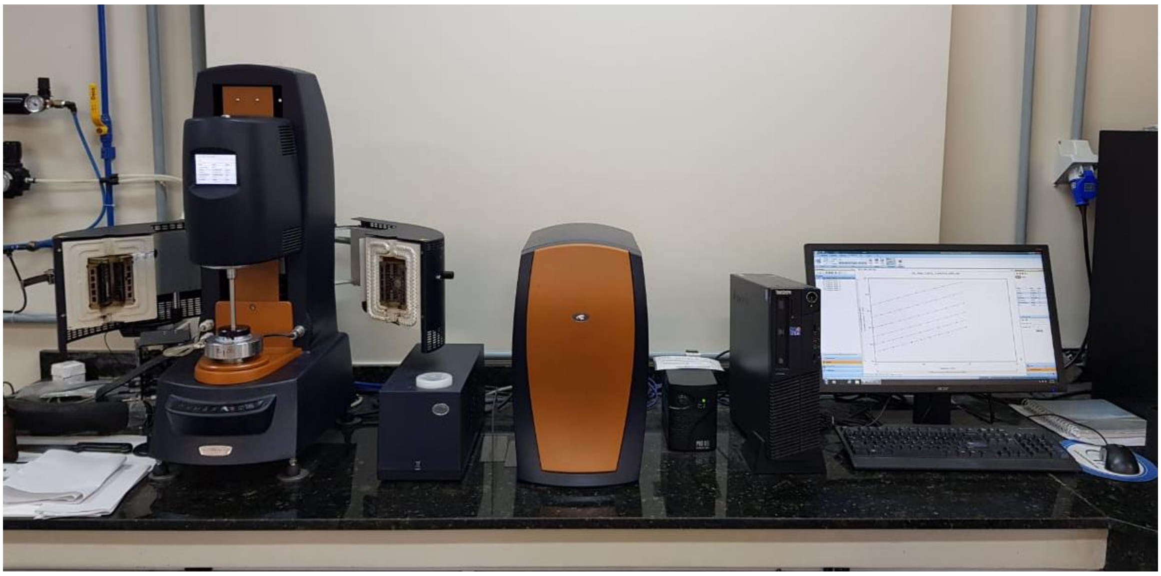
However, as mention in chapter 1, there are few studies with bio-binders for total replacement of asphalt binder regarding to their characterization. In this context, this paper presents a comparison between a wood-based asphalt binder and a neat asphalt binder, in order to evaluate the potential use of the bio-binder as 100% substitute of the asphalt. The comparison is made throughout rheological and performance tests and thermo-gravimetric analysis of the binders.

3.2 MATERIALS AND METHODS

Two binders were studied in this research. The first one is a neat asphalt binder of penetration grade AC 30/45, with penetration at 25°C of 25 0.1mm, softening point of 55°C and rotational viscosity at 135°C of 361cP. The second binder is a bio-binder (BioB) produced from plant biomass, by-product of the treatment of pine wood resin. The penetration at 25°C of the bio-binder was of 21 0.1 mm, softening point of 57°C and rotational viscosity at 135°C of 638.3cP.

The short-term aging of both binders was simulated using the *Rolling thin film oven* (RTFO) test, according to the ASTM D 2872-12. The *Pressure aging vessel* (PAV) test was used to simulate the long-term aging also for both binders, following the standard ASTM D 6521-18. The rheological behavior of the unaged and aged binders studied was observed using the DSR (Figure 18) with the test methods described below.

Figure 18 – Dynamic Shear Rheometer Model DHR-3 used in the study.



Source: Author (2020)

Frequency sweep test. The deformation rate adopted for the test was 0.01%, with the frequency range between 1 and 100 rad/s. The test temperature varied from 10°C to 80°C. The variation of the dynamic shear modulus with the frequency, for two samples of each binder at the different aging stages, was plotted for each temperature and then, the master curves were constructed at the reference temperature (RT) of 40°C, based on the time-temperature superposition principle.

The performance grade (PG) of both binders was determined using the AASHTO M332-141-2014 procedure, and the linearity was assessed by the determination of the rheological properties following the standard specification ASTM D 7175-15.

Multiple stress creep and recovery (MSCR) test. The susceptibility to rutting of the short-term aged binders was analyzed by performing the MSCR test according to the ASTM D 7405-15. The test temperature was 70°C and the non-recoverable compliance (J_{nr}) and the recovery (R) were calculated for three samples of each binder.

The fatigue behavior of the PAV aged samples of both binders were evaluated with the *Linear Amplitude Sweep (LAS) test*. Three samples were tested for each binder following the AASTHO TP 101-2014. According to Safaei and Castorena (2016), in order to avoid the effects of flow or adhesion loss during the test, the temperature chosen for the test is such that the linear dynamic shear modulus of the sample ranges between 12 to 60 MPa. Thus, the test temperature for the bio-binder was 35°C and for the AC 30/45 was 20°C. The Viscoelastic Continuous Damage (VECD) theory was used to analyze the test results, adopting as rupture criterion the maximum value of the shear stress.

Thermo-gravimetric analysis (TGA). The TGA is a thermal analysis technique in which the variation in the mass of a sample is determined as a function of time and/or temperature, while the sample is subjected to a controlled increase of temperature (CINCOTTO, 2014), obtaining thermo-gravimetric (TG) curves. The DTG is the first derivative of the TG curve and it allows separation of the overlapping reactions in a TG curve, leading to the identification of the temperatures where thermal decomposition starts and ends. As a complement, the differential scanning calorimetry (DSC) was used to identify the type of reaction occurring during the test. The thermal analyzer shown in Figure 19 was used to the TGA of the binders involved in this study. The test was carried out in a nitrogen atmosphere for the neat asphalt and the bio-binder, and in an oxygen atmosphere for the bio-binder, with a heat rate of 10°C/min.

Figure 19 – Thermal analyzer NETZSCH STA 409 PC/PG used in the study.

Source: Author (2020)

3.3 RESULTS AND DISCUSSION

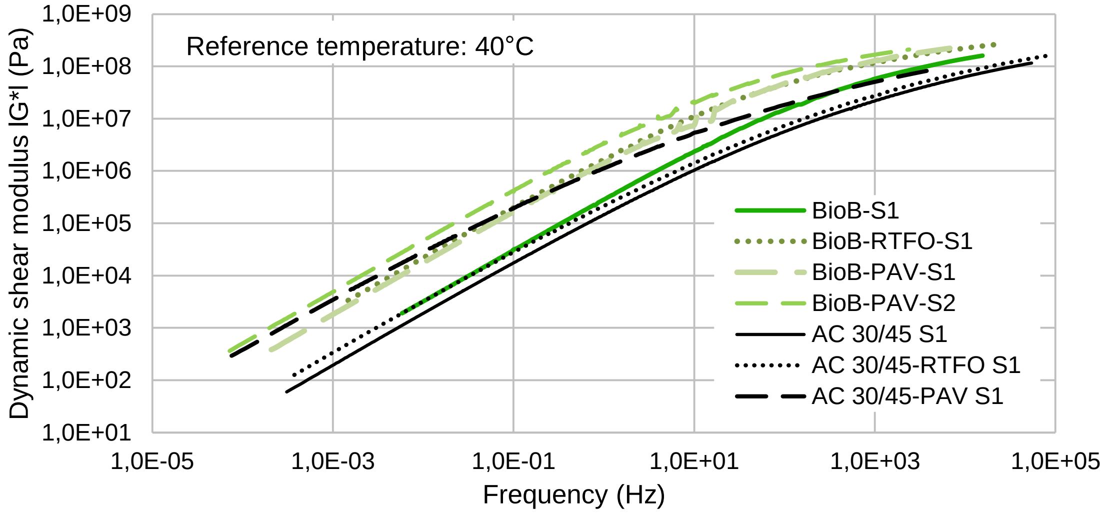
3.3.1 Linear viscoelastic characterization

The master curves of the dynamic shear modulus (│G*│) for both binders are shown in Figure 20. The three samples studied for each binder showed no variation between the same material and same aged stage, except for the two samples of PAV aged BioB. In order to discuss that variation, Figure 20 presents one sample for each material and two samples for PAV aged BioB.

It can be seen in Figure 20 that BioB presented higher │G*│ values than AC 30/45, under unaged and aged conditions. The RTFO aging increased the stiffness of both binders. However, its effect on the BioB was more remarkable than on the AC 30/45, with │G*│ increase of 570% versus 80% for the asphalt binder at lower reduced frequencies (higher temperatures), and 220% versus 23% at higher reduced frequencies (lower temperatures), respectively. That might be an indicator that the aging mechanisms are different for both types of binders. Camargo, Bernucci and Vasconcelos (2019) studied a similar bio-binder for total replacement of the neat asphalt binder and Yang et al. (2014) showed the results of a bio-binder as an extensor or modifier of asphalt binders, both binders were wood-based and it was found on both studies that the aging effect was higher in the bio-binder blends. This suggests that certain compounds on wood-based binders would be more susceptible to aging that the asphalt binders.

PAV aged BioB samples presented different tendencies (Figure 20). One of them exhibited smaller values of │G*│than the RTFO aged BioB (different from the neat asphalt binder behavior), and the other one presented higher values of │G*│than the RTFO aged BioB. This suggest that the long-term aging simulated in laboratory with the PAV test might be aggressive to the bio-binder studied, causing some structural degradation. That may be due to the differences between the sources of both binders. The bio-binder compounds may undergo structural changes during the test due to their different composition, as Dalmazzo et al. 2020 suggested to the different trends found in the results of another wood-base bio-binder.

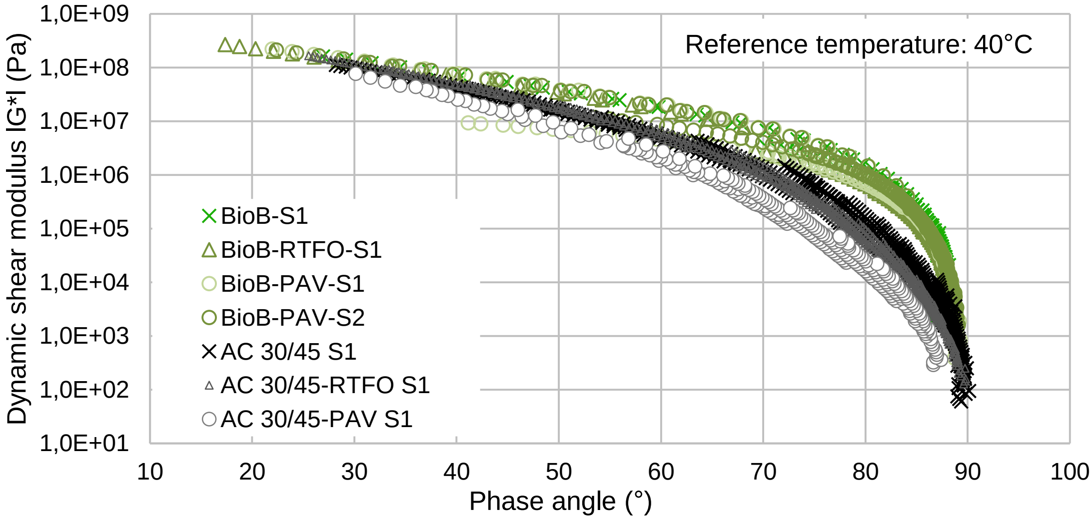
Figure 20 – Master curves for the AC 30/45 and BioB.



Source: Author (2020)

Figure 21 presents the Black space curves for both binders. It was found that the AC 30/45 exhibited a gradual transition from the glassy to the viscous state. While for the BioB, the transition was not smooth and, despite of its more viscous condition, the BioB presented higher stiffness, as also showed in Figure 20. The PAV aged bio-binder black curve did not exhibit a well-defined trend, another indication that the PAV aging test may have caused some degradation in the internal structure of the material. These outcomes mean that time-temperature superposition principle (TTSP) may not be applied on the BioB under this aged condition. Similar results were found by Dalmazzo et al. (2020), where the wood-based bio-binder studied did not show common trends as those of the asphalt binder in all aged stages, preventing the application of the TTSP. However, the bio-binder tested in that study showed a more rheological simple behavior in the curves when the aged stage increased, the opposite of the bio-binder assessed in the current research.

Figure 21 – Black space for the AC 30/45 and BioA.



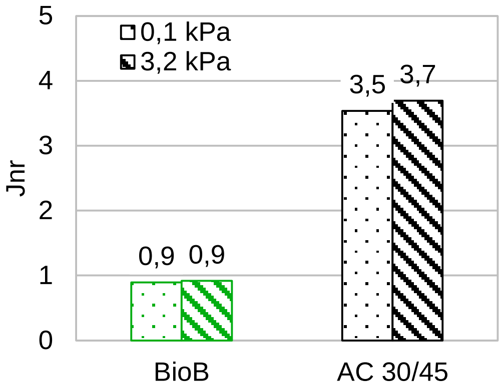
Source: Author (2020)

The performance grade (PG) was determined for both binders. The high PG temperature (HPG) of the AC 30/45 for heavy traffic was 64°C and the intermediate temperature was 28°C. The HPG of the BioB for standard traffic was 76°C and 70°C for heavy traffic. However, the intermediate temperature could not be identified, as the rheological properties (i.e., |G*|.sinδ) in the range of temperatures tested (19 to 37°C) of the PAV aged BioB was above the specified limit (5000kPa for standard traffic and 6000kPa for heavy traffic). Due to that limitation, it was not possible to determine its PG lower temperature.

