MSc Thesis

Recycling of SBS Asphalt Mixture with Polymer Network Reconstructive Rejuvenators

Final Report

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Summary

Styrene-Butadiene-Styrene (SBS) modified bitumen is a pivotal binder in road construction, with its superior performance largely attributed to the incorporated SBS polymer network. Despite its advantages, the efficacy of SBS modified bitumen is compromised due to oxidative, thermal, and UV-induced aging, leading to a degradation in polymer network. Existing commercial rejuvenators mainly replenish the light components but fall short in restoring the degraded polymer network. To address this, the present master thesis introduces an innovative rejuvenator that not only supplements these light components but also integrates fresh polymers and mends the compromised SBS polymer network through specially designed chemical connecting agents. This research complements existing evaluation methodologies by incorporating Dynamic Mechanical Analyzer (DMA) for cohesive/adhesive characterization, Fourier-Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Flame Ionization Detector (GC-FID) for chemical analytics, and Environmental Scanning Electron Microscopy (ESEM) for morphological assessment. Building on this foundation, the research elucidates the underlying rejuvenation mechanisms, particularly focusing on the rejuvenator's chemical reactivity. Further assessments regarding compatibility, storage stability, and aging durability substantiate the rejuvenated bitumen's operational viability and long-term durability. Finally, a 50% RAP recycling mixture is prepared using field-collected Reclaimed Asphalt Pavement (RAP) that contains SBS modified bitumen. This mixture is then subjected to comprehensive tests for ravelling resistance, cracking resistance, and moisture durability to evaluate the efficacy of the rejuvenator. This study aims to enhance the recyclability of RAP with polymer modified bitumen and explores its potential application in surface layers, particularly in the Netherlands.

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Chapter 1. Introduction and Literature Review

This Chapter introduced the background information and the necessity of SBS modified bitumen rejuvenation. Three distinct rejuvenator types – pure oil rejuvenator, physical rejuvenator, and chemical rejuvenator – representing three distinct rejuvenation routes, are reviewed. In the end, the research objective and methodology of this MSc thesis were explained.

1.1. Research Background

The Netherlands is a rainy country due to its oceanic climate. According to KNMI, the Royal Netherlands Meteorological Institute, the majority of Dutch regions have experienced an annual average of more than 170 rainy days over the past three decades [1]. Moreover, the average yearly precipitation in the Netherlands has also grown by 25% over the past 100 years to the current level of 795 millimetres due to the influence of the sea [2,3]. Such high precipitation levels and frequent precipitation events place higher demands on the drainage performance of Dutch pavements. In addition, as road traffic increases, the number of dwellings along roads exposed to noise pollution also increases. More than 12,000 households in the Netherlands were subjected to excessive road traffic noise pollution in 2012 [4].

To deal with both of these problems, porous asphalt has been utilized in the Netherlands since the 1980s, and as of today more than 85% of the pavements in this country are constructed with porous asphalt [5]. Along with the benefits of water permeability and noise absorption, porous asphalt also provides the added advantages of enhancing friction performance, lowering glare, minimizing soil erosion, and reducing the urban heat island effect [6,7]. However, on the other side, porous asphalt is more prone to oxidation because its open-graded structure and high porosity [6,8]. The amount of asphaltene in bitumen rises with continued environmental exposure, making it more hard and brittle [6]. Combined with the effects of climate conditions and vehicle loads, ravelling become the major problem for porous asphalt [8].

In order to improve ravelling resistance, polymer modified bitumen (PMB) is employed to strengthen the interaction between binder and aggregate, reducing the likelihood of abrasion of the porous asphalt mixture [8]. Additionally, the high temperature rutting resistance and low temperature cracking resistance of the mixture are both enhanced by PMB's higher temperature stability and increased elasticity [9,10]. Among all the well-known bitumen modification polymers such as styrene-isoprene-styrene (SIS), ethylene butyl acrylate (EBA), and polypropylene (PP), styrene-butadiene-styrene (SBS) has attracted widespread interest because its comparative ease of dispersion in bitumen as well as the comparably superior performance and affordable cost of the SBS modified bitumen [11].

Unfortunately, just like base bitumen, SBS modified bitumen also ages as a result of environmental factors involving oxygen, heat, and UV light, which can furthermore lead to pavement problems as well [12]. Therefore, the asphalt pavement will need to be replaced after a long period of use, leading to a sizeable amount of asphalt waste. It is essential to recycle these asphalt wastes as a way to reduce the costs associated with building and maintaining roads, conserve raw materials and protect the environment [13]. However, to avoid affecting the overall performance of the pavement, many transportation authorities and departments limited the amount of recycled asphalt used to the new mixtures as a result of recycled asphalt waste inevitably deteriorates over time [14]. Moreover, it is typically restricted or prohibited to use recycled asphalt in the surface layer, and if the recycled asphalt which contained high-valued PMB can only be used in the base layer, this is essentially a capital destruction [15]. Therefore, the challenge now is to be able to replace part of the fresh PMB in the asphalt mixtures with recycled asphalt that contains PMB and without sacrificing performance. As a solution to this issue, rejuvenators can be used to recycled asphalt to recover its viscoelastic and rheological properties [16].

In light of this, this MSc thesis research will focus on the rejuvenation of aged SBS modified bitumen and aim to investigate the impacts of rejuvenator components on rejuvenation effects, also to develop a trustworthy evaluation system to characterize the rejuvenation effects. The significance of this project is to improve the recycling ability of aged PMB to make it not only easy to reuse but also can be fully utilized the add-on value.

1.2. Current Aging Research on SBS Modified Bitumen

Although the aging mechanism of SBS modified bitumen is complicated, it may be roughly categorized into base bitumen aging and SBS polymer modifier degradation [17,18].

Bitumen aging is influenced by a number of mechanisms, including thermal oxidation, photooxidation, volatile component loss, and physical hardening [19]. Hardening, which can be further separated into reversible hardening and irreversible hardening, is the most significant of all impacts of aging since it lessens the crack resistance of the asphalt mixture and makes it more susceptible to cracking in low temperature conditions [20]. Reversible hardening is brought on by molecular reorientation or wax crystallization of bitumen and is typically recoverable by increasing the temperature of the bitumen [21,22]. Irreversible hardening is commonly caused by evaporation of light components, exudation of oil components, polymerization, and oxidation [20,23]. Compounds like ketone and sulfoxide are produced during the oxidation of bitumen, and the production of ketone is associated with the viscosity and asphaltenes increasing of the bitumen [20]. Undoubtedly the type of bitumen oxidation products is constant across all sources and varieties of bitumen, but their amount could differ, particularly between base bitumen and polymer modified bitumen [19]. Additionally, the oxidation of bitumen and the concentration of these oxidation products are influenced by the crude oil source as well [24].

For SBS polymer modifier, it ages differently depending on the polymer structure, including the polymer molecular weight, block ratio, and polybutadiene (PB) phase saturation [18]. In general, although some cross-linking reaction take place, aging primarily broken down the polymer into small molecules [25]. Furthermore, Chen *et al.* [26] indicate that the chain scission reaction of the PB segment plays a significant role in the degradation of SBS polymer given that the unsaturated carbon-carbon double bonds (C=C) in the PB segment can readily become oxygen targets and degrade when exposed to heat and UV light. Moreover, Xu *et al.* [27] discovered that throughout the aging process of SBS polymers, the content of C=C dropped while substantial amounts of active oxygen-containing groups including -OH, -COOH, and C=O were generated. **Figure 1-1** below illustrates the SBS aging mechanism and process.

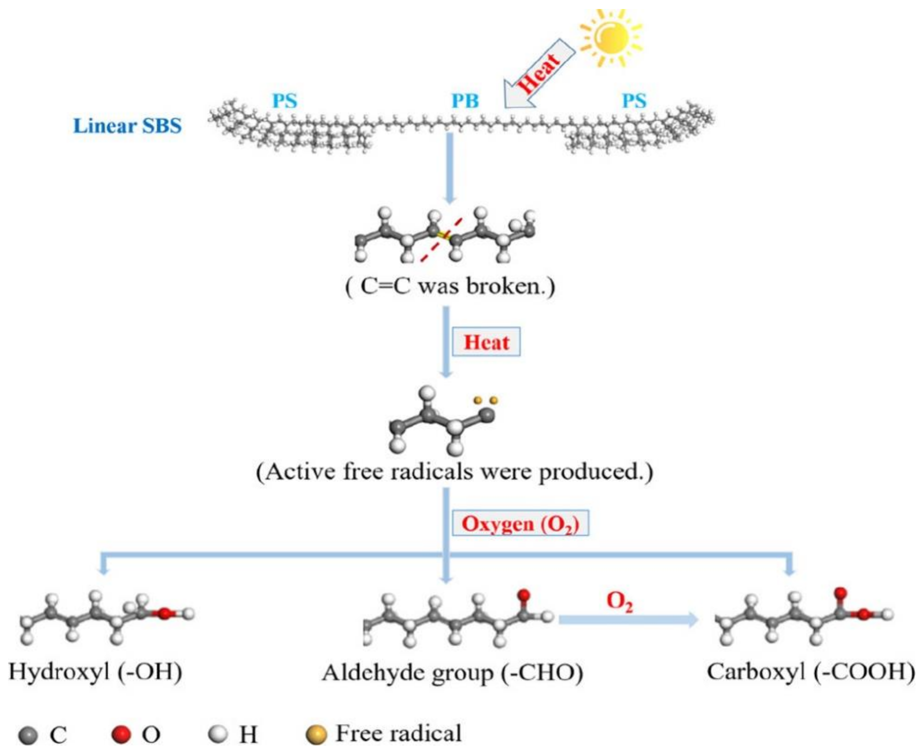

Figure 1-1. SBS aging mechanism and process [28].

However, in addition to bitumen aging and SBS polymer degradation, the presence of SBS also distinguishes the aging process of the polymer modified bitumen from that of the base bitumen [29]. For instance, during the production of SBS modified bitumen, the polymer swells by absorbing the lighter/oily components of the bitumen, preventing them from contacting oxygen, thereby limiting the oxidation process and enhancing the aging resistance [30]. The fact is that the aging rate of the SBS polymer and the bitumen together is much lower than the aging rate of either one separately due to their mutual protection [18]. Whereas when aging occurs, the bitumen molecular weight increases and the SBS polymer degrades to form SBS copolymer particles dispersed in the bitumen, the rheological properties of aged modified bitumen are influenced by the combined effects of bitumen oxidation and polymer degradation [29]. In light of this, it is important to take both bitumen and SBS polymer into consideration when researching and implementing rejuvenators based on aged SBS modified bitumen.

1.3. Current Rejuvenation Research on Aged SBS Modified Bitumen

As was previously indicated, both the aged base bitumen and the degraded SBS polymer should be taken into account when rejuvenating the aged SBS modified bitumen. However, there is no obvious distinction between the rejuvenation trajectories for base bitumen and SBS modified bitumen in practical experiments [31]. In general, some researchers have concentrated on the use of oils or other substances to rejuvenate the base bitumen phase while ignoring the polymer phase in the study of SBS modified bitumen rejuvenation. Others have added fresh SBS modifiers along with oil-based substances with a view to targeting the simultaneous rejuvenation of the base bitumen phase and the polymer phase. There have also been some studies that utilise reactive rejuvenators for degraded SBS to directly repair the polymer phase.

For clarity, throughout the following sections of this thesis, rejuvenators will be classified into three groups: pure oil rejuvenators, physical rejuvenators, and chemical rejuvenators.

- Pure oil rejuvenators are groups of rejuvenators that consist solely of one or more types of oils, without any other additives or components.
- Physical rejuvenators are groups of rejuvenators that contain oil and fresh SBS polymer as their main ingredients. The term physical implies that the fresh SBS polymer restores the degraded SBS polymer network structure through a physical interaction.
- Chemical rejuvenators are groups of rejuvenators that comprise reactive chemical compounds, and may also include oil and fresh SBS polymer. The term chemical indicates that the reactive chemical compounds recover the degraded SBS polymer network structure through a chemical reaction.

Figure 1-2 below has further illustrated this classification.

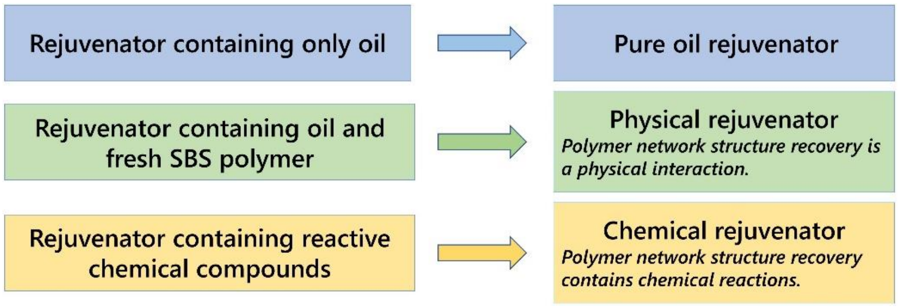

Figure 1-2. Rejuvenator classification.