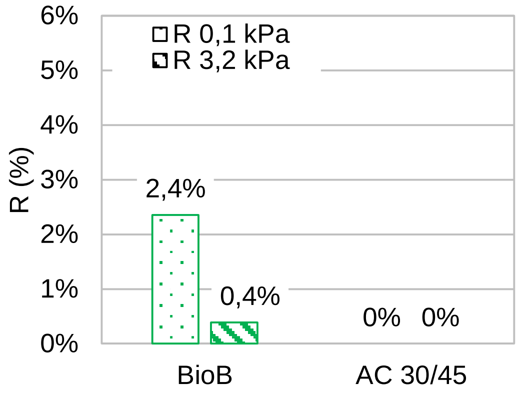
3.3.2 Permanent deformation

The results of the MSCR, presented in Figure 22, shows that the BioB is less susceptible to permanent deformation when compared to the AC 30/45, as it presented lower average Jnr value. The results presented in Figure 22b show that the recovery is similar for both binders and has very small values, as none modifier was added to the binders. The COV for the Jnr values for BioB was 4% and for AC 30/45 was 1%, 3 samples were tested. Camargo (2018) and Camargo, Bernucci and Vasconcelos (2019) also found that a wood-based bio-binder presented a similar permanent deformation susceptibility to the asphalt binder taken as reference. The literature also shows that when used as modifier and/or extensors, it is possible to observe that wood-based bio-binders might improve the elastic recovery (despite the very low numbers) and reduce the non-recoverable deformation (Xu; WANG; ZHU, 2017; YANG; SUCIPTAN, 2016).

Figure 22 – MSCR test results for BioA and the AC 30/45.



(a)



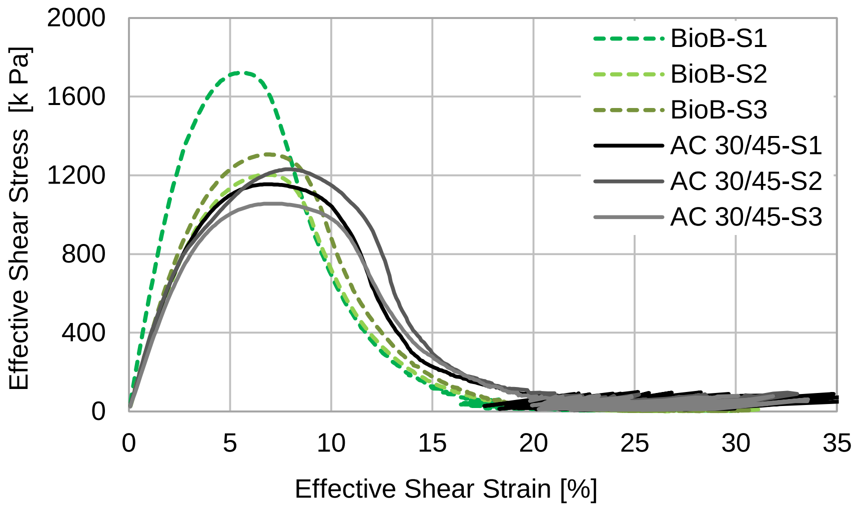
(b)

Source: Author (2020)

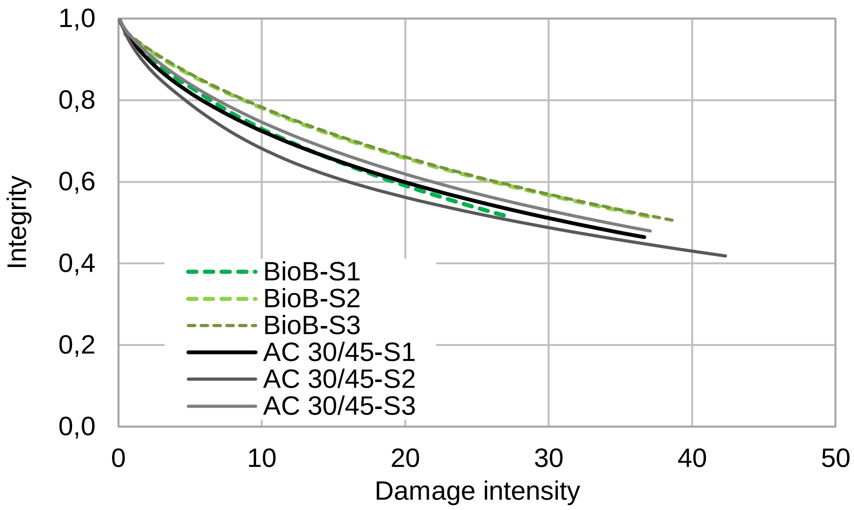
3.3.3 Fatigue life

The LAS test results are shown in Figure 23. The test temperature for BioB was 35°C and for AC 30/45 was 20°C. It can be seen that BioB resists more shear stress when compared with the AC 30/45, but the damage occurs at smaller values of strains (Figure 23a). This, added to the higher test temperature required, show that the bio-binder exhibited a more brittle behavior. However, the VECD analysis, shown in the damage characteristic curves (Figure 23b), suggests that both binders have similar damage resistance in terms of fatigue. The variability and the brittleness of the bio-binder samples might be linked to the aging process (PAV test), in which the test conditions would be inducing damage in the material.

Figure 23 – Binders fatigue results in terms of (a) Effective shear stress and (b) Integrity curves.



(a)

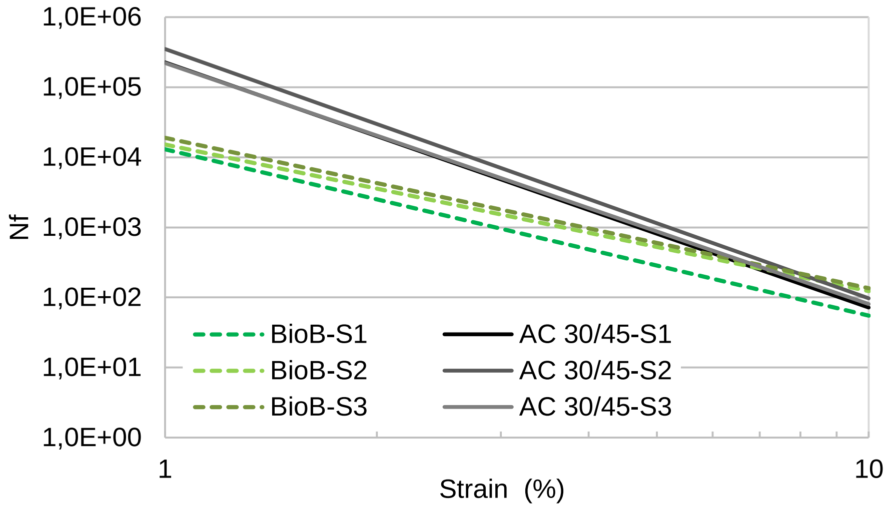


(b)

Source: Author (2020)

The fatigue life of the binders studied in this research are summarized in Figure 24. Three samples of each material were tested. The COV for the parameter A of BioB samples was 19% and for AC30/45 samples was 28%. The COV for the parameter B for BioB samples was 15% while for AC 30/45 samples was 6%. AC 30/45 showed higher fatigue resistance compared to BioB for the strain rates up to 10%. The results presented in Figure 23b and Figure 24 suggest that the bio-binder had lower performance when compared with the neat asphalt binder in terms of fatigue. The slope of the curves shows that the AC 30/45 is more sensitive to the applied strain rate than the Bio, but although an increase on the strain rate would decrease more the fatigue life of the AC 30/45, its performance remains superior to that of the BioB.

Figure 24 ─ Number of cycles to fracture (Nf) for the AC 30/45 and the BioB.



Source: Author (2020)

The differences in the fatigue life between both binders may be also related to the difference in the test temperature. The criterion chosen to select this temperature, as explained in section 3.2, required the │G*│ to be between 12 and 60MPa, for the bio-binder, this temperature was of 35°C. Additionally, the PAV test might have caused damage in the BioB samples, causing a lower performance in comparison with the AC 30/45.

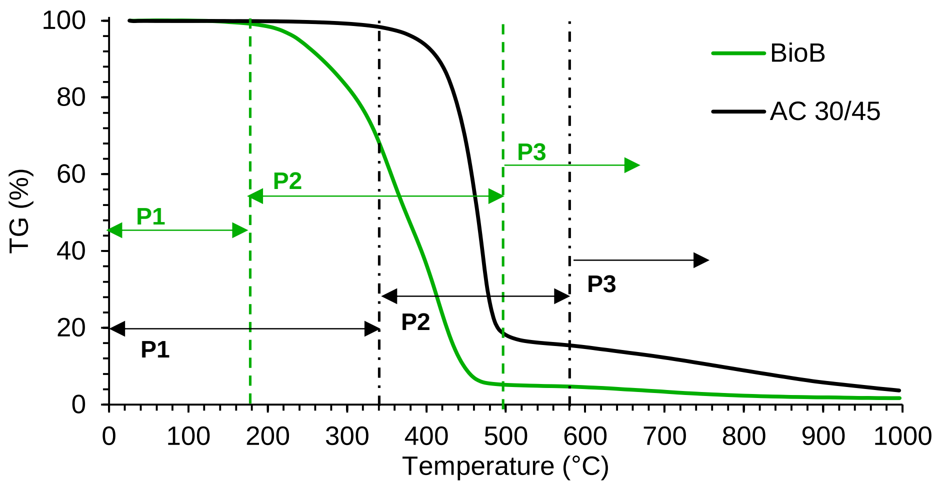
3.3.4 Thermo-gravimetric analysis

TGA for BioB and AC 30/45 in nitrogen atmosphere are shown in Figure 25. One sample was tested for each binder. Nitrogen is known as an inert atmosphere, where there is no burning of the material during the test, therefore, the result obtained is the decomposition of carbon dioxide (CO_2), water or organic material.

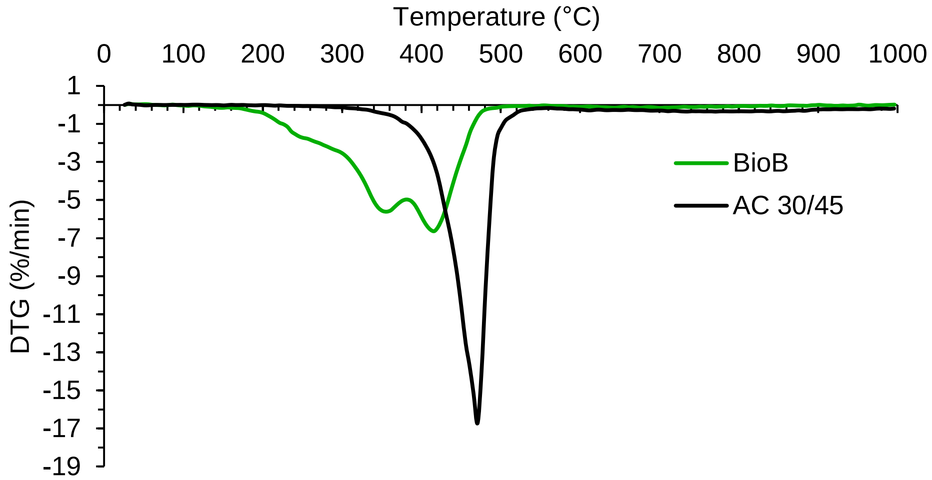
There are three phases during the test. In phase 1 (P1) occurs the loss of volatile elements, phase 2 (P2) corresponds to the decomposition of the material and, in phase 3 (P3) the loss of mass stabilizes because only inert and inorganic compounds remain in the sample. In Figure 25a it is possible to observe that the decomposition phase (P2) starts earlier in BioB than in the AC 30/45, as the thermal degradation of BioB begins at around 190°C and for AC 30/45 format around 340°C, indicating that there is higher content of light components in the BioB (LI et al., 2019). However, the temperature range where the decomposition occurs is wider in the BioB, showing a gradual loss of mass. During that process, Figure 25b shows that there are two partially overlapping reactions occurring in the BioB and one single reaction occurring in the AC 30/45.