1.3.1. Pure oil rejuvenator research

Research on waste cooking oil (WCO) by Azahar *et al.* [32] discovered that WCO after chemical modified acid reduction treatment could enhance the rutting resistance and lessen the temperature sensitivity of aged bitumen. Another study on waste edible vegetable oil (WEVO) by Chen *et al.* [33] illustrated that although WEVO can successfully soften and improve the physical and rheological characteristics of aged bitumen, it is still necessary to increase the elasticity, low temperature flexibility, and thermal stability. Yan *et al.* [34] compared tung oil and waste cooking oil and the results showed that rejuvenated bitumen with tung oil performed better at high temperatures and had greater low temperature ductility, whereas rejuvenated bitumen using waste cooking oil had a longer fatigue life.

In a comparison of aromatic oil and waste engine oil, Qiu *et al.* [35] found that while waste engine oil can only provide enhanced fatigue resistance at large strain, aromatic oil extended the fatigue life of rejuvenated bitumen at both low and high strain levels. In addition, the rejuvenated bitumen using these two oils had different ductility characteristics, which might be because rejuvenated bitumen with waste engine oil shows more gelatinization transitions than rejuvenated bitumen with aromatic oil, as demonstrated in the following figure.

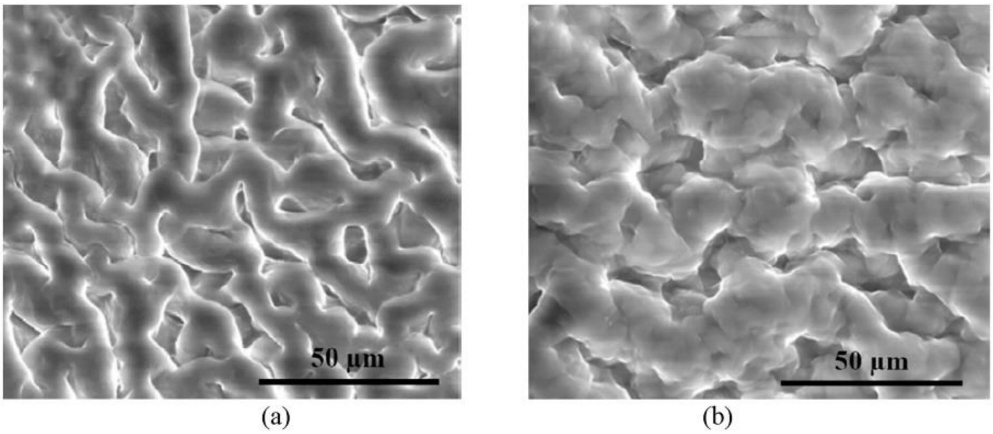

Figure 1-3. Environmental scanning electron microscopy (ESEM) maps of rejuvenated bitumen with (a) aromatic oil and (b) waste engine oil [31,35].

Cao *et al.* [36] chose vacuum steam oil, cashew shell oil, corn oil and waste engine oil to rejuvenate the aged SBS modified bitumen. According to their experiments, in contrast to the nonpolar molecular structure of vacuum steam oil and the strong polarity of engine oil with high viscosity, the cashew shell oil containing weak polar aromatic derivatives had the best softening effect on aged bitumen. In addition, rejuvenated bitumen with corn oil and cashew shell oil has better low temperature cracking resistance, and rejuvenated bitumen with cashew shell oil has better viscoelasticity after re-aging than samples with the other three types of oil.

Three rejuvenators were tested on aged SBS modified bitumen by Lin *et al.* [37], and the results showed that the low viscosity rejuvenator rich in saturated components was significantly more effective at reducing the complex modulus and increasing the phase angle of the aged bitumen, whereas the linear amplitude sweep (LAS) experiments indicated that rejuvenators that contain aromatic components are less effective at enhancing fatigue performance.

Zhu *et al.* [38] investigated bio-binder/plasticizer-based rejuvenator and demonstrated that it can enhance the fatigue resistance of aged bitumen, though not to its original level, and restore the viscosity to its prior stage. Additionally, the use of bio-rejuvenator can lower the asphaltene concentration, as well as the carbonyl and sulfoxide indices of aged bitumen. Cai *et al.* [39] also studied bio-rejuvenators and identified that the rejuvenation process of bio-rejuvenators is utterly a physical behaviour, with no chemical functional groups changed, indicating that bio-rejuvenators cannot repair the broken SBS polymer and restore the cross-linked structure in aged SBS modified bitumen.

In general, pure oil rejuvenators are basically based on the compatibility theory and the component regulation theory to restore the performance of aged bitumen [31]. Pure oil rejuvenators can be beneficial on the base bitumen phase of aged SBS modified bitumen, but the degraded SBS polymer phase could not be recovered.

1.3.2. Physical rejuvenator research

The effectiveness of utilizing oil rejuvenated SBS modified bitumen is limited because, as was previously mentioned, pure oil rejuvenators can only essentially work on the base bitumen phase. As a result, some of the properties of aged SBS modified bitumen, such as fatigue resistance and cracking resistance, cannot be efficiently restored [31]. To recover the polymer phase of SBS modified bitumen, some researchers have also sought to introduce fresh SBS polymer in addition to the usage of the aforementioned oils.

Hong *et al.* [40] employed a physical rejuvenator with 77% aromatic oil and 23% SBS polymer and contrasted it with using only aromatic oil. The outcomes demonstrated that this physical rejuvenator further enhanced the ductility and softening point of the aged bitumen, and that the plateau region of the phase angle master curves was regained. According to the FTIR (Fourier transform infrared) results, introducing this physical rejuvenator increased the SBS index of aged bitumen, indicating that it can successfully replenish the degraded polymer phase. Similarly, a physical rejuvenator consisting of 75% aromatic oil and 25% SBS polymer was used on binders and mixtures containing reclaimed asphalt pavement (RAP) by Eltwati *et al.* [41]. The experiment data revealed that this rejuvenator significantly softened the binder, reestablished the low temperature cracking resistance and high temperature rutting resistance. As for the asphalt mixture level, this rejuvenator increased the fatigue deformation resistance and rutting resistance while lowering the possibility of water damage. Another physical rejuvenator that included aromatic oil, light oil, corn oil and SBS polymer was prepared by Cong, Guo and Mei [42]. Investigations showed that the ductility, elasticity, and low temperature cracking resistance of aged bitumen were significantly improved by the use of this physical rejuvenator. Additionally, microscopic examinations revealed that this physical rejuvenator could restore the polymer network structure as well as adjust the internal composition of aged bitumen.

Zhao, Shen and Ding [43] used a physical rejuvenator containing second-line extract oil, C9 aromatics petroleum resin, SBS polymer, stabilizing agent and dispersing agent. The findings revealed that this rejuvenator can not only disperse the light components into the aged bitumen, but also form a polymer network to enhance its high and low temperature performance, ductility, as well as deformation resistance. Wang *et al.* [44] produced a physical rejuvenator consisting of bio-oil, polymer modifier, plasticizer and cross-linking agent. Studies have shown that this rejuvenator not only restores the cracking resistance of aged bitumen to its original level, but also provides better elastic recovery, as well as reduces the damage rate and increases the fatigue life by improving the bitumen colloid structure and restoring the polymer network structure. Furthermore, the FTIR measurements revealed a reduction of ─CH═CH─ vibration and an increase of C─S stretching vibration, which may have resulted from the network structure reformation of aged bitumen by the physical rejuvenator.

1.3.3. Chemical rejuvenator research

In addition to the conventional rejuvenators mentioned in the above sections, reactive chemical compounds are also becoming more and more popular for bitumen rejuvenation. As illustrated in **Figure 1-1**, active oxidative functional groups like hydroxyl and carboxyl will appear at the fracture side of the broken SBS polymer segment as it degrades. Some chemical compounds can react with these functional groups thereby reconnecting the degraded SBS polymer, as demonstrated in **Figure 1-4** below.

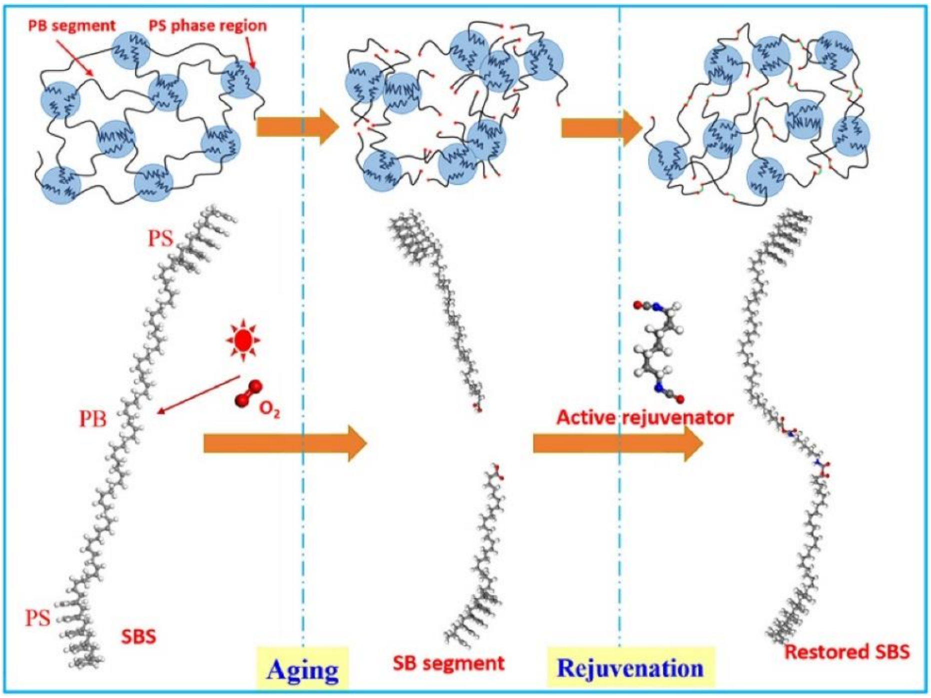

Figure 1-4. Schematic diagram of degradation and reconstruction of SBS polymer [45].

For instance, Xu *et al.* [46] used 1, 4-butanediol diglycidyl ether (BUDGE) and trimethylolpropane triglycidyl ether (TMPGE) as rejuvenators for SBS modified bitumen, respectively. The results revealed that both rejuvenators could improve the low temperature ductility and cracking resistance of aged bitumen, though BUDGE performed better. Experiments with FTIR and fluorescence microscopy further demonstrated that the terminated reactive groups on the epoxy molecule chemically reacted with the reactive functional groups on the degraded SBS polymer. In another study, Xu *et al.* [47] compared the rejuvenation effects of BUDGE with another compound, diphenyl methane diisocyanate (MDI). According to the findings, BUDGE can enhance the ductility, viscosity properties, and fatigue resistance of aged bitumen. MDI, on the other hand, improves softening point, elasticity, and rutting resistance. Unfortunately, these two compounds will only benefit the low and high temperature performance of aged bitumen, respectively. The rejuvenation mechanisms of BUDGE and MDI, which are the condensation reaction mechanism and the addition reaction mechanism, respectively, are shown in **Figure 1-5** below.

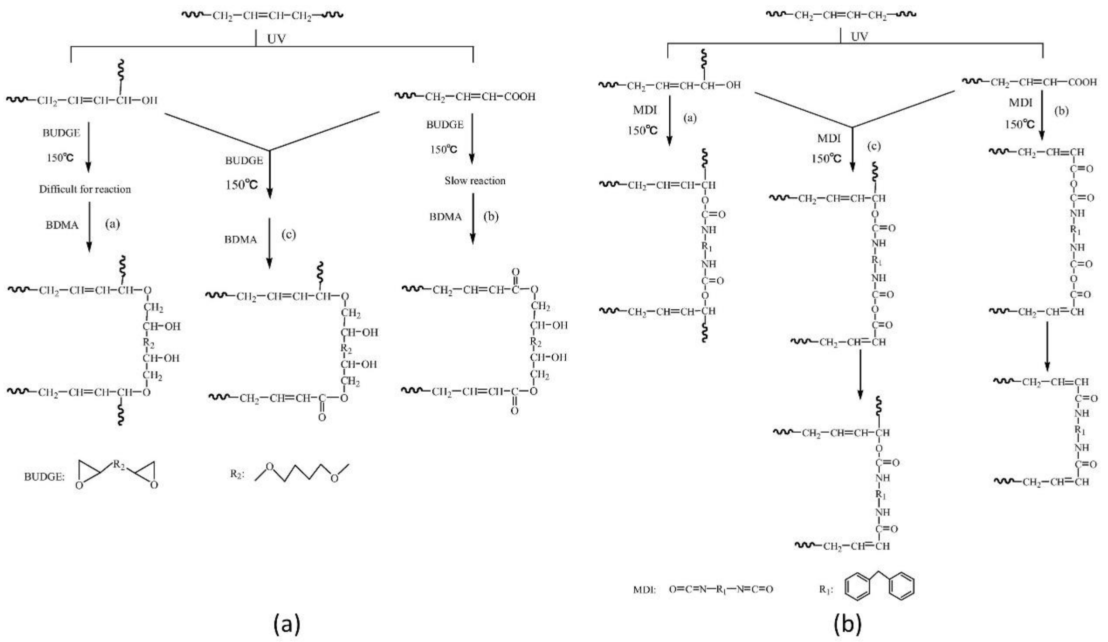

Figure 1-5. Rejuvenation mechanisms of (a) BUDGE and (b) MDI [47].

Three different active compounds, hexamethylene diisocyanate (HDI), MDI, and toluene-2, 6-diisocyanate (TDI), were compared by Cao *et al.* [45]. The results demonstrate that all three isocyanate compounds, with MDI being the most notable, can dramatically raise the softening point of aged bitumen. Additionally, the ductility of HDI rejuvenated bitumen is better. According to the rheological outcomes, MDI can greatly increase the elastic recovery and deformation resistance of aged bitumen, whereas HDI is more suited to enhancing the low temperature cracking resistance. Considering that HDI and TDI are extremely hazardous and their direct use is harmful to personnel and the environment, Han *et al.* [28] developed a new series of chemical rejuvenators based on polyethylene glycol (PEG400/PEG1000), HDI, and TDI, namely reactive chain extension rejuvenators (RCERs). In comparison to HDI or TDI added with aromatic hydrocarbon oil, they revealed that RCERs plus aromatic hydrocarbon oil may better recover the physical characteristics of aged bitumen, including softening point, penetration, and ductility. In a different project, Han *et al.* [12] prepared two novel chemical rejuvenators by reacting HDI and TDI with hydroxyl terminated polybutadiene (HTPB), namely H-HTPB and T-HTPB, as demonstrated in **Figure 1-6**. The experiments showed that both chemical rejuvenators can restore the physical properties of aged bitumen to the origin level, and that the rejuvenated bitumen performed well in both high and low temperatures. Meanwhile, according to the BBR (bending beam rheometer) results, the creep stiffness and m-value of rejuvenated bitumen at -12 ℃ and -18 ℃ satisfy the SHRP (Strategic Highway Research Program) specifications. Additionally, under the comprehensive analysis, T-HTPB has a greater rejuvenation effect than H-HTPB.

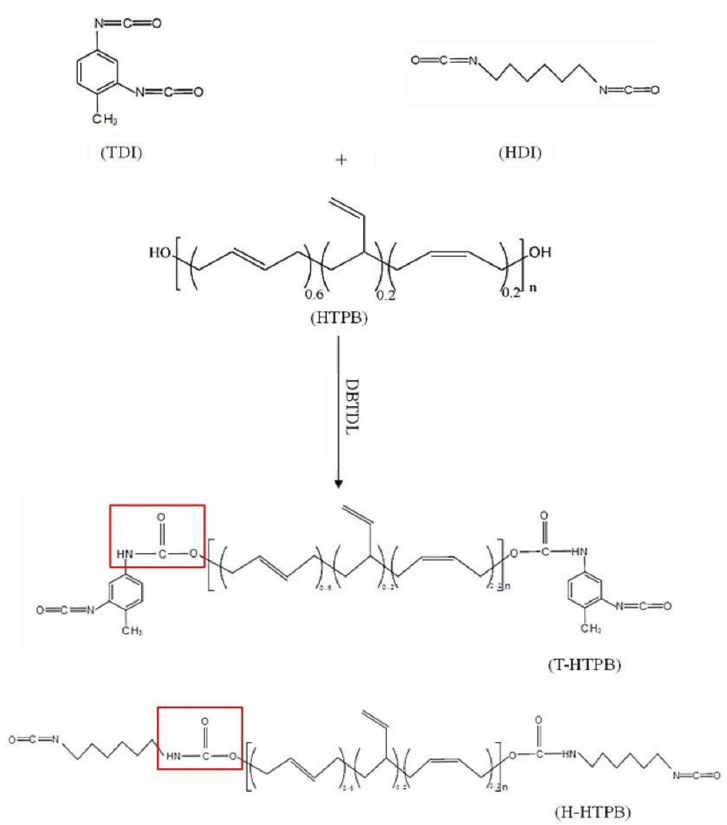

Figure 1-6. Synthetic mechanisms of H-HTPB and T-HTPB [12].

Wei, Zhang and Duan [29] rejuvenated aged SBS modified bitumen using epoxidized soybean oil (ESO) and triphenyl phosphine (TPP) as a catalyst. The functional groups C−O−C and −OH in the FTIR results proved that the catalyst TPP can open the epoxy groups of ESO, which can then react with the hydroxyl groups of the degraded SBS segments to restore the polymer network structure. The ductility and BBR experiments demonstrated that adding more catalyst enhanced the flexibility of rejuvenated bitumen at low temperatures. The softening points and the viscoelastic properties from the DSR (dynamic shear rheometer) tests also improved at first, but then decreased incrementally. Those results indicate that this catalyst TPP has multiple effects on binder softening and SBS structure repairing.

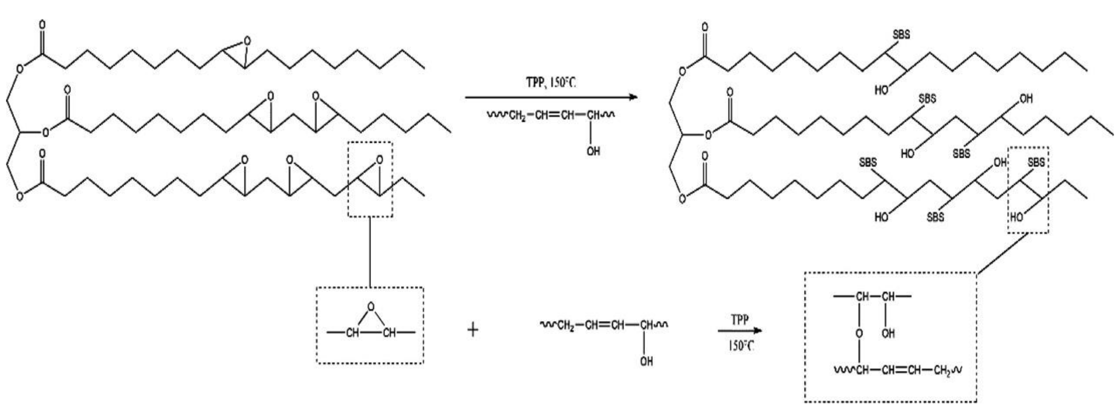

Figure 1-7. Rejuvenation mechanism of ESO and catalyst TPP [29].

In another project, Wei, Zhang and Duan [48] added aromatic oil in addition to ESO and TPP. The experiment results demonstrated that the ductility of rejuvenated bitumen could be improved while the high temperature performance was ensured when the ratio of aromatic oil to ESO(TPP) was 1:1. Furthermore, the addition of aromatic oil also provides better high and low temperature performance than the previous rejuvenated bitumen with ESO and TPP alone.

Besides the use of catalysts to open up the epoxy groups of ESO and then allow it to repair the degraded SBS segment, some studies have utilized ESO as a base oil and added other reactive compounds to it that can directly react with fractured SBS polymer. Yang *et al.* [49], for example, created a new chemical rejuvenator by combining ESO with epoxidized polybutadiene resin (EPR) and maleic anhydride (MA). According to the results, this new chemical rejuvenator has two benefits for aged SBS modified bitumen. First, it improves the physical properties of aged bitumen. Second, it helps the aged bitumen regain the phase angle plateau region and SBS polymer molecular weight peak. This demonstrates that both bitumen matrix component regulation and SBS structural reconstruction are effective for rejuvenating aged bitumen. Moreover, the fluorescence microscopy (FM) result confirms that this rejuvenator can rebuild the damaged polymer network structure. In another research, Shi *et al.* [50] added methylene-bis(4-cyclohexylisocyanate) (HMDI) and 1,6-hexanediol diglycidyl ether (HDE) to ESO. According to their findings, ESO could improve the low temperature performance of aged bitumen, but HMDI is needed to enhance the high temperature performance. Furthermore, HMDI rejuvenated bitumen has better permanent deformation resistance and elastic recovery properties than others. HMDI increased the asphaltene content in rejuvenated bitumen, while HDE increased the aromatic fraction content, as shown by the SARA fraction results. The FTIR results revealed that HMDI reacted with degraded SBS polymer to create carbamate bonds with a stable chemical structure, and both HMDI and HDE could partially rebuild the broken SBS chain structure.

Li *et al.* [51] synthesized a new chemical rejuvenator using fluid catalytic cracking slurry (FCC slurry), C12–14 aliphatic glycidyl ether (AGE), and MDI. The results demonstrated that this rejuvenator can enhance the overall physical properties of aged bitumen, while slightly lowering the softening point. By reducing the high temperature deformation resistance, lowering the high viscous-elastic temperature caused by bitumen molecules clumping and improving the low temperature cracking resistance, this rejuvenator can make the aged bitumen more similar to fresh PMB. Shu *et al.* [52] attempted to use aromatic oil as the base oil to fill the lost light compound in the bitumen phase and polyurethane (PU) as the reactive compound to repair the degraded polymer phase. The experiment findings revealed that the high temperature stability of the rejuvenated bitumen was mainly determined by the chemical reaction between degraded SBS polymer and PU, while the aromatic oil replenished the lost light component and enhanced the fatigue performance. Additionally, rejuvenated bitumen performs similarly viscoelastically at low temperatures to that of fresh PMB while being more resistant to elastic deformation at mid and high temperatures.

1.3.4. Rejuvenator research summary

By studying the bitumen aging mechanism and various rejuvenation approaches, it was discovered that pure oil rejuvenators enhance the performance of aged bitumen by introducing aromatic compounds, light compounds, or by rebalancing the compounds in the aged bitumen. This type of rejuvenator can improve the low temperature cracking resistance and fatigue life of aged bitumen, but it cannot repair the degraded SBS polymers or restore the cross-linked polymer network structure, which gives the exceptional performance of SBS modified bitumen [11,31]. As a result, the high temperature performance and elasticity of aged bitumen were unable to recover, leading to an insufficient rejuvenation of aged PMB [28,31].

In order to further improve the rejuvenation effects, it is crucial to take into account repairing the degraded polymer network structure while rejuvenating the base bitumen phase. There are currently two approaches that can be used to achieve this goal: either by using physical rejuvenators to supply fresh SBS polymers or by employing chemical rejuvenators to directly reassemble degraded SBS segments. Manually adding fresh SBS polymer is simple and effective, but this method neglects the repair and reuse of degraded SBS, which actually results in a waste of material. An innovative approach of utilizing reactive chemical compounds to restore degraded polymers provided a new direction for bitumen rejuvenation. As previously described, these compounds can have chemical reactions with hydroxyl and carboxyl groups generated on the fracture sides of degraded SBS polymer to reconnect the broken chains. This approach achieves the reuse of aged polymers, but most studies have ignored the influence of the interaction between reactive chemical compounds and conventional rejuvenators on the rejuvenation effects [31].

Table 1 has summarized all the rejuvenators that have been studied in this literature review section, their types, ingredients, and the research findings.

Table 1. Rejuvenators summary.

Type	Researchers	Ingredient	Research finding
Pure oil rejuvenator	Azahar *et al.* (2016)	Waste cooking oil	Improve rutting resistance, reduce temperature sensitivity.
	Chen *et al.* (2014)	Waste edible vegetable oil	Improve physical and rheological properties, but still necessary to improve elasticity and low temperature flexibility.