The first reaction in BioB occurs slowly, with a peak at 356 °C, and the second reaction happens more quickly, with a peak at 416 °C. In the AC 30/45 the single reaction occurs quickly and the peak is at 470°C-480°C. The DSC curve (Figure 25c) shows that the reactions in both materials release energy through heat (exothermic reactions), but when the reaction on the AC 30/45 reaches its peak, it starts an endothermic process in the sample. It suggests that the AC 30/45 is more thermally stable than BioB, which could be linked with the content of asphaltenes in asphalt binders, which are thermally stable at high temperatures (ELKASHEF; WILLIAMS; COCHRAN, 2018).

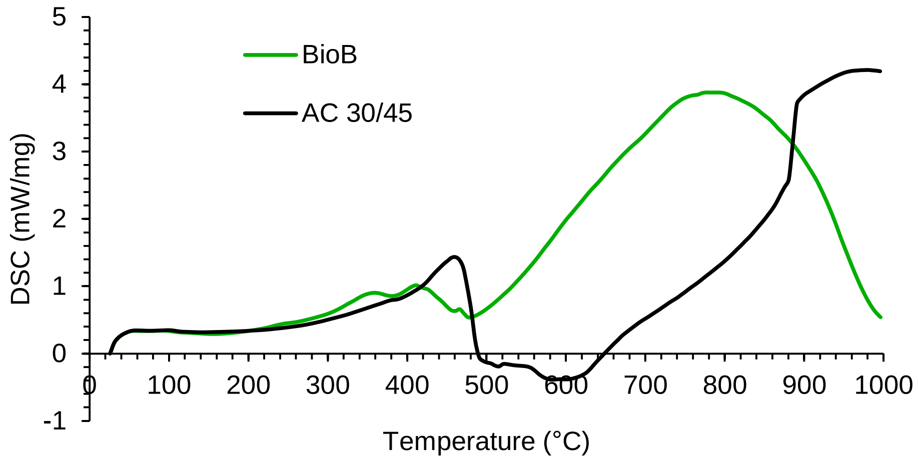
Figure 25 –Thermo-gravimetric analysis in nitrogen atmosphere of the binders studied, in terms of a) Thermo-gravimetric curves, b) DTG curves and c) DSC curves.



(a)



(b)

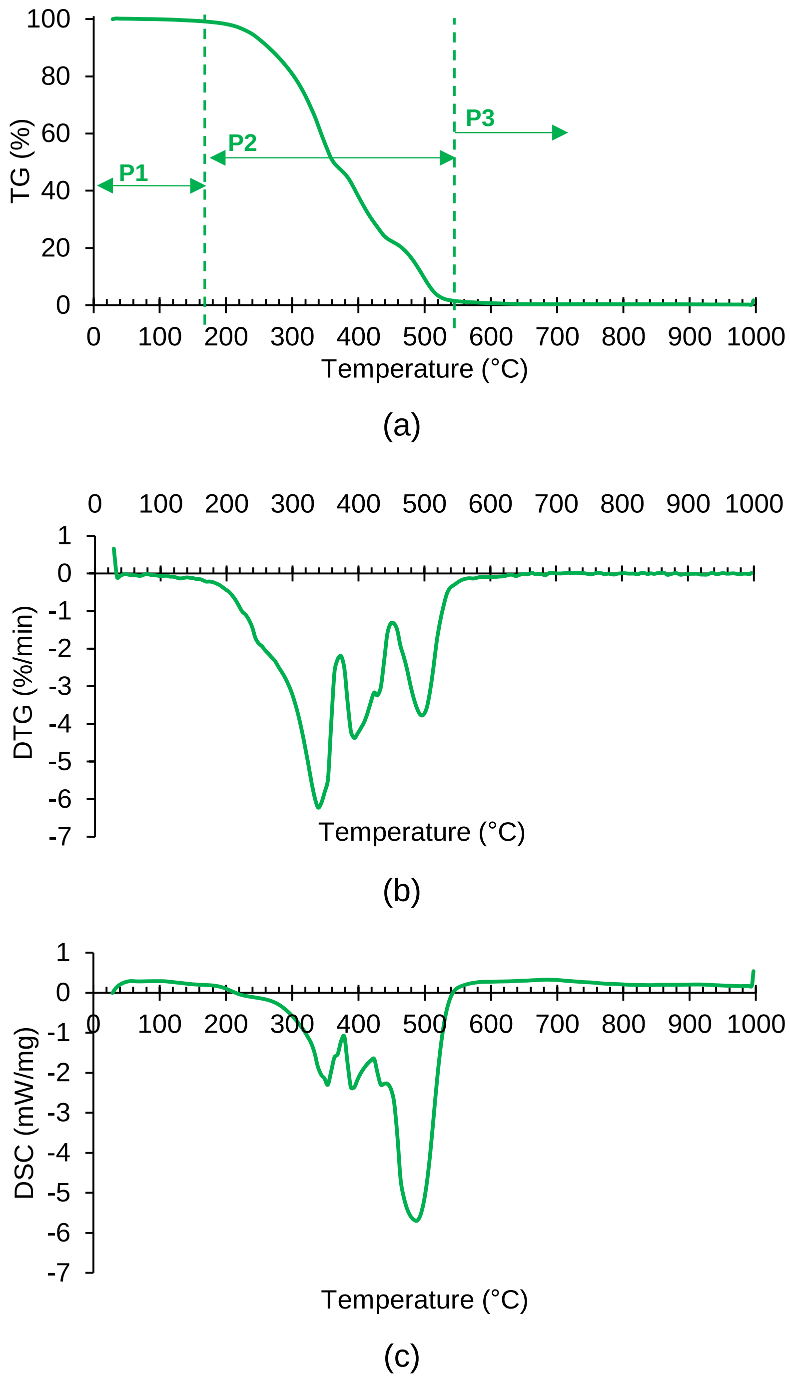


(c)

Source: Author (2020)

On the other hand, the oxygen atmosphere in the test generates a decomposition in a different temperature range, as part of the material burns during the test (oxidation process). Figure 26 presents the TGA in oxygen atmosphere for one sample of BioB. In this atmosphere, BioB starts to decompose in lower temperatures than in nitrogen atmosphere, beginning at 165°C. At the mixing and compaction temperatures (165°C-170°C) the TG curve (Figure 26a) shows that the loss of mass was of 0,9%, which correspond to the mass of volatile elements. The DTG curve (Figure 26b) identifies three reactions occurring during the decomposition of the material. The first one happens slowly with peak at 338°C, and the second and third occur faster, with peaks at 393°C and 493°C, respectively. Elkashef, Williams and Cochran (2019) studied the oxidative stability of a bio-rejuvenator made from soybean oil and found similar curves to the one presented in the Figure 26b for the one studied in the current research (i.e. two peaks). The authors attribute the first peak to the thermal oxidation of the main components of the bio-material, and the second one occurs due to the combustion of the remaining chart residue. Different from the reactions in the nitrogen atmosphere (Figure 25c), the DSC curve (Figure 26c) shows these reactions are accompanied by heat absorption by the sample.

Figure 26 ─ Thermo-gravimetric analysis in oxygen atmosphere of BioA, in terms of a) Thermo-gravimetric curves, b) DTG curves and c) DSC curves.



Source: Author (2020)

3.4 SUMMARY AND CONCLUSIONS

Rheological behavior of one wood-based bio-binder analyzed in this research showed that this material has potential for 100% replacement of the petroleum-based asphalt binders. The stiffness dependency on frequency/temperature and the permanent deformation susceptibility presented by the bio-binder are comparable, with the behavior exhibited by the asphalt binder, but in terms of fatigue resistance the bio-binder showed lower performance.

According to the results, the PG classification could not be applied to the bio-binder studied, due to the high stiffness and low elasticity ($|G^*|.\sin\delta$) of the PAV aged material under the imposed condition of strain, temperature and frequency evaluated. It prevents the identification of the intermediate and, as a consequence, the low PG temperature. The results also suggested that PAV test could cause damage to the internal structure of the material. Although, two samples by test might not be enough to reach this conclusion, more tests in PAV aged bio-binder would be carried out, including rheological tests, LAS test and TGA simulating the PAV test temperature conditions, in order to better understand the variability showed by this material after PAV aged stage. However, conditions external to this research (COVID-19 pandemic) restricted the use of laboratory facilities.

The TGA showed that the neat asphalt binder is thermally stable at higher temperatures than the bio-binder studied. However, in the temperature of mixing and compaction, the BioB remains thermally stable as the neat asphalt binder.

Further research work involving field test and durability aspects are needed in order to confirm the feasibility of the use of this bio-binder as a total substitute for the neat asphalt binder.

4 MOISTURE DAMAGE SUSCEPTIBILITY OF BIO-BINDERS

4.1 INTRODUCTION

Bio-binders and bio-oils -binders made from biomass- have become in an interesting alternative to reduce the petroleum-based asphalt binders. Literature shows that bio-binder from plant resources have higher potential to totally replace asphalt binder than those biomaterials from animal and waste cooking oil sources (CAMARGO, 2018; CAMARGO; BERNUCCI; VASCONCELOS, 2019; CHAILLEUX et al., 2012; PERALTA et al., 2012b; POUGET; LOUP, 2013)

However, one of the main concern towards the implementation of mixtures with bio-binders is the uncertainty in their overall durability (PERALTA et al., 2012b). In this regard, moisture damage resistance is one aspect of interest. Some authors point out that some compound in bio-oils may be harmful to the overall moisture susceptibility of asphalt binder, when used as a modifier, due to their solubility in water (GONG et al., 2016).

However, direct evaluation on the moisture damage resistance of mixtures made with bio-modified asphalt binder showed that the incorporation of the biomaterial do not adversely affect the moisture sensitivity of the mixtures. For example, a product obtained by the fast pyrolysis of pine wood chips, added to the mixture in proportions of 20%, 25.5% and 50% (by weight) was studied in Mohammad et al. (2013). The authors found that the moisture damage resistance of the mixtures with more than 30% of bio-binder would be reduced when compared with the reference mixture, nevertheless, it could be enhanced by the incorporation of an anti-stripping agent. On the other side, Wen, Bhusal and Wen (2013) found that mixtures with up to 60% (by weight) of a bio-binder (from waste cooking oil) passed the requirements for moisture damage resistance.

In regard of bio-binder in recycled mixture, Jimenez et al. (2019) studied the addition of plant-based bio-binders as fresh binder (i.e., new binder to be incorporated in the mixture), to the binder of the reclaimed asphalt (RA). They found that the bio-bidner generally improves the cohesion and adhesion of the RA binder or keep it up to an equivalent level to a neat asphalt binder. On the other side, Gong et al. (2016) added 3% of a bio-oil from the pre-treatment of biodiesel residue from waste cooking oil to an aged binder and found that the moisture sensitivity of the aged binder increased.

Regarding to bio-binder for total replacement of asphalt binder, there is a lack in the literature about the evaluation of moisture damage resistance.

In general, the moisture damage in a flexible pavement is the loss of structural capacity of the mixture induced by the presence of water. It is normally related to a cohesion failure (failure in the binder) or an adhesion failure (failure in the interface binder-aggregate) (TAN; GUO, 2013). Therefore, in order to characterize the moisture sensitivity of the materials, their cohesive and adhesive properties need to be assessed.

In this context, this paper presents an evaluation of the intrinsic cohesive and adhesion properties of a wood-based bio-binder for total replacement of asphalt binder compared with the properties of a neat and a highly modified asphalt binders, in combination with seven aggregates from different origins. As previous research showed that there is a good correlation of between Surface Free Energy parameters and energy ratios and moisture sensitivity of asphalt mixtures (GHABCHI; SINGH; HOSSAIN, 2016; LIU et al., 2014), these parameters were used in the current study.

4.2 MATERIALS AND METHODS

4.2.1 Materials

4.2.1.1 Binders

The bio-binder studied (BioB) was made from the treatment of pine wood resin. This product was designed for total substitution of asphalt binder in mixtures for surface layers, and it is the second generation of a bio-material studied before (CAMARGO; BERNUCCI; VASCONCELOS, 2019) and in the chapter 2 of this dissertation. As reference, an AC 30/45 and a highly modified asphalt (HiMA) binder were characterized. The HiMA correspond to an asphalt binder modified by a high percentage of elastomeric polymer SBS. Table 5 presents the conventional characterization of the binders studied.

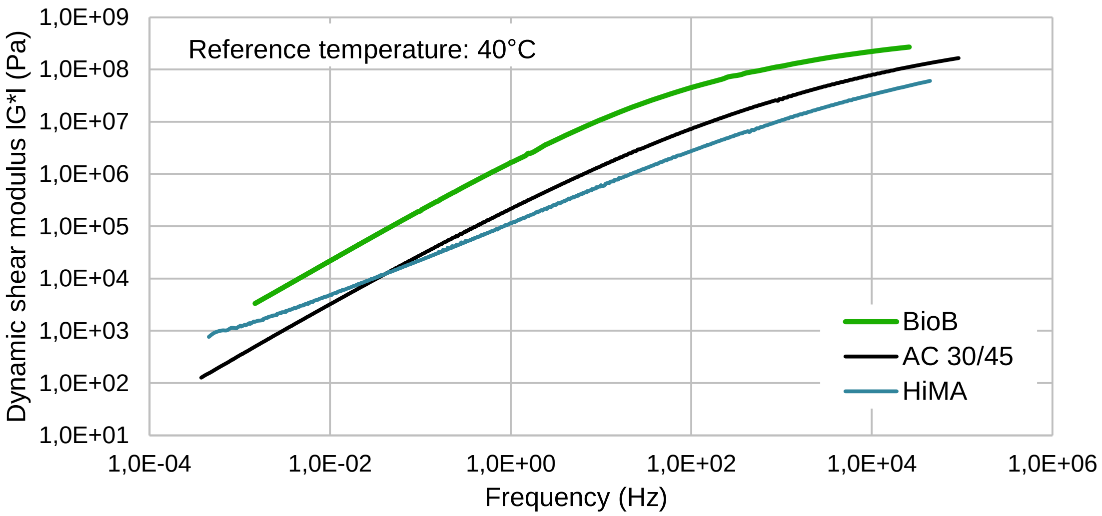
Table 5 — Conventional characterization of binders studied.

Test	Standard	BioB	AC 30/45	HiMA
Penetration at 25°C (1/10mm)	ASTM D5M - 13	21	25	45
Softening point (°C)	ASTM D36M-14	57	55	84
Rotational viscosity at 135°C (cP)	ASTM D4402M-15	638	361	2170

Source: Author (2020)

The three binders studied were subjected to short-term aging simulated in laboratory following the standard ASTM D 2872-12. Then, the linear viscoelastic characterization was made based on the results of a Frequency Sweep Test, with deformation rate of 0.01%, frequency range between 1 and 100 rad/s, and temperature varying from 10°C to 80°C. This characterization is showed in Figure 27.

Figure 27 — Viscoelastic characterization of the aged binders studied.



Source: Author (2020)

4.2.1.2 Aggregates

Table 6 presents the information of the aggregates used to calculated the adhesion with the binders studied. The seven aggregates are from available sources in the United States.

Table 6 ─ Origin of aggregates used in the current study.

ID	ORIGIN	TYPE
AG 1	El Paso, TX	Limestone
AG2	Brownwood, TX	Limestone
AG3	Knippa, TX	Traprock
AG4	Murphy, TX	River Gravel
AG5	Snyder, OK	Granite
AG6	Jones Mill, AK	Quartzite
AG7	Sawyer, OK	Sandstone

Source: Author (2020)

4.2.2 Methods

The SFE components of the binders involved in the current research were computed using the Wilhelmy plate method results. This method allows the determination of the contact angle between a liquid with known SFE components and a solid binder surface (HEFER; BHASIN; LITTLE, 2006). With these measurements and based on the Good-van Oss-Chaudhury theory (SCHAPERY, 1984), the calculation of the SFE of the binder it is possible. For this study, four liquids were used: formamide, ethylene glycol, distilled water, and glycerol, and with each liquid were tested for samples of each binder.

The aggregates SFE components were taken from the Database presented in FHWA/TX-09/5-4524 (FHWA, 2009). The authors used the Universal Sorption Device, which uses the gas adsorption characteristics of three solvents (i.e. nHexane, methyl propyl ketone and water) to compute the aggregate SFE components.

4.2.3 Energy parameters: cohesion and adhesion characteristics of binder-aggregate systems

The SFE is known as the work required to create a unit area of surface in a material (BHASIN et al., 2007). The total SFE (Γ) of a material is the combination of three components: a nonpolar component, also known as Lifshitz-van der Waals component (Γ^{LW}), a monopolar acid (Γ^{+}) and a monopolar basic (Γ^{-}) (VAN OSS, 1994; VAN OSS; CHAUDHURY; GOOD, 1988). Equation 1 shows the relationships between these components.

$$\Gamma = \Gamma^{LW} + 2\sqrt{\Gamma^{+}\Gamma^{-}} = \Gamma^{LW} + \Gamma^{AB} \tag{1}$$

When the SFE components of the materials in a system are known, it is possible determine the amount of work required to separate them. Thus, the work of adhesion in an binder-aggregate system and the work of cohesion of a binder can be calculated as a combination of the SFE components of the binder (subscript B) and the aggregate (subscript A) as describe below.

The work of cohesion (W_{BB}) is the necessary energy to separate a unit area of a binder into two new surfaces and it is computed using Equation (2).

$$W_{BB} = 2\Gamma_{B}^{LW} + 4\sqrt{\Gamma_{B}^{+}\Gamma_{B}^{-}} \tag{2}$$

The work of adhesion (W_{BA}) is the energy required to separate the binder-aggregate system at the interface, by creating two new surfaces of unite area, and it is calculated using the Equation (3).

$$W_{BA} = 2\sqrt{\Gamma_{B}^{LW}\Gamma_{A}^{LW}} + 2\sqrt{\Gamma_{B}^{+}\Gamma_{A}^{-}} + 2\sqrt{\Gamma_{B}^{-}\Gamma_{A}^{+}} \tag{3}$$

The presence of water in the interface binder-aggregate reduces the work of adhesion system, since the aggregate has a greater affinity for water than for the binder. Therefore, the work of adhesion in wet condition or work of debonding (W_{BAW}^{wet}), is calculated as a combination of the interfacial energies in the water-binder (W_{WB}), water-aggregate (W_{WA}) and binder-aggregate (W_{BA}) systems, as described in Equation (4).

$$W_{BAW}^{wet} = W_{WB} + W_{WA} - W_{BA} \tag{4}$$

Where W_{WB} and W_{WA} are calculated by replacing the SFE components of the aggregate and the binder for those of the water in Equation (3), respectively.

Finally, the moisture damage susceptibility of the binder-aggregate systems is assessed by the ER_1 and the ER_2 indexes (Equations (5) and (6)) (BASHIN et al., 2007). High values of ER_1 are associated with system that develop interfaces with high resistance to debonding in dry conditions and at the same time, reduced susceptibility to the effect of water. The ER_2 is a modification of the ER_1 to include the wettability, which is the ability of a binder to adequately coat the aggregate (LIU; YU; DONG, 2017).

$$ER_1 = \left|\frac{W_{AS}^{dry}}{W_{WAS}^{wet}}\right| \tag{5}$$

$$ER_2 = \left|\frac{W_{AS}^{dry} - W_{AA}}{W_{WAS}^{wet}}\right| \quad (6)$$

4.3 RESULTS AND DISCUSSIONS

4.3.1 Surface free energy and energy parameters

The COV for the contact angles for BioB samples ranged between 1.8% and 5.7%. For AC 30/45 samples that range was from 0.5% to 2.4%. COV of HiMA samples ranged between 0.5% and 9%. The total SFE and SFE components of binders and aggregates are summarized in Table 7. BioB is the binder with highest total SFE, making it the most cohesive binder when compared with the HiMA and AC 30/45, as seen in Figure 28 (Work of cohesion). HiMA presented the lowest SFE, the non-polar component (Γ^{LW}) is the most significant contributor to the total SFE, this suggests that HiMA could present a poor compatibility with polar aggregates, based on the principle of similarity and intermiscibility (LIU; YU; DONG, 2017). According to this, it is expected that HiMA present a better bonding with the AG1, which is the aggregate with the SFE commanded by the non-polar component. Meanwhile, BioB presents similar values of non-polar and polar components, with suggests that this bio-material will have a well bonding potential with polar and non-polar aggregates.

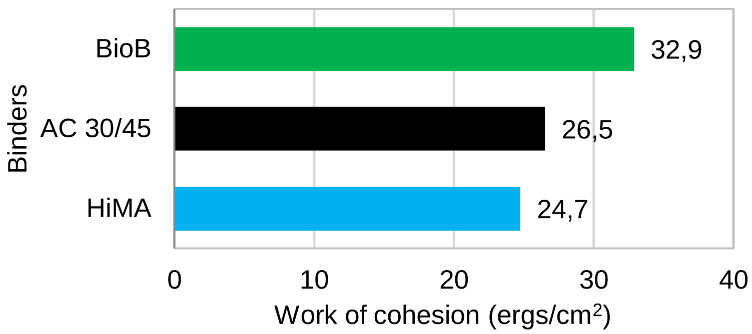
Table 7 – Surface free energy components of binders and aggregates.

Materials	Γ	Γ^{LW}	Γ^{AB}
BioB	16,4	8,1	8,3
AC 30/45	13,3	3,1	10,2
HiMA	12,4	7,0	5,4
AG1	271,0	152,0	119,0
AG2	124,8	52,0	72,9
AG3	521,7	53,4	468,3
AG4	162,0	50,2	111,8
AG5	425,2	56,4	368,8
AG6	265,4	59,9	205,5
AG7	94,8	41,5	53,3

Source: Author (2020)

The main moisture damage causes in flexible pavements are failures in the cohesion (inside the binder) and in the adhesion (binder-aggregate interface), as describe in section 4.2, the SFE influences those aspects (TAN; GUO, 2013). The work of cohesion of the binders studied is presented in Figure 28. As can be seen, BioB has the highest work of cohesion and HiMA the lowest. According to Liu, Yu and Dong (2017), materials with higher cohesive energy would present a higher resistance to moisture damage. This suggests that between the binders studied, BioB has a higher potential to develop a better resistance to the water effect. However, it depends on the combination with the aggregates and the compatibility of the system.

Figure 28 – Work of cohesion of the bio-binder, the neat asphalt binder and the highly modified asphalt binder.

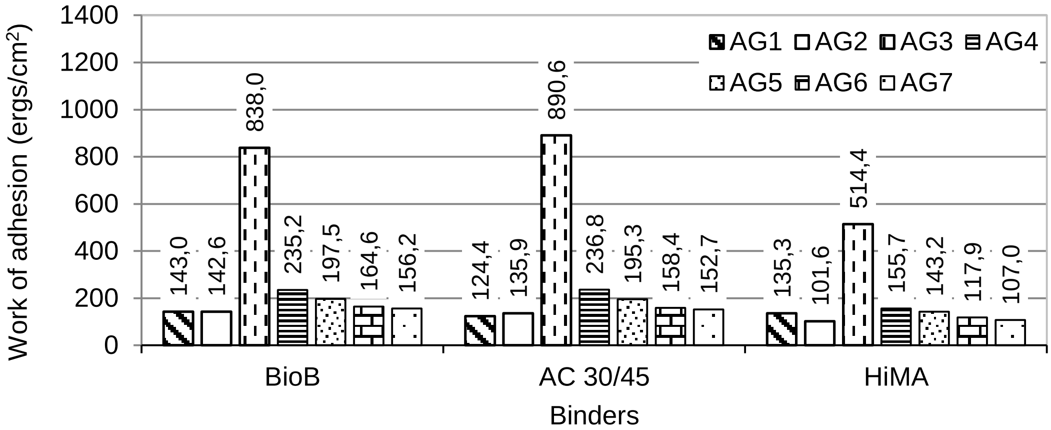


Source: Author (2020)

In order to assess the compatibility of the binders with aggregates from different origin, the Work of adhesion (W_{BA}) between BioB, AC 30/45 and HiMA with seven aggregates was calculated and Figure 29 shows the results. As expected, AG1 presented higher adhesion with HiMA that the combinations with the other binders. HiMA presents a lower compatibility with rest of the aggregates. The three binders evaluated presented the higher W_{BA} in dry condition with AG3, a traprock aggregate with the highest SFE among the materials studied (Table 7). BioB presented similar trends to the neat asphalt binder in all the combinations binder-aggregate. Jimenez et al. (2019) studied two bio-binder from plant biomass to be used as fresh binder in recycled mixtures, the W_{BA} analysis presented showed that the bio-binders studied had more affinity with the limestone aggregate than the granite. The opposite trends was found in the current study, as seen in Figure 29, the granite (AG5) showed higher W_{BA} than the limestones

(AG1 and AG2) in combination with BioB. This could be due to the mineralogical composition of the biomaterials and aggregates used in both studies.

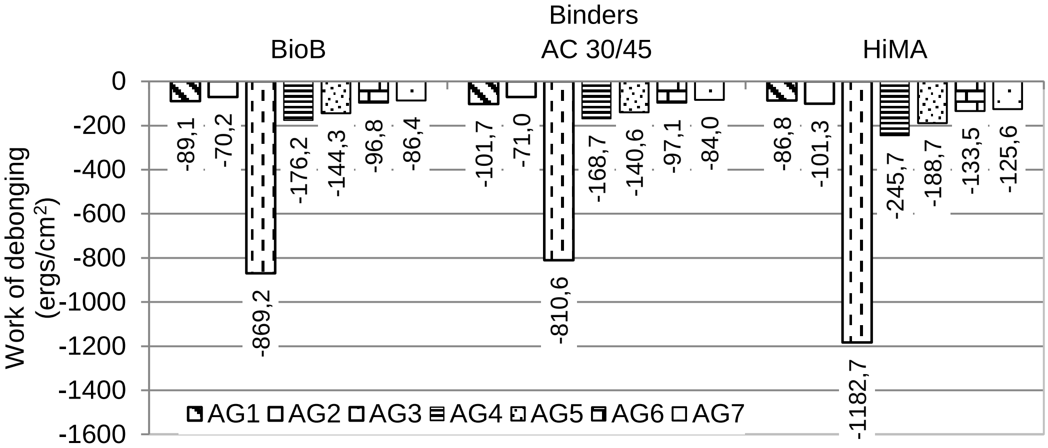
Figure 29 ─ Work of adhesion of the binder-aggregate systems studied.