	Yan *et al.* (2021)	Tung oil / waste cooking oil	Tung oil has better high temp performance and low temp ductility. Waste cooking oil has longer fatigue life.
	Qiu *et al.* (2018)	Aromatic oil / waste engine oil	Aromatic oil has better fatigue resistance than waste engine oil.
	Cao *et al.* (2019)	Vacuum steam oil / cashew shell oil / corn oil / waste engine oil	Cashew shell oil has the best soften effect. Cashew shell oil and corn oil have better low temperature cracking resistance. Cashew shell oil has better viscoelasticity after re-aging.
	Zhu et al. (2017)	Bio-rejuvenator	Improve fatigue resistance.
	Cai et al. (2019)	Bio-rejuvenator	Bio-rejuvenator cannot repair broken SBS and restore polymer network structure.
Physical rejuvenator	Hong et al. (2020)	Aromatic oil, SBS	Improve ductility and softening point. Recover plateau region.
	Eltwati et al. (2022)	Aromatic oil, SBS	Reestablished cracking resistance and rutting resistance.
	Cong, Guo and Mei (2020)	Aromatic oil, light oil, corn oil, SBS	Improve ductility, elasticity, cracking resistance. Restore polymer network structure. Adjust internal composition.
	Zhao, Shen and Ding (2018)	Second-line extract oil, resin, SBS, additives	Enhance high and low temperature performance, ductility, deformation resistance.
	Wang et al. (2021)	Bio-oil, polymer, additives	Restore cracking resistance, provide better elastic recovery, fatigue life.
Chemical rejuvenator	Xu, Yu, Xue, et al. (2017)	BUDGE / TMPGE	Both can improve low temperature ductility and cracking resistance, with BUDGE better.
	Xu, Yu, Zhang, et al. (2017)	BUDGE / MDI	BUDGE improve ductility, viscosity properties, fatigue resistance. MDI improve softening point, elasticity, rutting resistance.
	Cao et al. (2020)	HDI / MDI / TDI	MDI improve elastic recovery and deformation resistance. HDI improve low temperature cracking resistance.
	Han et al. (2021)	PEG400/PEG1000, HDI, TDI	Improve physical properties: softening point, penetration, ductility.
	Han et al. (2022)	H-HTPB / T-HTPB	Both can restore physical properties, improve performance in high and low temperatures. T-HTPB better overall.
	Wei, Zhang and Duan (2020)	ESO, TPP	Restore polymer network. More TPP improve flexibility. Softening point and

		viscoelastic properties improve first then decrease as TPP increase.
Wei, Zhang and Duan (2022)	Aromatic oil, ESO, TPP	Aromatic oil to ESO(TPP) ratio is 1:1, ductility improved with high temperature performance ensured.
Yang et al. (2022)	ESO, EPR, MA	Improve physical properties, regain plateau region.
Shi et al. (2022)	ESO, HMDI, HDE	HMDI improve permanent deformation resistance and elastic recovery properties.
Li et al. (2019)	FCC slurry, AGE, MDI	Improve overall physical properties, lower softening point, high temperature deformation resistance, high viscoelastic temperature.
Shu et al. (2023)	Aromatic oil, PU	Have similar viscoelastic properties to fresh PMB at low temperatures. Become more resistant to elastic deformation at mid and high temperatures.

1.4. Methodology of This MSc Thesis Research

The formation of the SBS polymer network structure in SBS modified bitumen is governed by the intermolecular interactions among the polystyrene (PS) domains in the polymer. During the blending stage of SBS modified bitumen production, the SBS polymer is homogeneously dispersed in the bitumen phase. As the blending stops and the temperature decreases, the PS blocks undergo physical crosslinking through intermolecular forces, leading to the development of PS domains that are uniformly distributed within the bitumen phase [11], as demonstrated in **Figure 1-8**. Besides the physically formed PS domains, sulfur vulcanisation is also employed in SBS modified bitumen to enhance the storage stability and high temperature performance of the bitumen through chemical reactions [11]. During the aging process, oxidative cleavage of the carbon-carbon double bonds in the polybutadiene chain segments of the SBS polymer leads to the degradation of the polymer network structure [18,27], as illustrated in **Figure 1-8**. In accordance with previously discussed, the SBS polymer and the polymer network structure are vital for the excellent performance of SBS modified bitumen [39]. Therefore, to effectively rejuvenate the aged SBS modified bitumen, it is essential to restore the SBS polymer and reconstruct the polymer network structure.

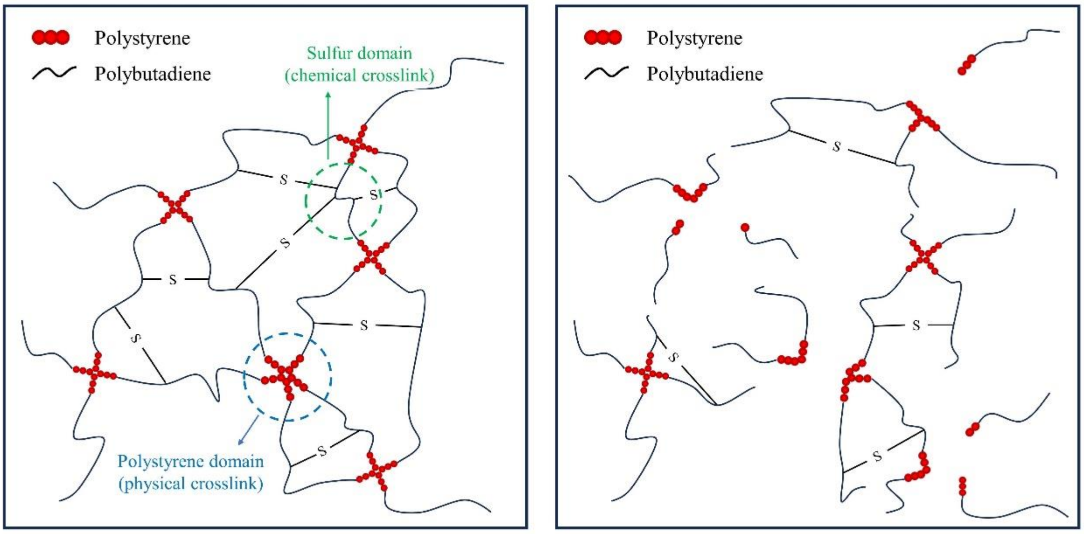

Figure 1-8. Schematic diagrams of polymer network structure in unaged PMB (left) and aged PMB (right).

As mentioned before, pure oil rejuvenators in development today physically function on the aged bitumen phase of the polymer modified bitumen. Although they may dramatically enhance the performance of the aged bitumen, they could not restore the degraded polymer network structure and resulted in further dilution of the existing polymers (**Figure 1-9**). Not to mention that some rejuvenators improve the performance of aged bitumen at low temperatures while degrading it at high temperatures [12].

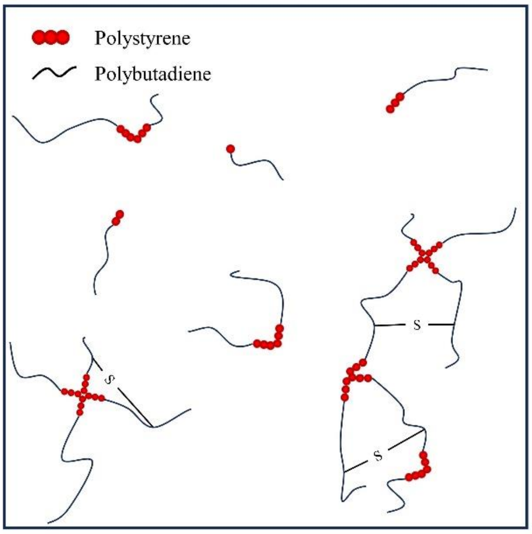

Figure 1-9. Pure oil rejuvenator fails to restore polymer network and dilutes existing polymers.

To achieve the objective of restoring SBS polymer and reconstructing polymer network structure, researchers have attempted to either directly replenish the fresh SBS polymer or employ the reactive chemical compounds for the aged polymer modified bitumen. The rejuvenation mechanism of fresh SBS polymers corresponds to the polymer network structure formation process in SBS modified bitumen production. During the blending stage, the added fresh SBS polymers are uniformly dispersed in the aged bitumen. As the blending stops and the temperature drops, the PS blocks of fresh SBS polymer form physical crosslinks with other PS blokes, either from fresh or aged polymers, through intermolecular interactions, to create PS domains and reconstruct the polymer network structure, as demonstrated in **Figure 1-10**. The rejuvenation mechanism of reactive chemical compounds is a series of chemical reactions. As illustrated in **Figure 1-1**, after the C=C in PB blocks broken, a substantial amount of active oxygen-containing groups including -OH, -COOH, and C=O were generated. The added reactive chemical compounds can have chemical reactions with these active oxygen-containing groups and reconnect the broken PB segments (**Figure 1-10**).

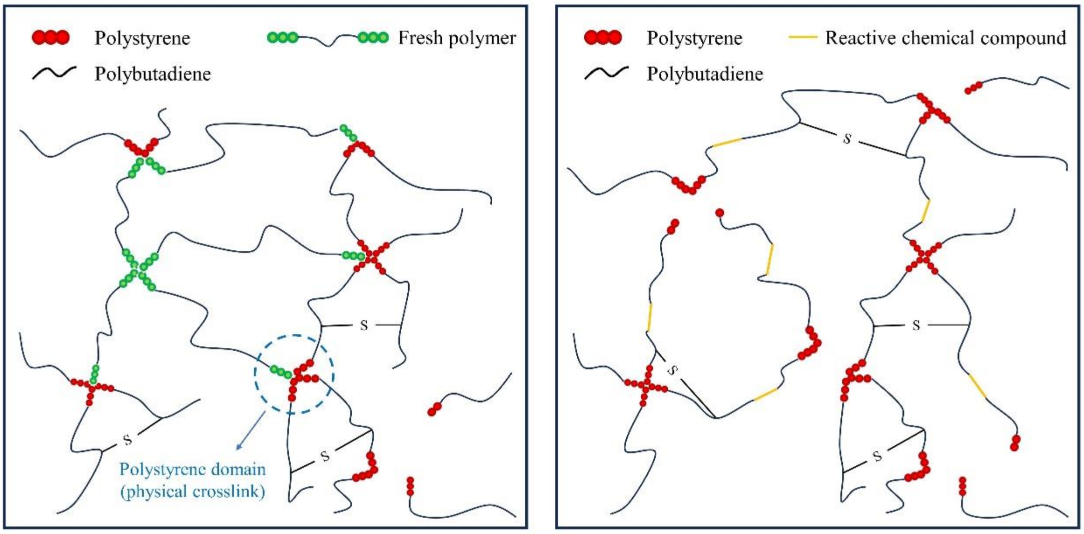

Figure 1-10. Schematic diagrams of the rejuvenation mechanisms of fresh SBS polymer (left) and reactive chemical compounds (right).

For both approaches, however, the problems are also obvious. It is a straightforward and efficient approach for adding fresh SBS polymers, but it wastes the original, degraded polymers by not reusing them. Although the existing polymers are used in the chemical rejuvenation approach, the degraded polymer network structure cannot be fully restored as the reactive chemical compounds can only reconnect the broken PB segments.

In light of this, the present master thesis introduces an innovative rejuvenator that not only softening the aged bitumen phase but also integrates fresh polymers and mends the compromised SBS polymer network through specially designed chemical connecting agents, as demonstrated in **Figure 1-11**.

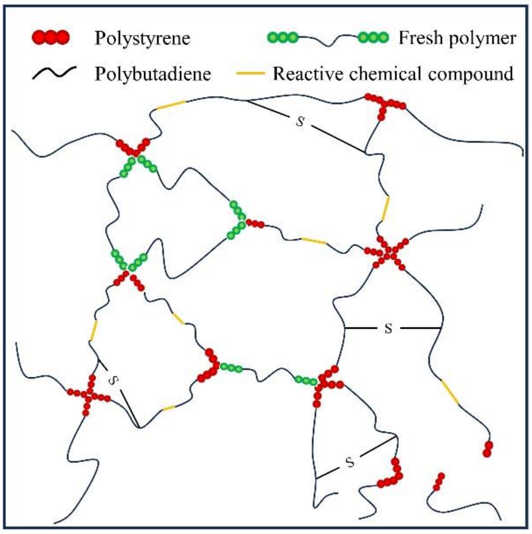

Figure 1-11. Rejuvenation mechanism schematic of the rejuvenator introduced in present master thesis.

Furthermore, to investigate impacts of rejuvenator components on rejuvenation effects and develop a trustworthy evaluation system, this research complements existing evaluation methodologies by incorporating Dynamic Mechanical Analyzer (DMA) for cohesive/adhesive characterization, Fourier-Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Flame Ionization Detector (GC-FID) for chemical analytics, and Environmental Scanning Electron Microscopy (ESEM) for morphological assessment. Building on this foundation, the research elucidates the underlying rejuvenation mechanisms, particularly focusing on the rejuvenator's chemical reactivity. Further assessments regarding compatibility, storage stability, and aging durability substantiate the rejuvenated bitumen's operational viability and long-term durability. Finally, a 50% RAP recycling mixture is prepared using field-collected Reclaimed Asphalt Pavement (RAP) that contains SBS modified bitumen. This mixture is then subjected to comprehensive tests for ravelling resistance, moisture durability, and cracking resistance to evaluate the efficacy of the rejuvenator. This study aims to enhance the recyclability of RAP with polymer-modified bitumen and explores its potential application in surface layers, particularly in the Netherlands. **Figure 1-12** has demonstrated the complete structure of this MSc thesis research project.