Source: Author (2020)

Figure 30 presents the work of debonding. Due to the high affinity of the aggregate with water, the work of debonding (W_{BAW}^{wet}) is always negative. Which means that without any external forces, the water is capable of separate the interface binder-aggregate. Therefore, for binder-aggregate systems with good resistance to moisture damage it is expected the smaller values of W_{BAW}^{wet}. As seen in Figure 30, the presence of water weaken the bonding of the AG3 with all binders, which had been stronger in the work of adhesion in dry condition. This may due to the polar nature of the water that is more compatible with the higher polar component of the AG3 (Table 7). For the three binder, the aggregate with less susceptibility to the water effect is the limestone (AG2). Between the binders studied, HiMA presented the higher values of W_{BAW}^{wet}, thus, it is the material with poorest potential to resist moisture damage. BioB showed similar tendencies to the AC 30/45.

Figure 30 ─ Work of debonding of the binder-aggregate systems studied.



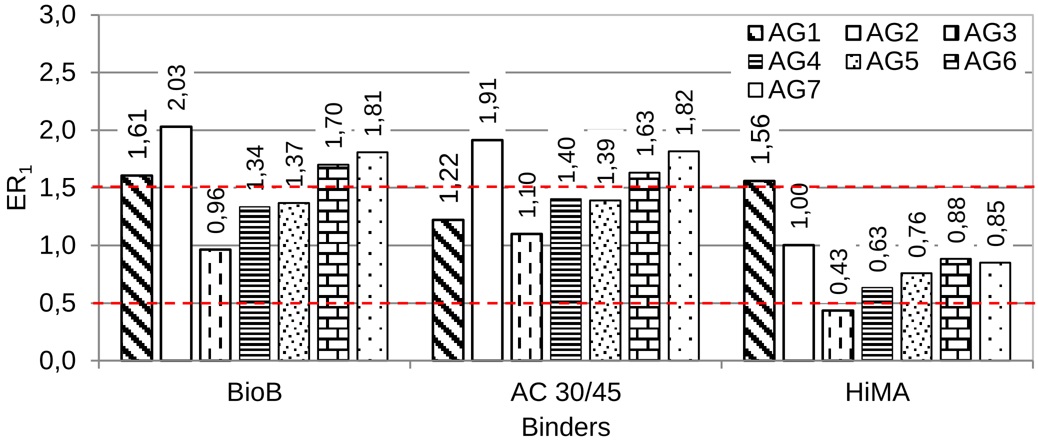
Source: Author (2020)

4.3.2 Moisture damage susceptibility: Energy ratios

Binder-aggregate interfaces with high resistance to be disrupted by the presence of water are expected to have work of adhesion as high as possible, while keeping the work of debonding as low as possible. Therefore, the higher ER_1 (Equation (5)) the higher the potential of the system to resist moisture damage. Figure 31 shows the ER_1 indexes of the binder-aggregate systems studied.

Bhasin et al. (2006) established thresholds to ER_1 results from the performance of the tested materials in the field. According to the authors, ER1 higher than 1.5 correspond to materials with good moisture damage resistances, materials with ER_1 between 0.5 and 1.5 have intermediate resistance to the deleterious water effect, and ER_1 less than 0.5 correspond to materials with poor resistance to this degradation phenomenon. As can be seen in Figure 31, BioB and AC 30/45 in combination with all aggregates presented similar tendencies, with ER_1 indexes in the intermediate and high resistance zone, while HiMA exhibited ER_1 indexes in the intermediate and poor resistance zone.

Figure 31 – ER_1 index of the binder-aggregate systems studied.

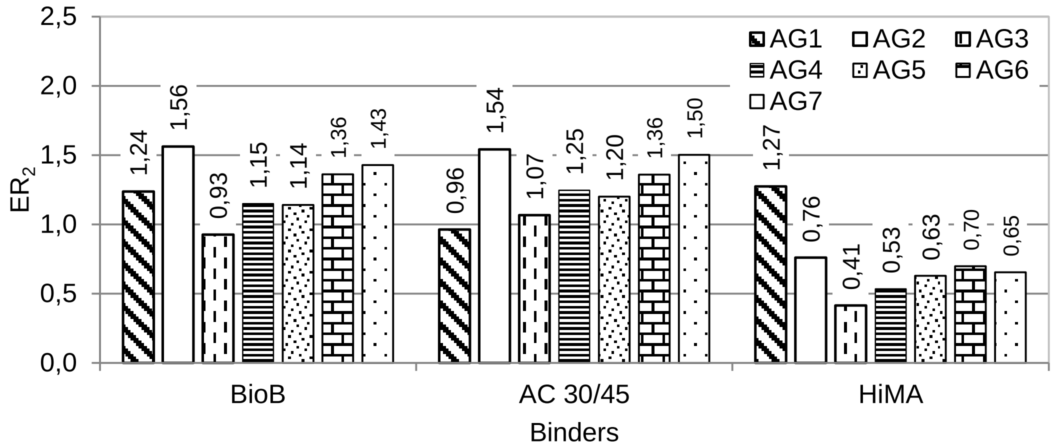


Source: Author (2020)

Figure 31 points the importance of choosing better the combination binder-aggregate to obtain mixtures with high moisture damage resistance. The bio-binder showed good indexes in all combinations, however, combination with AG2 presented an ER_1 twice as high as combination with AG3, that would be the difference between a mixture with a high or intermediate resistance to the effect of water.

The ER_2 presented in Figure 32 allows identifying material combinations that can develop at the same time proper wettability and resistance to moisture damage. Results in Figure 32 suggest that the bio-binder has a wettability as good as the neat asphalt binder, and in most of combinations, higher than the highly modified asphalt binder.

Figure 32 – ER_2 index of the binder-aggregate systems studied.



Source: Author (2020)

According to the results in the energy parameters, BioB presented a moisture damage susceptibility similar with the presented by the neat asphalt binder. An asphalt binder modified by a bio-oil from sawdust and by polymer showed similar results, with good moisture damage resistance (ZHANG et al., 2017).

4.4 SUMMARY AND CONCLUSIONS

The moisture damage sensitivity of a wood-based bio-binder (BioB) for total substitution of asphalt binder in mixtures for surface layers was evaluated using energy parameters based on the Surface Free Energy (SFE) components. The SFE components of seven aggregates from different sources were used to evaluate the adhesive bond with the bio-binder. The results were compared with a neat asphalt binder (AC 30/45) and a highly modified asphalt binder (HiMA), taken as reference.

The evaluation of the Work of cohesion showed that BioB is the most cohesive among the binders studied. This, added to the results of the work of adhesion and the energy ratios, showed that this biomaterial has potential to develop high resistance to moisture damage. The trends exhibited for the BioB are similar to those of the AC 30/45, which is an indicator that this bio-binder may be as durable as asphalt binders in terms of moisture damage resistance, while HiMA exhibited the least resistant bonds in presence of water.

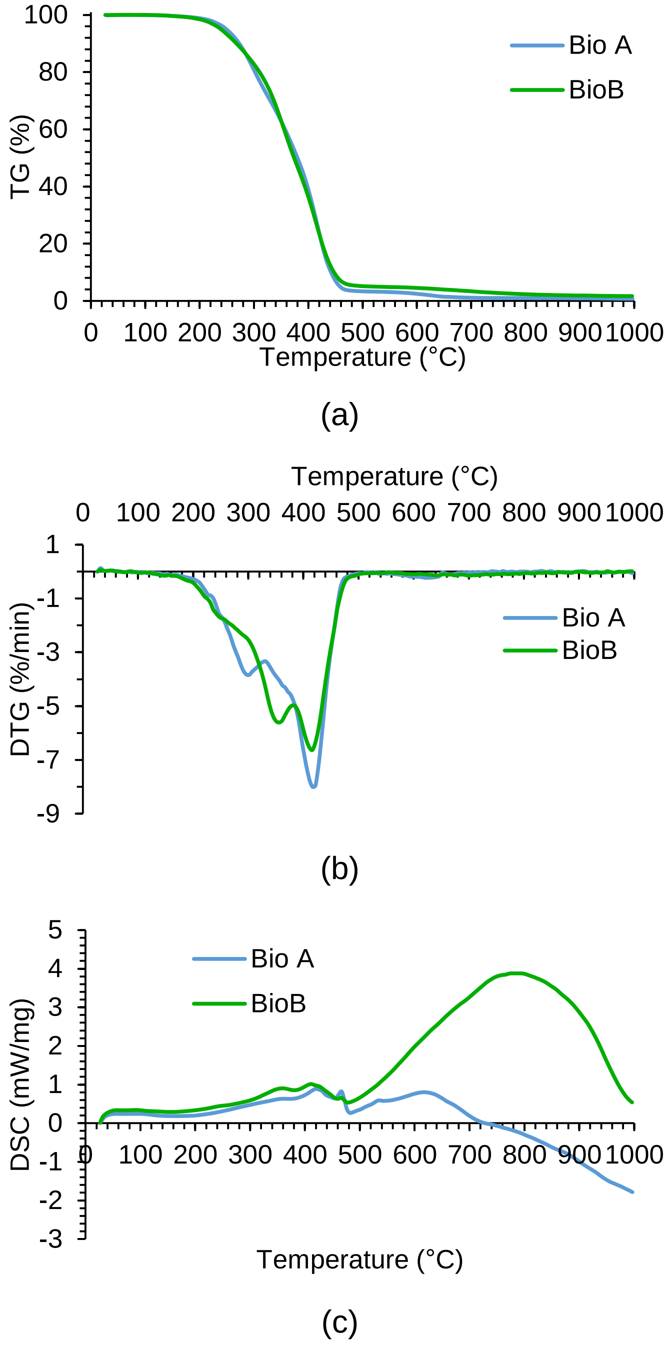
According to the above, the total substitution of asphalt binder by the bio-binder studied would not affect the moisture damage sensitive of the surface layer. However, it would be necessary further study in the behavior of mixtures manufactured with this material, in order to determine if the potential of the combination computed by the SFE components is reflected in the mixture behavior.

5 COMPARISION BETWEEN THE BIO-BINDERS STUDIED

As mentioned in section 1.7, both bio-binders studied, BioA and BioB, are successive generations of the same product. The difference in formulation led to a difference in the behavior of both bio-binders. This chapter discuses those differences and the key points that may be improved to get a final product with enhanced characteristics.

Figure 33 presents the thermogravimetric analysis of both bio-binders in a nitrogen atmosphere. It is possible to observe that the thermal degradation of both materials begins at the same temperature, around 190°C (Figure 33a). However, the DTG curve (Figure 33b) shows that the reactions occurring in both binders are different, specially the first reaction. For BioA, the reactions occurs more rapidly with peak at 290°C, while for BioB is at 340°C. The second reaction has peak at the same temperature for both binders, however, the mass loss rate is higher in the BioA. The DSC curve (Figure 33c) shows that the reactions in both materials release energy through heat (exothermic reactions). The nature of those reactions remains unknown, as the composition of both materials are not available to discuss.

Figure 33 ─ Thermogravimetric analysis of BioA and BioB.

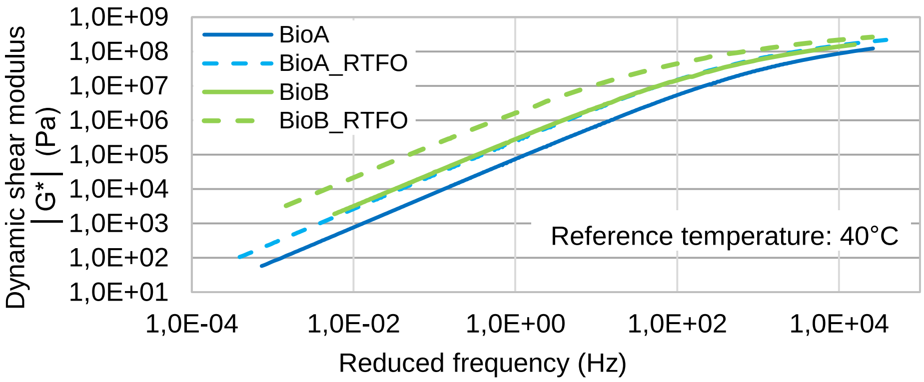


Source: Author (2020)

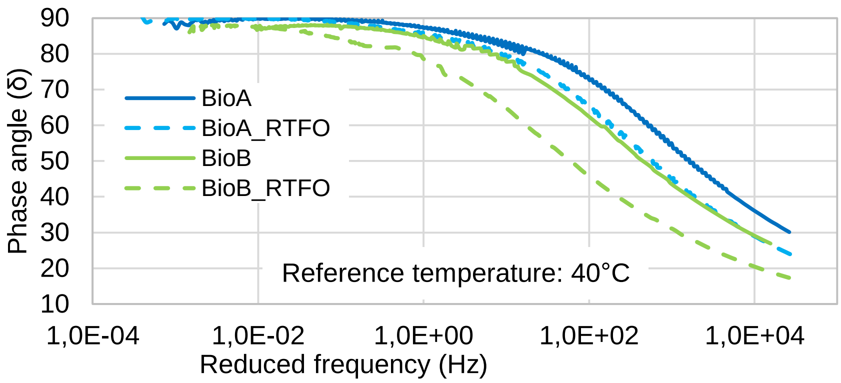
The viscoelastic characterization of both bio-binders in unaged and short-term aged conditions is shown in Figure 34. It can be seen that BioB is stiffer than BioA in all aged stages (Figure 34a). The short-term aging (RTFO) increased the stiffness of both materials, nevertheless, the effect in BioB was more remarkable, with increases of more than 220% up to 570%, while for BioA the increase was from 150% to 250%. The mass loss determined after the RTFO test was higher for BioB, which obtained a 0,50% versus a 0,27% of BioB. These results suggest that the modifications on BioA to obtain BioB increased the stiffness of the material whereas increased the effect of aging.

The phase angle master curves presented in Figure 34b, shows that BioB presented more elastic behavior than BioA. The short-term aging effect in both binders is the same, the RTFO samples are more elastic than the unaged ones, however this effect is higher on BioB. One alternative to reduce the aging effect would be the reduction on the temperatures for mixing and compaction. For BioA, the temperature was 150°C and for BioB was 165°C, and it could be seen that BioB was more prone to aging. The addition of a modifier to reduce the viscosity of the biomaterial would help on this aspect.

Figure 34 – Viscoelastic characterization of BioA and BioB.



(a)

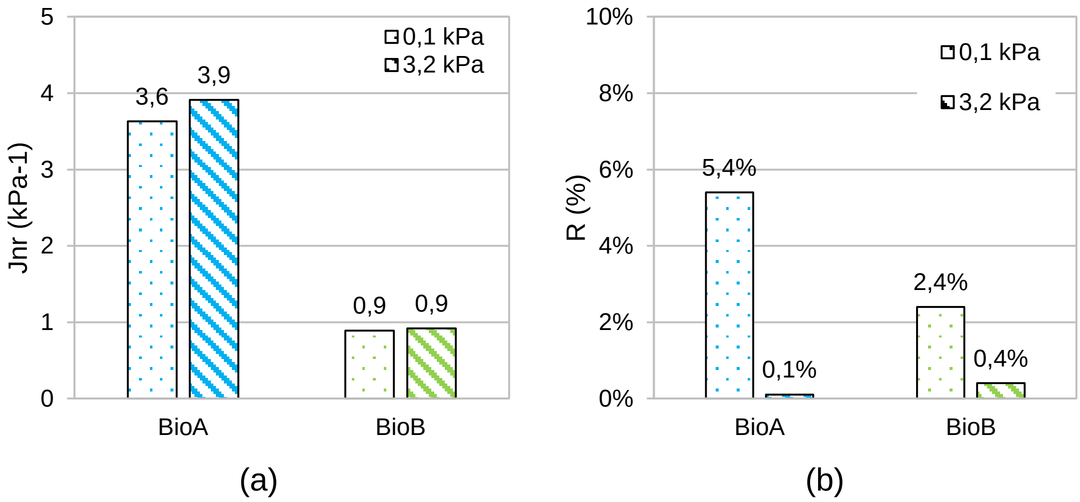


(b)

Source: Author (2020)

The MSCR test was used to determine the permanent deformation susceptibility of the binders. Figure 35 presents the results of the test in terms of non-recoverable compliance (Jnr) and the recovery (R). Both binders were tested at 70°C in order to compare their results at the same temperature. It is possible to see that BioB presented a better resistance to permanent deformation, obtaining the lower values in Jnr. This represent an improvement of the final product, however the recovery remained the same for both binders. The addition of a modifier to improve the recovery of the material may be consider.

Figure 35 – MSCR at 70°C results of BioA and BioB.



Source: Author (2020)

The change in formulation of BioA, which resulted in BioB, showed that the performance of the material improved in terms of stiffness and permanent deformation. However, the discussion on fatigue life presented in chapters 2 and 3 showed that the resistance to fatigue of both binders is lower than that of the asphalt binder. The comparison is not presented in this chapter because both materials were tested at different aged conditions and, due to pandemic COVID 19, it was not possible to repeat the tests in order to directly compare them.

The moisture susceptibility of BioB, assessed in chapter 4 showed that this material has the potential to be as durable as asphalt binder, in terms of moisture damage resistance. However, the mechanical evaluation of mixtures presented in chapter 2 with BioA showed that the bio-binder presented higher sensibility to moisture, when compared with the asphalt mixture. This difference may be due to the difference in the composition of the bio-binders and the difference in the aggregates studied. Nevertheless, it is necessary to undergo the mechanical evaluation of the combinations of BioB with local aggregates to determine if the product would perform in the same way.

On the other hand, while producing the samples for all test reported in this thesis, it was evidenced that the high temperatures generate gases emissions with a peculiar strong smell. It is necessary to study the nature of those emissions, and determine if they have adverse effect on the environment and/or human health. The reduction on the mixing and compaction temperatures would help in this regard.

6 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Bio-binders for pavement application present an environmentally friend alternative to the high petroleum-based asphalt binder dependency. Among its advantages are the reduced consumption of non-renewable sources and reduction of greenhouse gases emissions, due to the decreased consumption of asphalt binders. However, its rheological and mechanical behavior need to be properly characterized, in order to better understand how the binder properties are transferred to the mixture.

In this sense, this thesis studied two nationally produced wood-based bio-binders as a total replacement for the conventional asphalt binder. The evaluation of each bio-binder showed:

- The two bio-binders studied in this research have rheological behavior similar to the asphalt binder, with dynamic shear modulus increasing with the increase of frequency. Phase angle analysis showed that BioA and BioB tend to have a more viscous behavior than the asphalt binder at high temperatures, but they behave more elastically at low temperatures.
- Evaluation of the PAV aged BioB showed that this test may be aggressive to this type of material, leading to the degradation of the binder. More research is need in order to better understand the PAV aging effect on this material, as it might be related to its durability.
- Analysis of BioB showed that the Performance Grade classification may not be suitable for this kind of bio-binder, due to the material variability and also its very high stiffness after the long-term PAV aging. TGA showed that there are more reactions occurring in bio-binders than in the asphalt binder during thermal degradation, related to the different composition of both materials, what might be the reason for its variability. However, for mixing and compaction temperatures, BioB and the neat asphalt binder remain thermally stable.
- In terms of permanent deformation, in the MSCR test, BioB showed a better performance while BioA showed no difference when compared with the neat

asphalt binder taken as reference. Fatigue resistance showed that both bio-binders presented lower performance when compared with the asphalt binder.

- Energy parameters based on the Surface Free Energy components suggest that BioB presents durability similar of the neat asphalt binder. It also showed that there exist more affinity with limestone aggregate and less with the river gravel aggregate.

The behavior of BioA was also evaluated in the mixture with aggregates and an experimental test site was constructed. The comparison was made using a hot mix asphalt (HMA) prepared with neat asphalt binder as the reference. This evaluation showed that:

- The mixture with BioA, called as BM, showed higher moisture damage susceptibility than the HMA and it was attributed to the organic composition of the bio-binder.
- The BM presented higher dynamic modulus at higher frequencies than the HMA. This trend was also observed in the binder master curves. As the aggregates source and gradation were the same for both mixtures, these differences are attributed to the binder itself. Thus, BM mixture has higher stiffness in low temperatures than the HMA, but presents a similar stiffness at high temperatures. Phase angle curves of the mixture showed the same tendencies of the binder, with BM presenting a more viscous behavior at low frequencies, and a more elastic one at high frequencies, when compared with the HMA. Permanent deformation results showed that BM and HMA had similar resistance, which reflected the binders' behavior in the MSCR test.
- The field performance of the BM was found to be comparable to that of an HMA surface layer, based on the FWD and IRI results gathered through three years of pavement monitoring.

These outcomes suggest that BioA and BioB have potential to be used as a total replacement for the neat asphalt binder. Evaluation of the combination with conventional modifiers, such as polymers, need to be studied to determine if some properties of the mixture may be improved in the same way as the properties of asphalt mixtures are improved by these additives. Future research is also needed to assess the durability and the emissions produced during the mixing and compaction process of mixtures produced with bio-binders.

REFERENCES

AFLAKI, S.; HAJIKARIMI, P.; FINI, E.; ZADA, B. **Comparing Effects of Biobinder with Other Asphalt Modifiers on Low-Temperature Characteristics of Asphalt**. Journal of Materials in Civil Engineering, v. 26(3). 2014

AIREY, G.; HUNTER, A.; RAHIMZADEH, B. The influence of geometry and sample preparation on dynamic shear rheometer testing. **Performance of bituminous and hydraulic materials in pavements,** pp. 3-12. 2002

AIREY, G.; MOHAMMED, M. **Rheological properties of polyacrylates used as synthetic road binders.** Rheological Acta, v. 47, pp. 751-763. 2008

AKCELRUD, L. **Fundamentos da ciência dos polímeros.** Editora Manole LTDA., 2007

ALAMAWI, M.; KHAIRUDDIN, F.; YUSOFF, N.; BADRI, K.; CEYLAN, H. **Investigation on physical, thermal and chemical properties of palm kernel oil polyol bio-based binder as a replacement for bituminous binder.** Construction and Building Materials, v. 204, pp. 122-131. 2019

AMERICAN ASSOCIATION OF STATE AND HIGHWAY TRANSPORTATION OFFICIALS. **AASHTO T 101-14**: Estimating Damage Tolerance of Asphalt Binders Using the Linear Amplitude Sweep. 2014

______. **AASHTO M 332-141-2014**: Standard specification for performance-graded asphalt binder using multiple stress creep recovery (mscr) test. 2014

______. **AASHTO M 320-09**: Standard Specification for Performance-Graded Asphalt Binder. 2009

______. AASHTO T 342-11: Standard Method of Test for Determining Dynamic Modulus of Hot-Mix Asphalt Concrete Mixtures. 2011

______. AASHTO T166-16: Standard Method of Test for Bulk Specific Gravity (Gmb) of Compacted Hot Mix Asphalt (HMA) Using Saturated Surface-Dry Specimens. 2016

______. ASTM D 1559/92: Resistance to plastic flow of bituminous mixture using Marshall apparatus. 1992

AMERICAN SOCIETY FOR TESTING AND MATERIALS. **ASTM D5M – 13**. Standard Test Method for Penetration of Bituminous Materials. 2013

______. **ASTM D36M-14**. Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus). 2014

______. **ASTM D4402M-15**. Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer. 2015

______.**ASTM D2872-12**: Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test). 2012

______. **ASTM D4867-14**: Standard Test Method for Effect of Moisture on Asphalt Concrete Paving Mixtures. 2014

______. **ASTM D6521-18**: Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV). 2018

______. **ASTM D7175-15**: Standard Test Method for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer. 2015

______. **ASTM D7405-15**: Standard Test Method For Multiple Stress Creep And Recovery (MSCR) Of Asphalt Binder Using A Dynamic Shear Rheometer. 2015

______. **ASTM-E-950/98**. Standard Test Method for Measuring the Longitudinal Profile of Traveled Surfaces with an Accelerometer Established Inertial Profiling Reference. 1998

AZIZ, M.; RAHMAN, T.; HAININ, R.; BAKAR, W. **An overview on alternative binders for flexible pavement.** Construction and Building Materials, v. 84, pp. 315-319. 2015. http://dx.doi.org/10.1016/j.conbuildmat.2015.03.068

BHASIN, A.; LITTLE, D.; VASCONCELOS, K.; MASAD, E. **Surface free energy to Identify moisture sensitivity of materials for asphalt Mixes.** Transportation Research Record: Journal of the Transportation Research Board, 2001, pp. 37–45. 2007. doi:10.3141/2001-05

BHASIN, A.; MASAD, E; LITTLE, D.; LYTTON, R. **Limits on adhesive bond energy for improved resistance of hot mix asphalt to moisture damage.** Transportation Research Record: Journal of the Transportation Research Board, 2006 (1970), pp. 3-13. 2006

BERNUCCI, L.; MOTTA, L.; CERATTTI, J.; SOARES, J. **Pavimentação asfáltica: formação básica para engenheiros.** Rio de Janeiro: PETROBRAS: ABEDA. 2008