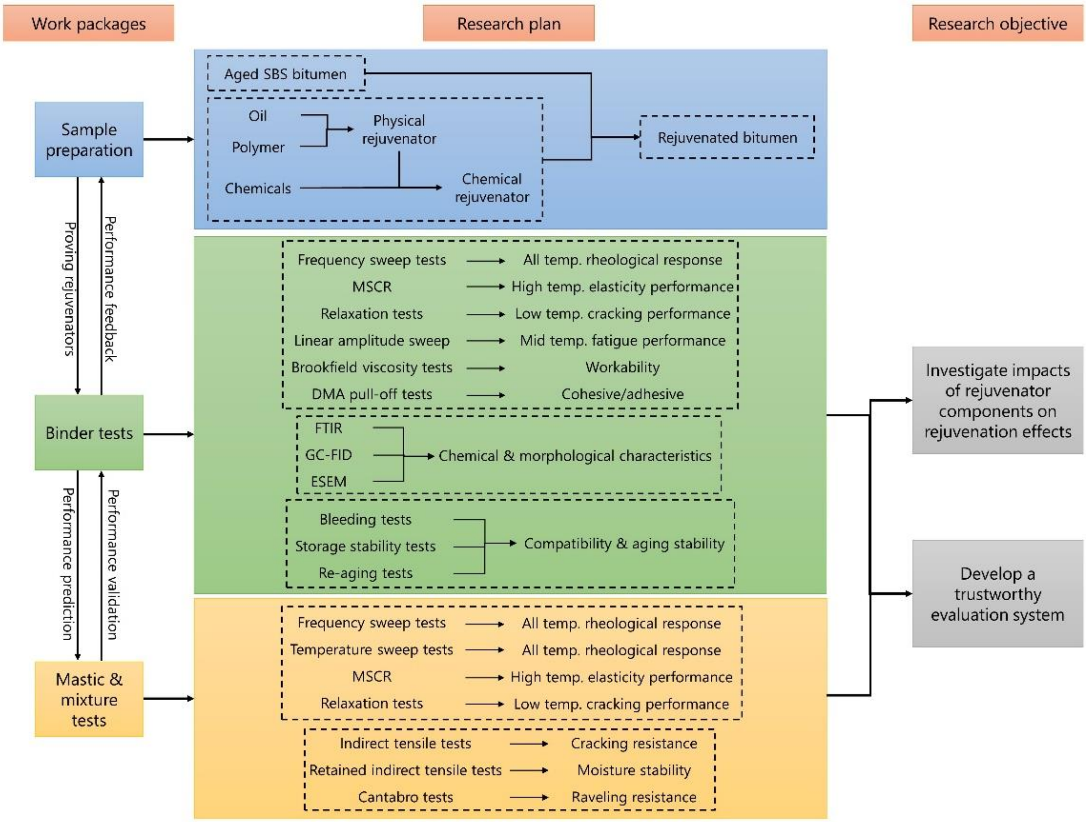

Figure 1-12. MSc thesis research structure.

Chapter 2. Sample Preparation

In this Chapter, the rejuvenators preparation and binder samples preparation procedure will be explained first, followed by a list which summarises rejuvenated bitumen binder samples with code name, corresponding rejuvenator and dosage. Additionally, the mastic samples preparation and mixture samples preparation process will be discussed as well.

2.1. Rejuvenators Preparation

Reference rejuvenators (pure oil rejuvenators), physical rejuvenators, and chemical rejuvenators are the three categories of rejuvenators employed in this project.

Reference rejuvenators include Aro oil, a petroleum-based oil produced through catalytic reforming and steam cracking, Rap oil, a type of vegetable oil that is extracted from the seeds of a plant, and LS oil or Liquid Resin, a by-product of the kraft process used for making wood pulp from primarily coniferous trees. The purpose of using reference rejuvenators is to examine the rejuvenation effects of various types of oil as well as compare those effects to physical and chemical rejuvenators developed through this project.

The term *physical* in physical rejuvenators implies that the fresh SBS polymer restores the degraded SBS polymer network structure through a physical interaction. Ingredients in this type of rejuvenator consist of Aro oil, Rap oil, LS oil, polymer and resin. For the polymer involved in this project, linear SBS was utilized. The production of physical rejuvenators was performed according to the following steps:

i. Oils were heated up to temperature T_1 and mixed with the high shear mixer.

ii. SBS polymer was added gradually to the oils, and shear blended at rotational speed S_1 for 40 min to evenly disperse the polymer.

iii. Oil-polymer mixtures were moved to the overhead stirrer and blended at temperature T_2 and rotational speed S_2 for 2 hours, resin was added during this process as well.

Figure 2-1 shows the shear mixing process with the high shear mixer.

Figure 2-1. shear mixing process with the high shear mixer.

The term *chemical rejuvenator* refers to a rejuvenator that uses reactive chemical compounds to have chemical reactions with some of the oxygen-containing groups in the degraded SBS polymer phase during the rejuvenation process to improve performance. The raw materials for chemical rejuvenators include the physical rejuvenators made previously as well as the reactive chemical compound M.

2.2. Binder Sample Preparation

2.2.1. Bitumen aging

TotalEnergies SE supplied the SBS modified bitumen used in this project. TFOT was performed on the fresh bitumen at 163°C for 5 hours to replicate the short-term aging of bitumen. Short-term aged bitumen was placed in PAV for 80 hours at 100°C and 300 psi to simulate the long-term aging.

For aging stability verification, selected rejuvenated bitumen binder samples were aged again following the above procedure.

2.2.2. Rejuvenated bitumen preparation

The preparation of rejuvenated bitumen has been divided into two categories, 100% recycling and 50% recycling.

The production of 100% recycling bitumen was performed according to the following steps:

i. The aged bitumen was redistributed into small metal cans.

ii. The rejuvenators were added to the small cans at the designed dosage.

iii. Thoroughly mixed with a hand-held mixer at 170°C for 15 minutes, and the produced rejuvenated bitumen was poured onto silicone paper for further testing.

The production of 50% recycling bitumen was performed according to the following steps:

i. Half of the final rejuvenated bitumen mass of the aged bitumen was mixed with the corresponding dosage of rejuvenators under the same conditions as described above.

ii. Unaged bitumen was used to fill in the remaining portion and mixing was continued for 10 minutes at 170°C until well mixed.

Table 2 below lists all the rejuvenated bitumen binder samples with their code name and the corresponding rejuvenator as well as dosage. The addition ratio of reactive chemical compound M is represented by a factor X_i, i ranging from 1 to 7 illustrating the addition ratio varying from 0.1% to 2%.

Table 2. Rejuvenated bitumen binder samples with code name, corresponding rejuvenator and dosage.

	Code name	Rejuvenator and dosage
Unaged bitumen	Unaged PMB	Fresh SBS modified bitumen
Aged bitumen	Aged PMB	80h PAV aged SBS modified bitumen
Pure oil rejuvenators	10Aro	10% Aro oil
	10Rap	10% Rap oil
	10LS	10% LS oil
Physical rejuvenators	10Aro-H	10% Aro oil with high polymer content
	10Rap-H	10% Rap oil with high polymer content
	10LS-H	10% LS oil with high polymer content
	10LS-M	10% LS oil with medium polymer content
	10LS-L	10% LS oil with low polymer content
Pure chemical compounds	10M	10% reactive chemical compound M
	5M + 5Rap	5% reactive chemical compound M plus 5% Rap oil
	1M + 9Rap	1% reactive chemical compound M plus 9% Rap oil
Chemo-oil rejuvenators	$10X_2M$ + Aro	10% rejuvenator dosage containing X_2% chemical compound M and rest Aro oil
	$10X_2M$ + Rap	10% rejuvenator dosage containing X_2% chemical compound M and rest Rap oil
	$10X_2M$ + LS	10% rejuvenator dosage containing X_2% chemical compound M and rest LS oil
Chemical rejuvenators	$10X_2M$ + Aro-H	10% rejuvenator dosage containing X_2% chemical compound M and rest physical rejuvenator Aro-H
	$10X_2M$ + Rap-H	10% rejuvenator dosage containing X_2% chemical compound M and rest physical rejuvenator Rap-H
	$10X_2M$ + LS-H	10% rejuvenator dosage containing X_2% chemical compound M and rest physical rejuvenator LS-H
	$10X_4M$ + Aro-H	10% rejuvenator dosage containing X_4% chemical compound M and rest physical rejuvenator Aro-H
	$10X_4M$ + Rap-H	10% rejuvenator dosage containing X_4% chemical compound M and rest physical rejuvenator Rap-H
	$10X_4M$ + LS-H	10% rejuvenator dosage containing X_4% chemical compound M and rest physical rejuvenator LS-H
	$10X_2M$ + LS-M	10% rejuvenator dosage containing X_2% chemical

		compound M and rest physical rejuvenator LS-M
	$10X_2M$ + LS-L	10% rejuvenator dosage containing X_2% chemical compound M and rest physical rejuvenator LS-L
	$10X_1M$ + LS-L	10% rejuvenator dosage containing X_1% chemical compound M and rest physical rejuvenator LS-L
	$10X_3M$ + LS-L	10% rejuvenator dosage containing X_3% chemical compound M and rest physical rejuvenator LS-L
	$10X_4M$ + LS-L	10% rejuvenator dosage containing X_4% chemical compound M and rest physical rejuvenator LS-L
	$10X_5M$ + T-L	10% rejuvenator dosage containing X_5% chemical compound M and rest physical rejuvenator LS-L
	$10X_6M$ + LS-L	10% rejuvenator dosage containing X_6% chemical compound M and rest physical rejuvenator LS-L
	$20X_2M$ + LS-L	20% rejuvenator dosage containing X_2% chemical compound M and rest physical rejuvenator LS-L
	$20X_4M$ + LS-L	20% rejuvenator dosage containing X_4% chemical compound M and rest physical rejuvenator LS-L
	$20X_6M$ + LS-L	20% rejuvenator dosage containing X_6% chemical compound M and rest physical rejuvenator LS-L
	$20X_7M$ + LS-L	20% rejuvenator dosage containing X_7% chemical compound M and rest physical rejuvenator LS-L
50% PMB RAP recycling	50AgedPMB + 50UnagedPMB	50% Aged PMB mixed with 50% Unaged PMB
	50AgedPMB + 5LS + 45UnagedPMB	50% Aged PMB mixed with 5% LS oil and 45% Unaged PMB
	50AgedPMB + 5LS-L + 45UnagedPMB	50% Aged PMB mixed with 5% physical rejuvenator LS-L and 45% Unaged PMB
	50AgedPMB + X_4M + LS-L + 45UnagedPMB	50% Aged PMB mixed with X_4% reactive chemical compound M and rest physical rejuvenator LS-L and 45% Unaged PMB
	50AgedPMB + X_6M + LS-L + 40UnagedPMB	50% Aged PMB mixed with X_6% reactive chemical compound M and rest physical rejuvenator LS-L and 40% Unaged PMB

2.3. Mastic Sample Preparation

The ingredients for mastic include bitumen, rejuvenators, and Wigras 50K filler, whose properties are shown in **Table 3** below.

Table 3. Properties of the Wigras 50K filler.

Filler properties		
Density	kg/m^3	2638
Calcium carbonate category		CC_{60}
Calcium hydroxide category		Ka5

The production of mastic samples was performed according to the following steps:

i. The bitumen and filler were heated to 170°C.

ii. The rejuvenator was added to the bitumen and mixed for 15 minutes with a hand-held mixer.

iii. The filler was added to the rejuvenated bitumen in a 1:1 weight ratio and mixed for 10 minutes with the hand-held mixer to ensure a homogenous blend was achieved.

iv. The mixtures were placed in the oven at 170°C for 30 minutes to enhance the bonding of the materials.

v. The mixtures were subjected to another minute of mixing with the hand-held mixer to prevent the possible migration of filler particles to the bottom of the metal can and ensure the homogeneity of the mixture.

vi. The well-mixed mixtures were poured into the preheated silicon mould with the metal rings pre-attached, as illustrated in **Figure 2-2(a)**. After the mastic had cooled down and been de-moulded, it was placed on sand and refrigerated to avoid deformation (**Figure 2-2(b)**).

Figure 2-2. (a) Mastic in the silicon mould and (b) de-moulded mastic.

The dimensions of produced mastic sample have demonstrated in **Figure 2-3**.

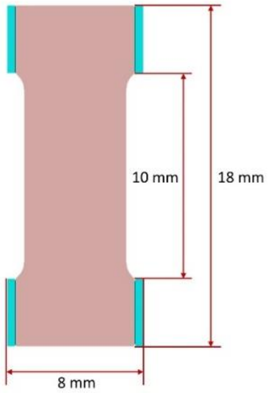

Figure 2-3. Schematic of produced mastic sample and its dimensions.