BLANC, J.; HORNYCH, P.; SOTOODEH-NIA, Z.; WILLIAMS, C.; POROT, L.; POUGET, S.; BOYSEN, R.; PLANCHE J.; LO PRESTI, D.; JIMENEZ, A; CHAILLEUX, E. **Full-scale validation of bio-recycled asphalt mixtures for road pavements**. Journal of Cleaner Production, v. 227, pp. 1068-1078. 2019

BRIDGWATER, A. V. **Review of fast pyrolysis of biomass and product upgrading**. Biomass and bioenergy, v. 38, pp. 68-94. 2012

CAMARGO, I. Potencial do emprego de misturas de bioligante e agregados usinadas a quente para revestimentos e bases de pavimentos. Master thesis, Universidade de São Paulo, São Paulo, Brazil. 2018

CAMARGO, I.; BERNUCCI, L.; VASCONCELOS, K. Aging characterization of Biobinder produced from renewable sources**. RILEM 252-CMB Symposium 2018**, RILEM Book series 20, pp. 1–6. 2019

CANEVAROLO, S. **Técnicas de Caracterização de Polímeros**. 1ra edição. São Paulo: Artiliber. 2003

CAO, X.; WANG, H.; CAO, X.; SUN, W.; ZHU, H., TANG, B. **Investigation of rheological and chemical properties asphalt binder rejuvenated with waste vegetable oil.** Construction and Building Materials, v. 180, pp. 455-463, 2018

CARO, S.; VEGA, N.; HUSSERL, J.; ALVAREZ, A. E. **Studying the impact of biomodifiers produced from agroindustrial wastes on asphalt binders**. Construction and Building Materials, v. 126, pp. 369-380. 2016

CHAILLEUX, E.; AUDO, M.; BUJOLI, B.; QUEFFELEC, C.; LEGRAND, J.; LÉPINE, O. Alternative Binder from Microalgae Algoroute Project. **In the workshop on alternative binders at the 91st Annual Meeting of the Transportation Research Board**. Transportation Research Circular Number E-C165, pp. 7-14. Washington D.C. 2012

CHEN, C.; HSEU, Y.; LIANG, S.; KUO, J. Assessment of genotoxicity of methyl-tert-butyl ether, benzene, toluene, ethylbenzene, and xylene to human lymphocytes using comet assay. Journal of hazardous materials, v. 153(1), pp. 351-356. 2008

CINCOTTO, M.A. **Capítulo 2: análise térmica dos ligantes e seus materiais**. Disciplina PCC 5042 "Ciência dos materiais aplicada aos ligantes inorgânicos" – Departamento de Engenharia de Construção Civil. Escola Politécnica da Universidade de São Paulo. 2014

CZERNIK, S.; JOHNSON, D. K.; BLACK, S. **Stability of wood fast pyrolysis oil**. Biomass Bioenergy, v. 7(1–6), pp. 187–192. 1994

CZERNIK, S.; BRIDGWATER, A. **Overview of Applications of Biomass Fast Pyrolysis Oil**. Energy & Fuels, v. 18, pp. 590-598. 2004

DA COSTA, L., GRANGEIRO DE BARROS, A., LUCENA, L., LUCENA, A. **Asphalt mixture reinforced with banana fibers**. Road Materials and Pavement Design. 2020. https://doi.org/10.1080/14680629.2020.1713866

DA SILVA, L.; FORTE, M.; VIGNOL, L.; CARDOZO, N. **Study of rheological properties of pure and polymer-modified Brazilian asphalt binders**. Journal of Materials Science, v. 39, pp. 539–546. 2004

DALMAZZO, D.; JIMENEZ DEL BARCO CARRIÓN, A.; TSANTILIS, L.; LO PRESTI, D.; SANTAGATA, E. Non-petroleum- based binder for paving applications: rheological and chemical Investigation on ageing effects. **Proceedings of the 5th International Symposium on Asphalt Pavements & Environment (APE)**. Lecture Notes in Civil Engineering, v. 48. 2020

DE SÁ ARAUJO, M.; LINS, V.; PASA, V.; LEITE, L. Weathering aging of modified asphalt binders. Fuel Processing Technology , v. 115, pp. 19-25, 2013.

DHASMANA, H.; OZER, H.; AL-QADI, I.L.; ZHANG Y, SCHIDEMAN, L.; SHARMA, B.K.; CHEM, W.T.; MINARICK, M.J.; ZHANG, P. **Rheological and chemical characterization of biobinders from different biomass resources.** Transportation Research Record. Journal of the Transportation Research Board 2505, v. 2505, pp. 121-129. 2015

DIEBOLD, J. **A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils**. Final report to U.S. Department of Energy, Rep. No. NREL/SR-570-27613, Thermalchemie, Inc., Golden, CO. 2000

DONG, Z., ZHOU, T., LUAN, H., YANG, C., WANG, P. Evaluation and improvement of moisture susceptibility of bio-asphalt incorporating chemical modifiers**. TRB 2019 98th Annual Meeting.** Paper Number: 19-01492. 2019

DONG, Z.; ZHOU, T.; WANG, H.; LUAN, H. **Performance Comparison between Different Sourced Bioasphalts and Asphalt Mixtures**. Journal of Materials in Civil Engineering, v. 30 (5), pp. 04018063. 2018

DORCHIES, P. The Environmental Road of the Future: Analysis of energy consumption and greenhouse gas emissions**. Annual Conference of Transportation Association of Canada**. Toronto, Canada, 2008.

ECOPAVE AUSTRALIA. (2009). **GEO320 master roller hybrid**. Ecopave Australia Bio-Bitumen Asphalt Concrete Research. 2009

EL-BADAWY, S., BAYOMY, F., AWED, A. **Performance of MEPDG dynamic modulus predictive models for asphalt concrete mixtures: local calibration for Idaho**. Journal of Materials in Civil Engineering, v. 24(11). 2012 https://doi.org/10.1061/(ASCE)MT.1943-5533.0000518

ELKASHEF, M.; WILLIAMS, C.; COCHRAN, E. **Thermal stability and evolved gas analysis of rejuvenated reclaimed asphalt pavement (RAP) bitumen using thermogravimetric analysis–Fourier transform infrared (TG–FTIR).** Journal of Thermal Analysis and Calorimetry, v. 131, pp. 865-871. 2018 https://doi.org/10.1007/s10973-017-6674-9

ELKASHEF, M.; WILLIAMS, C.; COCHRAN, E. **Thermal and cold flow properties of bio-derived rejuvenators and their impact on the properties of rejuvenated asphalt binders.** Thermochimica Acta, v. 671, pp. 48-53. 2019. https://doi.org/10.1016/j.tca.2018.11.011

FEDERAL HIGHWAY ADMINISTRATION. Teach Brief- Asphalt Mixture Performance Tester (AMPT). Office of Pavement Technology. **FHWA -HIF-13-005**. February 2013

______. Development of a database for surface energy of aggregates and asphalt binders**. FHWA/TX-09/5-4524**. 2009

FINI, E.; AL-QADI, I.; YOU, Z.; ZADA, B.; MILLS-BEALE, J. **Partial replacement of asphalt binder with bio-binder: characterisation and modification. International** Journal of Pavement Engineering, v. 13 (6). 2012

FINI, E. H.; KALBERER, E. W.; SHAHBAZI, C. Application of Bio-Binder from Swine Manure in Asphalt Binder. In: **Transportation Research Board 90th Annual Meeting**. Washington: DC. 2011.

FINI, E.; KALBERER, E. W.; SHAHBAZI, A.; BASTI, M.; YOU, Z., OZER, H.; AURANGZEB, Q. **Chemical characterization of biobinder from swine manure: Sustainable modifier for asphalt binder**. Journal of Materials in Civil Engineering, v. 23(11), pp. 1506-1513. 2011

FINI, E.; HOSSEINNEZHAD, S.; OLDHAM, D.; CHAILLEUX, E.; GAUDEFROY, V. **Source dependency of rheological and surface characteristics of bio-modified asphalts.** Road Materials and Pavement Design, v. 18. 2017

FINI, E.; KHODAII, A.; HAJIKARIMI, P. **Fractional viscoelastic study of low-temperature characteristics of biomodified asphalt binder**. Journal of Materials in Civil Engineering, v. 28 (9), pp. 04016078. 2016

FINI, E. H.; YANG, S.; XIU, S. Characterization and application of manure-based bio-binder in asphalt industry. In: **Transportation Research Board 89th Annual Meeting.** (No. 10-2871). 2010.

GHABCHI, R.; SINGH, D.; HOSSAIN, Z. **Micro-structural analysis of moisture-induced damage potential of asphalt mixes containing RAP**. Journal of Testing and Evaluation, v. 44(1). 2016
doi:10.1520/JTE20140018

GONG, M.; YANG, J.; ZHANG, J.; ZHU, H.; TONG, T. **Physical–chemical properties of aged asphalt rejuvenated by bio-oil derived from biodiesel residue**. Construction and Building Materials, v. 105, pp. 35–45. 2016

HAJJ, E., SOULIMAN, M., ALAVI, M., LORIA, L. **Influence of hydrogreen bioasphalt on viscoelastic properties of reclaimed asphalt mixtures**. Transportation Research Record: Journal of the Transportation Research Board, v. 2371 (1), pp.13–22. 2013. https://doi.org/10.3141/2371-02

HE, M., TU, C., CAO, D.W., CHEN, Y.J. **Comparative analysis of bio-binder properties derived from different sources**. International Journal of Pavement Engineering, 20 (7), pp. 792-800. 2019.
https://doi.org/10.1080/10298436.2017.1347434

HEFER, A.; BHASIN, A.; LITTLE, D. **Bitumen surface energy characterization using a contact angle approach**. Journal of Material of Civil Engineering, v.18 (6), pp. 759-767. 2006

HICKS, R. Moisture damage in asphalt concrete. **Transportation Research Board,** n. 175, 1991

HILL, B.; OLDHAM, D.; BEHNIA, B.; FINI, E.; BUTTLAR, W.; REIS, H. Low-temperature performance characterization of biomodified asphalt mixtures that contain reclaimed asphalt pavement. **Transportation Research Record**: Journal of the Transportation Research Board, n. 2371, p. 49-57, 2013.

HINTZ, C.; VELASQUEZ, R.; JOHNSON, C.; BAHIA, H. Modification and validation of linear amplitude sweep test for binder fatigue specification. **Transportation Research Record**: Journal of the Transportation Research Board, n. 2207, pp. 99-106, 2011

HOSSEINNEZHAD, S.; JOHNSON, C.; OLDHAM, D.; FINI, E. H. Investigating the Effect of Processing Parameters on Bio-binder Characteristics. In: **Transportation Research Board 95th Annual Meeting** (No. 16-5535). 2016

HUANG, B.; YE, X. P.; ZHAO, S.; SHU, X. **Preparing a bio-modifier composition used for asphalt comprises providing a non-wood biomass material and treating the non-wood bio-mass material to produce a bio-modifier composition comprising bio-char**. Depositante: B. Huang, X. P. Ye, S. Zhao e X. Shu. US2015128829-A1. Depósito: 08 nov. 2013. Publicação: 14 mai. 2015

JIMENEZ, A.; CARVAJAL-MUÑOZ, S.; LO PRESTI, D.; AIREY, G. **Intrinsic adhesive and cohesive assessment of the moisture sensitivity of bio-rejuvenated recycled asphalt binders**. Road Materials and Pavement Design, v. 20(1), pp. S347-S364. 2019

JIMENEZ, A.; LO PRESTI, D.; POUGET, S.; AIREY, G.; CHAILLEUX, E**. Linear viscoelastic propreties of high reclaimed asphalt content mixes with biobinders**. Road Materials and Pavement Design, v. 18, pp. 241-251. 2017a

JIMENEZ, A.; PÉREZ-MARTÍNEZ, M.; THEMELI, A.; LO PRESTI, D.; MARSAC, P.; POUGET, S.; HAMMOUM, F.; CHAILLEUX, E.; AIREY, G. **Evaluation of bio-materials' rejuvenating effect on binders for high-reclaimed asphalt content mixtures**. Materiales de Construcción, v. 67(327), pp. 04516. 2017b

JOHNSON, C. **Estimating asphalt binder fatigue resistance using and accelerated test method.** Thesis (Doctorate) - University of Wisconsin-Madison. 2010

KALOUSH, K.; WITCZAK, M.; SULLIVAN, B. Simple performance test for permanent deformation evaluation of asphalt mixtures. **In Performance testing and evaluation of bituminous materials PTEBM-03. Proceedings of the 6th international RILEM symposium, Zurich, Switzerland.** pp. 14-16. 2003

KIM, Y. R. **Modeling of asphalt concrete**. New York: McGraw-Hill, 2009

KHOSHHESAB, Z. M. **Reflectance IR Spectroscopy, Infrared Spectroscopy** - Materials Science, Engineering and Technology, Prof. Theophanides Theophile (Ed.), InTech, 2012

LAMONTAGNE, J. DUMAS, P. MOUILLET, V., KISTER, J. **Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques: application to road bitumens**. Fuel, v. 80(4), pp. 483-488. 2001

LAVIN, P. **Asphalt pavements: A practical guide to design, production and maintenance for engineers and architects.** CRC Press, 2003

LENNOX, R.; MACKENZIE, M. Eco-Road Building for Emerging Economies: An Initial Scan for Promising Alternative Technologies. **Geneva: Global Transport Knowledge Partnership**. 2008

LI, J.; ZHANG, F.; LIU, Y.; MUHAMMAD, Y.; SU, Z.; MENG, F.; CHEN, X. **Preparation and properties of soybean bio-asphalt/SBS modified petroleum asphalt.** Construction and Building Materials, v. 201, pp. 268-277. 2019 https://doi.org/10.1016/j.conbuildmat.2018.12.206

LIU, Y.; APEAGYEI, A.; AHMAD, N.; GRENFELL, J.; AIREY, G. **Examination of moisture sensitivity of aggregate-bitumen bonding strength using loose asphalt mixture and physico-chemical surface energy property tests**. International Journal of Pavement Engineering, v. 15(7), pp. 657–670. 2014 doi:10.1080/10298436.2013.855312

LIU, S.; YU, X.; DONG, F. **Evaluation of moisture susceptibility of foamed warm asphalt producedby water injection using surface free energy method**. Construction and Building Materials, v. 131, pp. 138–145. 2017 doi:10.1016/j.conbuildmat.2016.11.072

LU, X.; ISACSSON, U. **Effect of aging on bitumen chemistry and rheology**. Construction and Building Materials, v. 16(1), pp. 15-22. 2002

MACEDO, I.; SEABRA, J.; SILVA, J. **Greenhouse gases emissions in the production and use of ethanol from sugarcane in Brazil**: the 2005/2006 averages and a prediction for 2020. Biomass and bioenergy, v. 32(7), pp. 582-595. 2008

MIAO, X.; WU, Q**. High yield bio-oil production from fast pyrolysis by metabolic controlling of Chlorella protothecoides**. Journal of Biotechnology, v. 110(1), pp. 85–93. 2004

MILLS-BEALE, J. Characterization of Asphalt Materials Containing Bio Oil from Michigan Wood. Ph.D. Dissertation, Michigan Technological University, Houghton. 2013

MILLS-BEALE, J.; YOU, Z.; FINI, E.; ZADA, B.; LEE, C. H.; YAP, Y. K. **Aging influence on rheology properties of petroleum-based asphalt modified with biobinder**. Journal of Materials in Civil Engineering, v. 26(2), pp. 358-366. 2012

MOGAWER, W. S.; FINI, E. H.; AUSTERMAN, A. J.; BOOSHEHRIAN, A.; ZADA, B. Performance characteristics of high RAP bio-modified asphalt mixtures. **Transportation Research Record** (No. 12-2411). 2012

MOGAWER, W.; FINI, E.; AUSTERMANA, A.; BOOSHEHRIANA, A.; ZADAB,B. **Performance characteristics of high reclaimed asphalt pavement containing bio-modifier**. Road Materials and Pavement Design, v. 17(3), pp. 753–767. 2016

MOHAMMAD, L. N.; ELSEIFI, M. A.; COOPER, S. B.; CHALLA, H.; NAIDOO, P. Laboratory evaluation of asphalt mixtures containing biobinder technologies. **Transportation Research Record:** Journal of the Transportation Research Board, no. 2371, pp. 58-65, 2013

MOUILLET, V.; LAMONTAGNE, J.; DURRIEU, F.; PLANCHE, J.P., LAPALU, L. **Infrared microscopy investigation of oxidation and phase evolution in bitumen modified with polymers**. Fuel, v. 87, pp. 1270-1280. 2008

NEWMAN, P.; HARGROVES, C.; DESHA, C.; KUMAR, A.; WHISTLER, L.; FARR, A.; WILSON, K.; BEAUSON, J.; MATAN, A.; SURAWSKI, L. **Reducing the environmental impact of road construction**. 2012

ONOCHIE, A.; FINI, E.; YANG, X.; MILLS-BEALE, J.; YOU, Z. Rheological characterization of nano-particle based bio-modified binder. In: **Transportation Research Board 92nd Annual Meeting**. 2013

OWERHALL, E. J. **Bio bitumen binder composition**. Depositante: Eerik Juhani Owerhall. AU2016100073. Depósito: 21 jan. 2016. Concessão: 11 fev. 2016

PERALTA, J.; WILLIAMS, C.; ROVER, M.; SILVA, H. Development of Rubber-Modified Fractionated Bio-Oil for Use as Noncrude Petroleum Binder in Flexible Pavements. **In the workshop on alternative binders at the 91st Annual Meeting of the Transportation Research Board**. Transportation Research Circular Number E-C165, Washington D.C. 2012a

PERALTA, J.; RAOUF, M. A.; TANG, S.; WILLIAMS, R. C. Bio-renewable asphalt modifiers and asphalt Substitutes. **In K. Gopalakrishnan (Ed.), Sustainable bioenergy and bioproducts. Green energy and technology**. pp. 89–115. London: Springer-Verlag. 2012b

POUGET S.; LOUP F. **Thermo-mechanical behaviour of mixtures containing bio-binders**. Road Materials and Pavement Design, v. 14(1), pp. 212-226. 2013

POURANIAN, M.R.; SHISHEHBOR, M. **Sustainability Assessment of Green Asphalt Mixtures**: A Review. Environments, v. 6, 73. 2019

QU, X; LIU, Q.; WANG, C.; WANG, D.; OESER, M. **Effect of Co-Production of Renewable Biomaterials on the Performance of Asphalt Binder in Macro and Micro Perspectives**. Materials, v. 11, 244, 2018

QUIMIGEL**. Composição de bioligantes, uso das mesmas em superfície**. Depositante: Quimigel Indústria, Comércio e Serviços Aéreos Especializados LTDA (BR/SP). BR 10 2016 017866 5. Depósito: 02 ago. 2016. Publicação: 06 mar. 2018

RAGAUSKAS, A.; BECKHAM, G.; BIDDY, M.; CHANDRA, R.; CHEN, F.; DAVIS, M.; DAVISON, B.; DIXON, R.; GILNA, P.; KELLER, M.; LANGAN, P.; NASKAR, A.; SADDLER, J.; TSCHAPLINSKI, T.; TUSKAN, G.; WYMAN, C. **Lignin valorization: improving lignin processing in the biorefinery**. Science, v. 344(6185), pp. 1246843. 2014

RAOUF, M. A.; WILLIAMS, R. **Determination of pre-treatment procedure required for developing bio-binders from bio-oils**. In: Proc., 2009 Mid-Continent Transportation Research Symposium. 2009.

RAOUF, M.A.; WILLIAMS, R. Development of non-petroleum based binders for use in flexible pavements. **Transportation project reports 17:** Flexible Pavements. 2010a

RAOUF, M.; WILLIAMS, R. **Temperature and shear susceptibility of a nonpetroleum binder as a pavement material**. Transportation Research Record: Journal of the Transportation Research Board, n. 2180, pp. 9-18, 2010b.

ROMERO, P.; MASAD, E. **Relationship between the representative volume element and mechanical properties of asphalt concrete.** Journal of Materials in Civil Engineering, v. 13(1), pp. 77-84. 2001

SAFAEI, F.; CASTORENA, C. **Temperature Effects of Linear Amplitude Sweep Testing and Analysis**. Transportation Research Record: Journal of the Transportation Research Board, v. 2574(1), pp. 92–100, 2016

SCHAPERY, R.A. **Correspondence Principles and a Generalized J Integral for Large Deformation and Fracture Analysis of Viscoelastic Media**. International Journal of Fracture, v. 25, pp.194-223. 1984

SCHWAB, A.; DYKSTRA, G.; SELKE, E.; SORENSON, S.; PRYDE, E**. Diesel fuel from thermal decomposition of soybean oil**. Journal of the American Oil Chemists' Society, v. 65(11), pp. 1781-1786. 1988

SIDDIQUI, M., ALI, M. **Studies on the aging behavior of the Arabian asphalts.** Fuel, v. 78(9), pp. 1005-1015. 1999

SILVA, C.; SILVA, A.; FROTA C. **Módulo Dinâmico de Compósitos Asfálticos com Agregados Sinterizados de Argila Calcinada**. CERÂMICA, v. 60, pp. 10-21. 2014.

SOARES, S.; LUCENA, M.; ALENCAR, A.; SOARES, J.; MORAES, R. Uso da Espectroscopia Vibracional (ATR-FTIR) no estudo do Envelhecimento de Asfaltos Modificados por EVA. In: **XLIV Congresso Brasileiro de Química da Associação Brasileira de Química (ABQ)**, Fortaleza. 2004

TANG, S.; WILLIAMS, R. Antioxidant effect of bio-oil additive ESP on asphalt binder. **Mid-Continent Transportation Research Symposium**, Iowa State Univiversity, IA. 2009

TAN, Y.; GUO, M. **Using surface free energy method to study the cohesion and adhesion of asphalt mastic.** Construction and Building Materials, v. 47(5), pp. 254-260. 2013

UNITED NATIONS-UN. **Transforming our world: the 2030 Agenda for Sustainable Development.** General Assembly. 2015

VAN OSS, C. Interfacial forces in aqueous media. New York, NY: **CRC Press - Taylor; Francis Group**. 1994

VAN OSS, C.; CHAUDHURY, M.; GOOD, R. **Interfacial Lifshitz – van der Waals and polar interactions in macroscopic systems**. Chemical Reviews, v. 88, pp. 927–941. 1988

WANG, C.; XUE, L.; XIE, W.; YOU, Z.; YANG, X. **Laboratory investigation on chemical andrheological properties of bioasphaltbinders incorporating waste cooking oil**. Construction and Building Materiais, v. 167, pp. 348-358, 2018.

WEN, H.; BHUSAL, S.; WEN, B. **Laboratory evaluation of waste cooking oil-based bioasphalt as an alternative binder for hot mix asphalt**. Journal of Materials on Civil Engineering, v. 25(10), pp. 1432-1437. 2013

WHITE, D. H.; COOPER, B. A. **Asphalt product for paving, roofing and sealing uses, contains thermoplastic bio-binder and asphalt**. Depositante: D. H. White e B. H. Cooper. WO200159008-A1. Depósito: 07 fev. 2001. Publicação: 16 ago. 2001

WHITE, D. H.; COOPER, B. A. **Process for producing improved petroleum asphalt product from biomass material useful to produce reactive bio-additive, comprises preparing liquefied bio-binder from the material, and blending the bio-binder**. Depositante: D. H. White e B. H. Cooper. US2008314294-A1. Depósito: 29 ago. 2008. Publicação: 25 dez. 2008

WITCZAK, M., FONSECA, O. **Revised Predictive Model for Dynamic (Complex) Modulus of Asphalt Mixtures.** Transportation Research Record, 1540(1), pp. 15–23. 1996. https://doi.org/10.1177/0361198196154000103

XU, G.; WANG, H.; ZHU, H. **Rheological properties and anti-aging performance of asphalt binder modified with wood lignin.** Construction and Building Materials, v. 151, pp. 801–808. 2017

YANG, S.; SUCIPTAN, T. **Rheological behavior of Japanese cedar-based biobinder as partial replacement for bituminous binder**. Construction and Building Materials, v. 114, pp. 127–133. 2016

YANG, X.; MILLS-BEALE, J.; YOU, Z. **Asphalt binders blended with a high percentage of biobinders: aging mechanism using FTIR and rheology**. Journal of Materials in Civil Engineering, v. 27(4), pp. 04014157, 2014

YANG, X.; MILLS-BEALE, J.; YOU, Z. **Chemical characterization and oxidative aging of bio-asphalt and its compatibility with petroleum asphalt**. Journal of Cleaner Production, v. 142, pp. 1837-1847. 2017

YANG, X.; YOU, Z.; DAI, Q.; MILLS-BEALE, J. **Mechanical performance of asphalt mixtures modified by bio-oils derived from waste wood resources**. Construction and Building Materials, v. 51, pp. 424-431, 2014

YANG, X.; YOU, Z. MILLS-BEALE, J. **Asphalt binders blended with a high percentage of Biobinders**: **Aging Mechanism Using FTIR and Rheology**. Journal of Materials in Civil Engineering, v. 27(4), pp. 04014157. 2015

YU, H., SHEN, S. **Impact of aggregate packing on dynamic modulus of hot mix asphalt mixtures using three-dimensional discrete element method**. Construction and Building Materials, v. 26(1), pp. 302-309. 2012. https://doi.org/10.1016/j.conbuildmat.2011.06.025

ZHANG, R.; WANG, H., GAO, J.; YANG, X.; YOU, Z. **Comprehensive Performance Evaluation and Cost Analysis of SBS-Modified Bioasphalt Binders and Mixtures**. Journal of Materials in Civil Engineering, v. 29(12), pp. 04017232. 2017