2.4. Mixtures Sample Preparation

According to the research plan, 50% RAP recycling mixtures will be prepared. The mixture sample consists of 50% field-collected Reclaimed Asphalt Pavement (RAP) that contains SBS modified bitumen, and the appropriate dosage of rejuvenators. The mixture design procedure, materials properties, and sample preparation procedure will be explained step by step.

A target gradation is established based on the Dutch RAW 2005 standard for PA 16 gradation requirements. The target gradation and required gradations are presented in **Table 4**, which illustrate the percentage passing.

Table 4. Gradation target and requirements for PA 16 (RAW 2005).

Gradation target and requirements			
Sieve opening (mm)	**% passing in each sieve**		
	Target	Min.	Max.
22.4	100	100	100
16.0	98.3	90	100
11.2	77.3	-	-
8.0	43.8	-	-
5.6	22.0	-	-
2.0	14.1	5	25
0.063	2.0	2	10

The SBS modified bitumen used for mixture preparation is provided by TotalEnergies SE. The filler properties are shown in **Table 3**, and the bulk specific gravities of fresh aggregates are listed in **Table 5**.

Table 5. Bulk specific gravities of fresh aggregates.

Aggregate size (mm)	22.4 - 16	16 - 11.2	11.2 - 8	8 - 5.6	5.6 - 2	2 - 0.063	Filler
Specific gravity	2.686	2.686	2.678	2.670	2.673	2.658	2.638

The RAP used in 50% recycling mixtures was provided by Latexfalt B.V. in the Netherlands, the specific gravity of RAP aggregates G_{RAP} was measured as 2.426. The bitumen ratio in RAP was determined as 5% after an extraction.

The maximum specific gravity of the compacted mixture G_{mm} can be calculated with the equation

$$G_{mm} = \frac{100}{\left(\frac{P_{s1}}{G_{s1}} + \frac{P_{s2}}{G_{s2}} + \cdots + \frac{P_{si}}{G_{si}} + \frac{P_b}{G_b}\right)} \tag{1}$$

where P_{si} is the weight % of aggregate i in the mixture, P_b is the weight % of bitumen in the mixture, G_{si} is the specific gravity of aggregate i, and G_b is the specific gravity of bitumen.

With the above equation, the maximum specific gravity of 50% recycled mixtures G_{mm} was determined as 2.452. Assume the air void content VA of the mixture is 20%, the weight of a 180 mm height mixture can be calculated with the equation

$$W = G_{mm} \times \left(H \times \frac{1}{4}\pi D^2\right) \times 0.8 \times \frac{1}{10^6} \tag{4}$$

where H is the height of the mixture and D is the diameter of the mixture.

The weight of the mixture can be calculated as 2772 grams.

The production of 50% RAP recycling mixtures was performed according to the following steps:

i. Before the mixing procedures, RAP was heated in an oven at 130°C for 2 hours, and the physical rejuvenator was preheated at the same temperature for 15 minutes.

ii. The chemical compound M was sprayed onto the RAP and mixed for 90 seconds.

iii. The physical rejuvenator was added to the RAP and mixed for 60 seconds.

iv. Fresh aggregates that had been preheated at 185°C for 3 hours and fresh bitumen that had been preheated at 140°C for 60 minutes were added to the rejuvenated RAP mixtures and thoroughly mixed for 45 seconds.

v. The filler which was preheated at 185°C for 3 hours was added to the mixtures and mixed for 60 seconds.

vi. The well-mixed mixtures were loaded into mould at the designed weight W and compacted with Servopac gyratory compactor to the intended height H.

Chapter 3. Evaluation Methodology Complementary

This Chapter discussed the current evaluation methodology for bitumen binder and asphalt mixture and analysed their limitations. Therefore, several experiments were conducted in the present master thesis as an evaluation methodology complementary, and those experiments were explained in detail later in this Chapter.

3.1. Introduction

The current common evaluation methodology for bitumen binder involves examining its rheological properties with Dynamic Shear Rheometer (DSR) and its chemical properties with Fourier Transform Infrared Spectroscopy (FTIR). However, many important and useful properties are not considered in these two evaluation methods. For example, compatibility is crucial for bitumen rejuvenated with oil based rejuvenators, as oil segregation may compromise the aggregate interface and reduce the asphalt mixture strength. Thus, the bleeding test was introduced in the present master thesis as an evaluation methodology complementary for compatibility characterization. Similarly, to complement the analysis of chemical properties, Gas Chromatography-Flame Ionization Detection (GC-FID) and Differential Scanning Calorimetry (DSC) were employed. Additionally, Environmental Scanning Electron Microscopy (ESEM) was utilized to characterize the morphological properties of the bitumen samples.

At the asphalt mixture level, the current evaluation methodology consists of Cantabro tests for characterizing ravelling resistance, indirect tensile strength tests for characterizing cracking resistance, and indirect tensile strength ratio for characterizing moisture resistance. However, a major limitation of the traditional indirect tensile strength test for characterizing rejuvenated asphalt mixtures is that it does not reflect the cracking resistance properly. The indirect tensile strength or ITS of the aged mixtures increases compared to the unaged ones, but this is due to the increased stiffness of aged bitumen, and not indicating an improved cracking resistance of the mixtures. Meanwhile, the indirect tensile strength test fails to validate the effects of different types of rejuvenators on the aged mixtures. Adding pure oil rejuvenators decreases the ITS, while adding pure chemical compounds increases it. However, the binder level results show that pure oil rejuvenators improve the cracking resistance, while pure chemical compounds harden the bitumen and make it more susceptible to cracking. Therefore, the indirect tensile strength test results and the binder level results are contradictory with each other. In light of this, the present master thesis suggests the use of Indirect Tensile Asphalt Cracking Tests or IDEAL-CT as a better method for characterizing the cracking resistance and validating the performance of rejuvenators at the asphalt mixtures level. This test can be performed on the traditional indirect tensile strength test equipment with the same cylindrical specimen, and several studies have confirmed its validity for characterizing the cracking resistance [53–57].

Furthermore, mastic experiments have been conducted to bridge the performance gap between bitumen binder and asphalt mixture. Mastic, which consists of bitumen and filler, can reflect the bitumen behaviour in the actual mixture. The frequency sweep test is the common evaluation methodology for mastic, but the present master thesis also employs Multiple Stress Creep Recovery (MSCR) tests, creep-relaxation tests, and temperature sweep tests as complementary evaluation methodologies. These three tests can characterize the high temperature elastic recovery, the low temperature cracking resistance, and the rheological properties variation along temperature, to evaluate the rejuvenators performance considering the filler influence and as a link between the bitumen binder and asphalt mixtures.

In the following sections of this Chapter, the current evaluation methodology will be presented in detail first, followed by a discussion of the complementary methods.

3.2. Current Evaluation Methodology on Bitumen Binder

3.2.1. Rheological properties experiments

Rheology is the study of the relationship between stress and strain of a material under particular loading and environmental circumstances [58]. It is critical to comprehend how the rheological properties of bitumen are characterized, even though the viscoelastic properties of bitumen are frequently described in terms of complex modulus and phase angle [58]. More importantly, the rheological properties of bitumen are related to a number of pavement distress issues, such as high temperature rutting and low temperature cracking [59]. In light of this, this section will introduce how to conduct tests on rejuvenated bitumen to characterize its rheological properties.

3.2.1.1. Frequency sweep tests

Rheological properties are studied based on the findings of DSR experiments performed on the Anton Paar Modular Compact Rheometer (MCR). DSR tests are typically divided into a pair of distinct groups: low temperatures (between 0 and 30°C) and high temperatures (above 40°C). For the low temperature tests, a spindle with an 8 mm diameter and a 2 mm gap between the parallel plates was employed. For the high temperature tests, a spindle with a 25 mm diameter and a 1 mm gap between the parallel plates were employed. Frequency sweep tests were conducted at temperatures of 0, 15, 30, 40, 60, and 80°C with a frequency range of 0.1 to 10 Hz.

The complex modulus master curves were built with the Sigmoidal model developed in the National Cooperative Highway Research Program (NCHRP) Project A-37A [60]. The Kramers-Kronig relations were used to construct the phase angle master curves [37,61]. The equations for plotting the master curves of complex modulus and phase angle were shown below.

$$\log|G^*| = \upsilon + \frac{\alpha}{1 + e^{(\beta + \gamma \log \omega)}} \tag{6}$$

$$\delta = 90 \times \frac{dlogG^*}{dlog\omega} = -90 \times \alpha\gamma \frac{e^{(\beta+\gamma \log \omega)}}{[1+e^{(\beta+\gamma \log \omega)}]^2} \quad (7)$$

where $|G^*|$ is the complex modulus (Pa), δ is the phase angle (degree), ω is the reduced frequency at the reference temperature (rad/s), υ is the lower asymptote, α is the difference between the values of the upper and lower asymptote, β and γ define the shape between the asymptotes and the location of the inflection point (inflection point obtained from $10^{(\beta/\gamma)}$).

The master curves for complex modulus and phase angle during the frequency sweep tests were constructed with the reference temperature set to 30°C.

3.2.1.2. Multiple Stress Creep Recovery (MSCR) tests

The MSCR tests were conducted on DSR using a spindle with 25 mm diameters and a gap of 1 mm between the parallel plates at 70°C, according to AASHTO TP 70-13. During the testing, the sample was subjected to stresses of 0.1 KPa and 3.2 KPa, respectively, for 1 second before receiving 9 seconds to recover. The tests were executed 30 times, and the specification described above was used to compute the average percent recovery R.

3.2.1.3. Creep-Relaxation tests

At 0°C temperature, the creep-relaxation tests were carried out on DSR using a spindle with 8 mm diameters and parallel plates with 2 mm spacing. In a couple of seconds (0.1s), the samples were subjected to 1% shear strain, followed by a 100-second relaxation period. The shear stresses of the samples were measured throughout the test, and as the relaxation rate accelerated quickly at the beginning of the test, the data collection frequency was set at a rate of 100 points per second [62].

3.2.1.4. Linear Amplitude Sweep (LAS) tests

The LAS tests were performed on DSR using a spindle with 8 mm diameters and parallel plates with 2 mm spacing at 20°C temperature, according to AASHTO TP 101-14. The tests were divided into two sections: frequency sweep and amplitude sweep. In order to determine the damage analysis parameter α, the samples were given 0.1% strain over a frequency range of 0.2 - 30 Hz during the frequency sweep phase. At the amplitude sweep phase, the applied strain was linearly increased from 0 to 30% while the frequency was set at 10Hz. The calculation of the LAS results adhered to the aforementioned standard.

3.2.2. Chemical properties experiments (FTIR tests)

The outcomes from rheological properties experiments will indicate that the performance of rejuvenated bitumen is closely related to the types, contents, and proportions of rejuvenators. In addition, the SBS segment and polymer network structure are crucial to the SBS modified bitumen performance [39]. If the rejuvenator is unable to rebuild the polymer network structure and restore the SBS content, the waste bitumen will not be utilized effectively [28]. To investigate a variety of chemical properties of rejuvenated bitumen, including SBS polymer chemical structure, using FTIR is one of the most practical methods.

Thermo Fisher FTIR equipment in attenuated total reflection (ATR) mode was used for the FTIR experiments. The scan resolution is 4 cm^{-1}, with a scan range from 4000 to 400 cm^{-1} and 32 scan numbers. OMNIC software was used to analyse the FTIR test data.

3.3. Current Evaluation Methodology on Asphalt Mixture

3.3.1. Cantabro tests

Cantabro tests were performed with the Los Angeles testing machine without the steel balls. The percentage of weight loss (Cantabro loss) can be used to characterize the mixture samples' ravelling resistance and durability.

At room temperature, the mixture sample was placed into the testing machine and the machine was rotated at a speed of 30 – 33 revolutions per minute for 300 revolutions. The sample weight before and after the test was recorded and the Cantabro loss can be calculated with the following equation:

$$CL = \frac{A - B}{A} \times 100 \quad (8)$$

where CL is the Cantabro loss (%), A is the sample weight before test and B is the sample weight after test.

3.3.2. Indirect tensile strength ratio (ITSR)

The indirect tensile strength ratio or ITSR is conducted based on the NEN-EN 12697-12: 2018 standard, it can be used to express the moisture resistance of the asphalt mixtures.

The cylindrical asphalt mixture specimens which have the same dimensions as specimens in **Section 3.6** were first placed on the perforated shelf in the vacuum container which was filled with water, then a vacuum was applied to the container and maintained for 30 minutes. After that the specimens were transported to a water bath at 40°C for a period of 72 hours. Before the test, the wet specimens were water bathed at 25°C to make them have the same temperature as the dry specimens. IDEAL-CT is also performed on wet specimens, and since the peak force is recorded, the indirect tensile strength or ITS can be calculated with the equation

$$ITS = \frac{2P}{\pi DH} \times 1000 \tag{9}$$

where P is the peak load, D is the diameter of the specimen and H is the height of the specimen.

The indirect tensile strength ratio, ITSR, can be calculated with the equation

$$ITSR = 100 \times \frac{ITS_w}{ITS_d} \tag{10}$$

where ITS_w is the average indirect tensile strength of the wet specimen group and ITS_d is the average indirect tensile strength of the dry specimen group.

3.4. Evaluation Methodology Complementary on Bitumen Binder

3.4.1. Compatibility experiment

Bleeding tests were conducted on rejuvenated bitumen samples to assess the compatibility between the bitumen and the rejuvenators. This test is particularly important for bitumen that has been rejuvenated with oil contained rejuvenators, as the oil may segregate from the rejuvenated bitumen and move towards the aggregate interface, which will loosen the compacted asphalt mixture and reduce the strength.

Bitumen samples were first poured into aluminium containers and a film thickness of 35 mm was controlled. After being cooled to room temperature, the samples were covered with filter paper and a constant pressure of 0.6 g/cm^2 was applied for 5 minutes (**Figure 3-1**).

Figure 3-1. Bleeding test samples before (left) and after (right) filter paper was applied.

The samples were then heated to 90°C for 2 hours in the oven. The blackness of the filter paper was visually evaluated for the bleeding test results. As demonstrated in **Figure 3-2**, the filter paper blackness before and after the bleeding tests exhibits a noticeable difference among various bitumen samples, which indicates the effectiveness of the bleeding tests for evaluating the compatibility properties.

Figure 3-2. Bitumen samples before (left) and after (right) bleeding tests.

3.4.2. GC-FID

Gas Chromatography-Flame Ionization Detection (GC-FID) is an analytical methodology that employs gas chromatography (GC) to separate the components from a bitumen sample and flame ionization detection (FID) to quantify their concentrations. This experiment provides complementary information on the chemical properties of rejuvenated bitumen.

The GC-FID sample was prepared by first weighing 15 mg of bitumen sample into a vial (2 ml), then adding 1.0 mL of cyclohexane and heating for 5 minutes. Prior to the test starting, 0.5 μL of cyclohexane was injected into the system for a zero-reading. The system was then injected with 0.5 μL of sample to run the test. The temperature of the column oven was increased from 90°C to 430°C at a rate of 10 °C/min. The temperature of the FID was 450°C, and the flow rates for the hydrogen, air, and makeup gas were

35 mL/min, 350 mL/min, and 40 mL/min, respectively. The sample has been transported through the column using helium as a carrier gas at a flow rate of 20 mL/min.

Figure 3-3 presents the GC-FID chromatogram of aged bitumen and rejuvenated bitumen samples with pure oil rejuvenators and physical rejuvenator. The molecular weight of the separated components from the bitumen sample is proportional to their retention time in the chromatogram. The aged PMB exhibits two distinct peaks, indicating the presence of two large fractions with different molecular weights. One fraction consists of relatively small molecules, while the other fraction comprises relatively large molecules. The rejuvenated bitumen samples with different types of oil show prominent peaks in the chromatogram, compared to the aged PMB sample. The Aro oil sample has a peak at the lowest retention time, indicating the smallest molecular weight. The Rap oil and LS oil samples have peaks at the same retention time as the first major peak of the aged PMB sample, suggesting similar molecular weights. Among the three oil samples, the Rap oil sample has the highest peak intensity, followed by the LS oil sample and the Aro oil sample. The peak intensity is related to the compatibility of the rejuvenators with the aged PMB, as confirmed by the bleeding tests described earlier. Higher peak intensity implies lower compatibility and vice versa. Moreover, adding extra SBS polymer to the pure oil rejuvenator (10LS), which is the physical rejuvenator (10LS-L), reduces the peak intensity, implying that the SBS polymer can absorb some small molecules in the oil and improve compatibility.

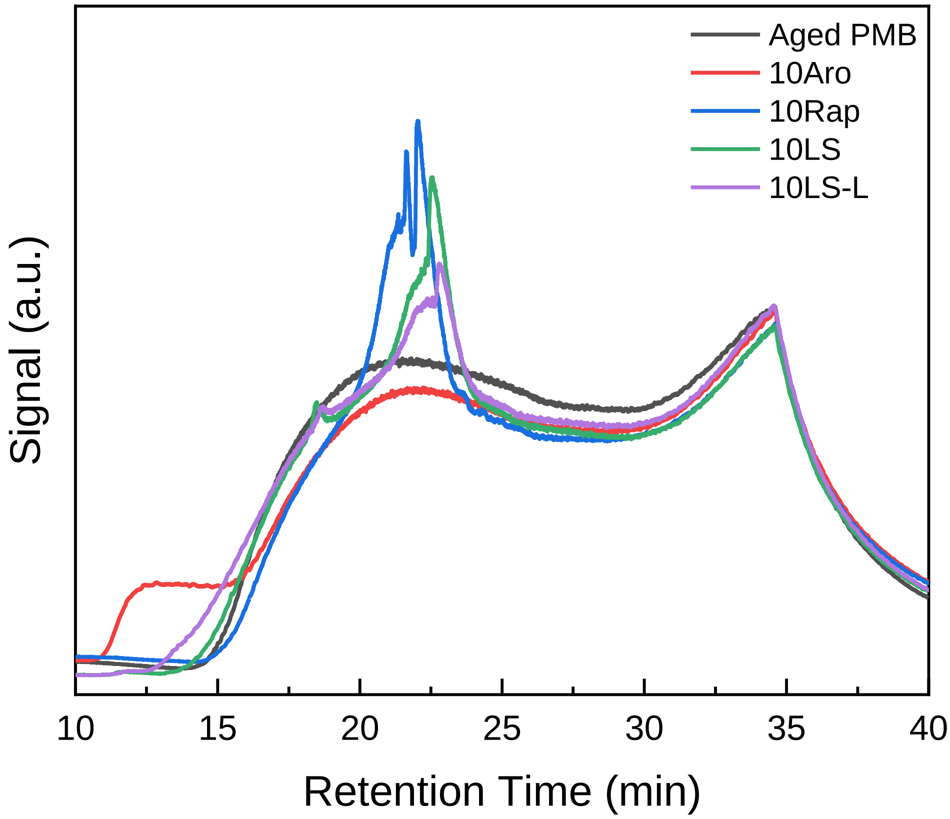

Figure 3-3. GC-FID chromatogram of various bitumen samples.

3.4.3. ESEM

ESEM stands for Environmental Scanning Electron Microscopy, which is a type of scanning electron microscopy that can produce high-resolution images of the surface and microstructure of the bitumen specimens without the need for special preparation or coating. The electron beam exposure for several minutes induced a surface modification of the bitumen films during the ESEM examination. The initially flat bitumen surface transformed into a random fibrillar network after the beam exposure. This phenomenon could be attributed to the selective removal of the low molecular weight oils (saturates and aromatics) from bitumen by the electron beam, leaving behind the higher molecular weight components, mainly the asphaltenes and resins [37]. The ESEM examination was used as an evaluation methodology complementary to the morphological properties of the bitumen specimen, and to study the effect of rejuvenators on the morphological properties and link to the chemical properties and rheological properties of the bitumen specimen.

Figure 3-4 demonstrates the fibrillar network morphology of the unaged PMB and aged PMB with different aging degrees. The results indicate that aging has a significant impact on the fibrillar network structure. The 20 h PAV aged PMB exhibits a smaller fibril diameter and a more disordered network than the unaged PMB. The 80 h PAV aged PMB loses its fibrillar network structure, which is attributed to the evaporation of low molecular weight oils during the prolonged aging process.

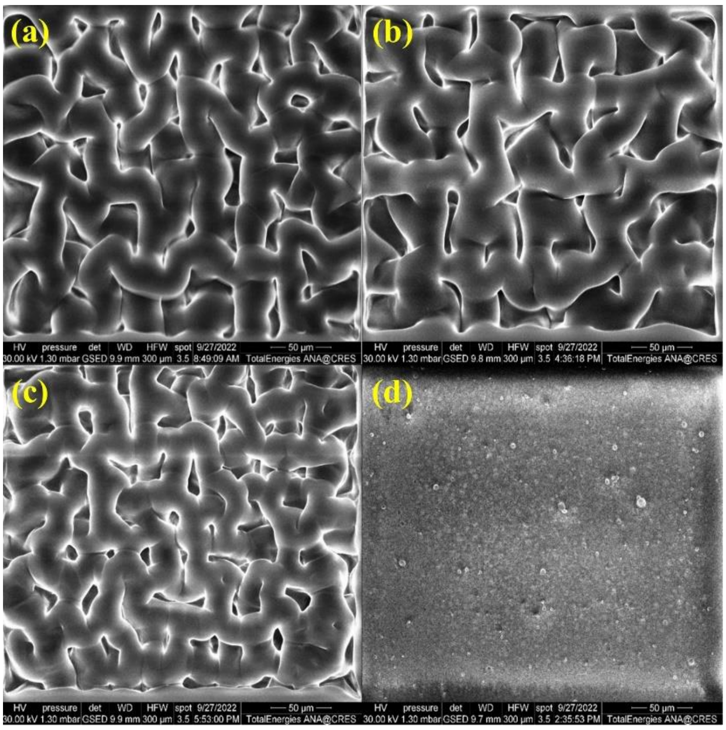

Figure 3-4. Fibrillar network morphology of (a) unaged PMB, (b) TFOT aged PMB, (c) 20 h PAV aged PMB and (d) 80 h PAV aged PMB.

Figure 3-5 presents the morphological changes of the aged PMB rejuvenated with different types of oils. The results indicate that the addition of oils can restore the fibrillar network structure of the aged PMB, but the morphology of the fibrils varies depending on the type of oil used. The rejuvenated PMB with Rap oil and LS oil have smoother fibrils than rejuvenated PMB with Aro oil, and their morphology is similar to that of the unaged PMB. This may be related to the prominent peak observed in the GC-FID chromatogram for Rap oil and LS oil, which indicates a higher content of light components.

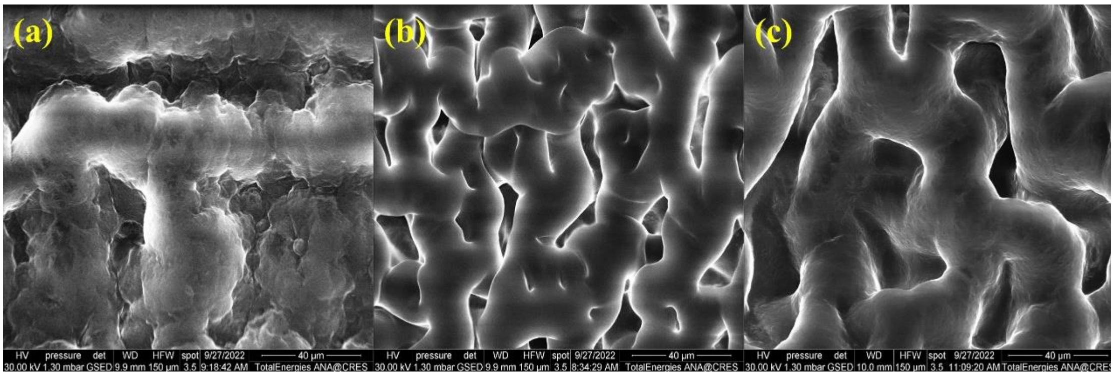

Figure 3-5. Fibrillar network morphology of (a) rejuvenated PMB with Aro oil, (b) rejuvenated PMB with Rap oil and (c) rejuvenated PMB with LS oil.

The effects of a physical rejuvenator and a chemical rejuvenator on the morphology of the aged PMB are illustrated in **Figure 3-6**. Both rejuvenators can recover the fibrillar network structure of the aged PMB, but there are many bubbles observed on the fibrils. These bubbles might relate to the fresh SBS polymer added with the rejuvenators, which indicates that the fresh SBS polymer does not blend well with the original polymers and forms crosslinks. However, the bubbles are significantly smaller when using the chemical rejuvenator, which suggests better compatibility and integration with the original polymers and a more effective restoration of the polymer network structure.

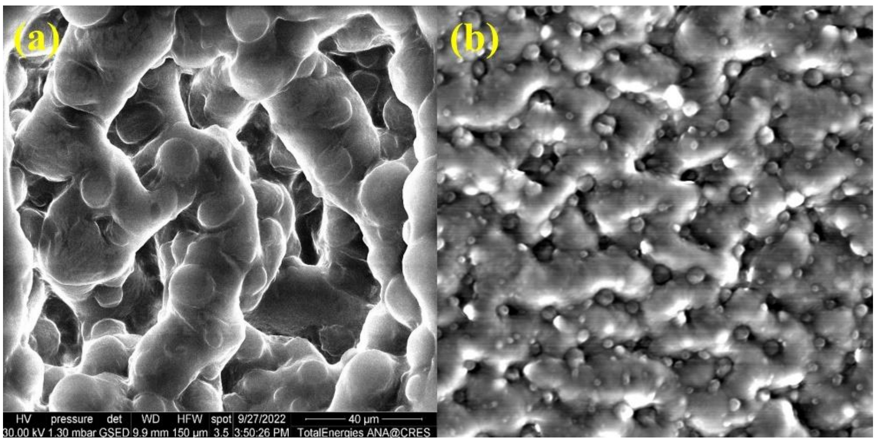

Figure 3-6. Fibrillar network morphology of (a) rejuvenated bitumen with a physical rejuvenator and (b) rejuvenated bitumen with a chemical rejuvenator.

3.4.4. Adhesion experiment

The adhesion properties of bitumen binder are closely related to the ravelling resistance of asphalt mixtures. In order to characterize the binder's adhesion, pull-off is conducted with DMA 3200 from TA Instruments (**Figure 3-7**). The stone columns employed in the pull-off tests have an 8-mm diameter, and their surfaces were polished to a flat level. The bitumen film has a thickness of 200 µm, and the test was carried out at 5°C. The load was displacement-controlled, and the speed was set to 10% strain per second.

Figure 3-7. Pull-off test with DMA.

Figure 3-8 presents the force versus displacement curves from the pull-off test with rejuvenated bitumen samples by pure oil rejuvenator, physical rejuvenator, and chemical rejuvenator, respectively. It can be seen that the rejuvenated bitumen with chemical rejuvenator has the highest peak force, indicating greater adhesive properties and ravelling resistance than bitumen that has been rejuvenated using the other two types of rejuvenators.

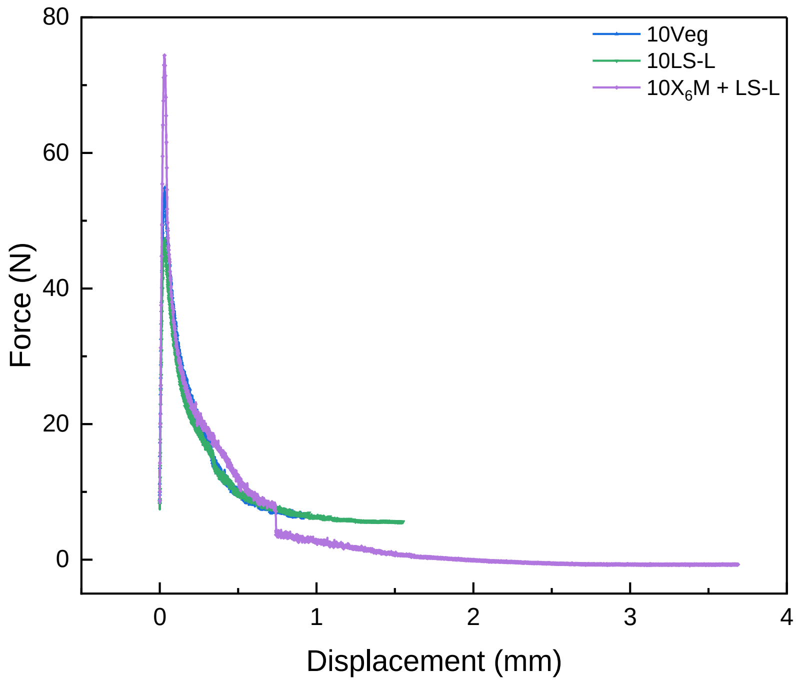

Figure 3-8. Force versus displacement curves from the pull-off tests.

3.5. Evaluation Methodology Complementary on Mastic

The mastic experimental method is substantially the same as the bitumen binder rheological properties experiments, with the exception that the frequency sweep test temperatures have been modified to 0, 15, 30, 45, and 60°C as the mastic could not withstand in high temperatures. The clamping system provided by Anton Paar was used to mount the mastic samples, as illustrated in **Figure 3-9**.

Figure 3-9. Mastic sample in DSR ready for testing.

3.6. Evaluation Methodology Complementary on Asphalt Mixture (IDEAL-CT)

According to the ASTM D8225-19 standard, IDEAL-CT is performed on the MTS 150 kN hydraulic actuator with a constant load-line displacement rate of 50.0 ± 2.0 mm/min at 25°C (**Figure 3-10**). The cylindrical asphalt mixture specimen has a 100 mm diameter and a 50 mm height.

Figure 3-10. IDEAL-CT setup.

The load and the displacement will be measured throughout the test, and a curve between the two can be plotted, as shown in **Figure 3-11**.

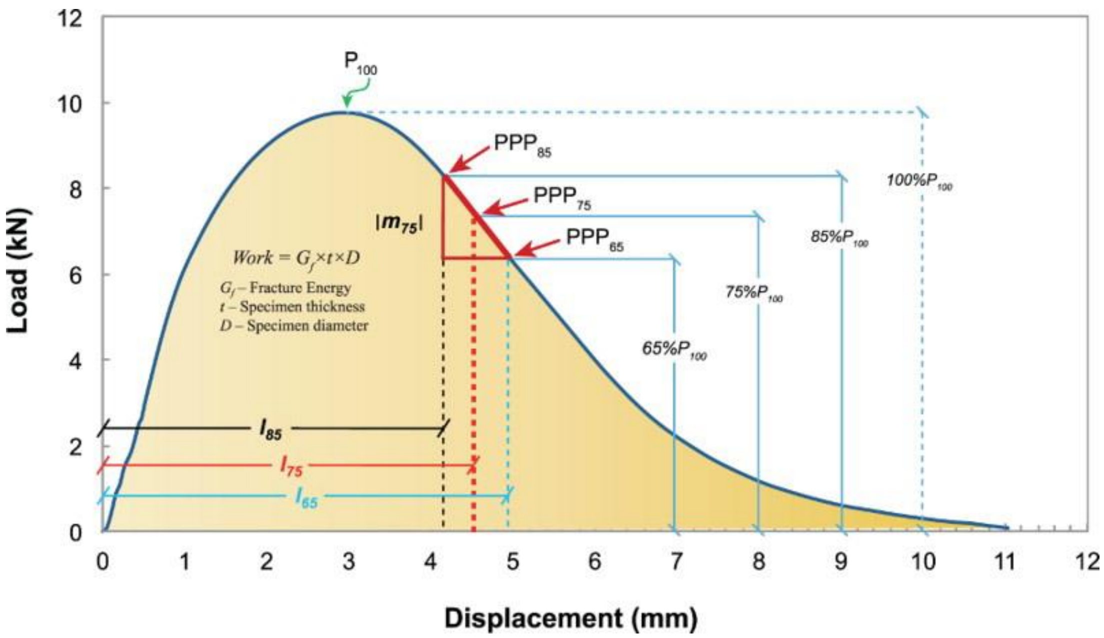

Figure 3-11. Recorded load (P) versus displacement (l) curve [53].

The cracking tolerance index CT_{index} can be calculated by using the failure energy, post peak slope, and deformation tolerance at 75% of the peak load obtained from the above plotted curve with the equation

$$CT_{index} = \frac{t}{62} \times \frac{l_{75}}{D} \times \frac{G_f}{|m_{75}|} \times 10^6 \quad (9)$$

where G_f is the failure energy, $|m_{75}|$ is the absolute value of the post peak slope at 75% peak load, l_{75} is the displacement at 75% peak load after the peak, D is the specimen diameter and t is the specimen thickness.

The calculated CT_{index} can be used to indicate the cracking resistance of the asphalt mixture, the higher the CT_{index}, the better the cracking resistance.

Chapter 4. Comparative Analysis of Three Primary Categories of Rejuvenators

This Chapter presents a comparative analysis of the rejuvenation effects of different types of rejuvenators on the rheological, mechanical, and chemical properties of rejuvenated bitumen. The analysis is based on the complex modulus and phase angle master curves, high temperature elasticity, low temperature cracking resistance, fatigue life performance, and Fourier transform infrared spectroscopy (FTIR) results.

4.1. Rheological Analysis Based on Master Curves

This section presents the analysis of the complex modulus and phase angle master curves, which were constructed based on the Sigmoidal model and the Kramers-Kronig relations as outlined in **Section 3.2.1.1**.

Figure 4-1 demonstrates the complex modulus and phase angle master curves of rejuvenated bitumen by pure oil rejuvenator, physical rejuvenator, and pure chemical compound. As presented in this figure, unaged PMB has a lower complex modulus, a significant phase angle downward trend at the low frequency range and a plateau region in the middle compared with aged PMB. The downward trend and plateau region disappeared with aging, proving that the polymer network structure has degraded [37,63]. For rejuvenated bitumen with pure oil rejuvenator (10LS), the complex modulus decreased a lot more than aged PMB and is even lower than unaged PMB, indicating that oil can help the aged bitumen become softer by supplying the diminished light components [28]. The phase angle results show that oil enhances the viscosity of aged bitumen, especially at low and high frequencies. This may benefit the low temperature cracking resistance, but may further reduce the high temperature elasticity. For the physical rejuvenator, 10LS-L still has a lower complex modulus than aged PMB, but the reduced range is less than with the pure oil rejuvenator, and the extra SBS polymer in the physical rejuvenator has provided this rejuvenated bitumen a little bit more stiffness. By looking at the phase angle results, the rejuvenated bitumen with physical rejuvenator and the rejuvenated bitumen with pure oil rejuvenator have similar phase angles at the high frequency range. However, as the frequency decreases, the rejuvenated bitumen with physical rejuvenator exhibits more elasticity than the rejuvenated bitumen with pure oil rejuvenator due to the additional SBS polymer, which may also imply a better high temperature performance. Moving to rejuvenation with pure chemical compound, the complex modulus of rejuvenated bitumen (10M) increased significantly, even surpassing that of aged PMB in the mid and low frequency range. The phase angle master curve of this rejuvenated bitumen showed essentially a flat line at a lower phase angle level, indicating that it had exceptional elasticity but lost the viscoelastic property as bitumen. Therefore, this rejuvenated bitumen may have an outstanding high temperature performance, but an unacceptable low temperature performance and fatigue life.

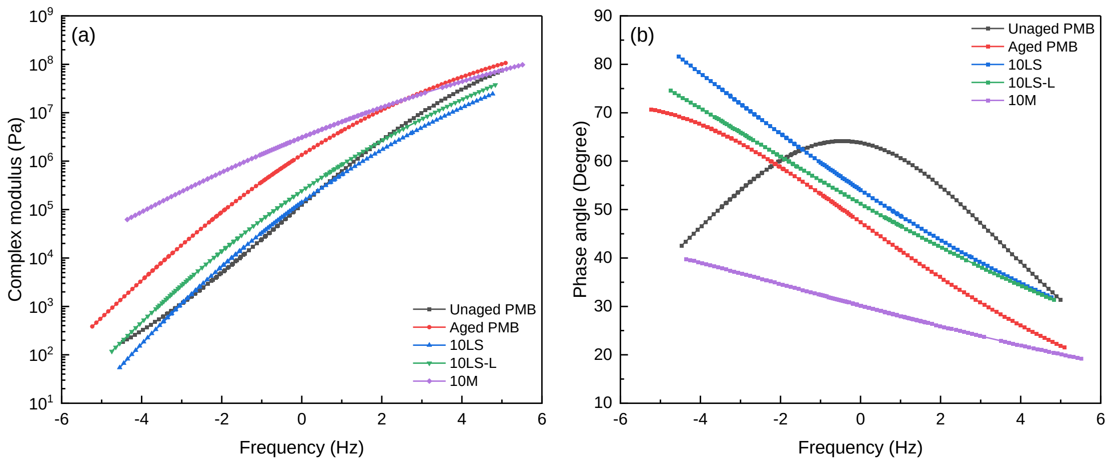

Figure 4-1. Complex modulus and phase angle master curves of rejuvenated bitumen by pure oil rejuvenator, physical rejuvenator and pure chemical compound.

Figure 4-2 compares the complex modulus and phase angle master curves of rejuvenated bitumen by pure oil rejuvenator added with chemical compound (chemo-oil rejuvenator) as well as physical rejuvenator added with chemical compound (chemical rejuvenator). It can be seen that the complex modulus of aged PMB is still able to be reduced by the chemo-oil rejuvenator. For the phase angle master curve, as presented in **Figure 4-2(b)**, the chemo-oil rejuvenator is able to increase viscosity at the mid to high frequency range and restore a downward trend at the low frequency range, which might be a sign that the chemical compound in the chemo-oil rejuvenator has reconstructed the degraded polymer network structure.

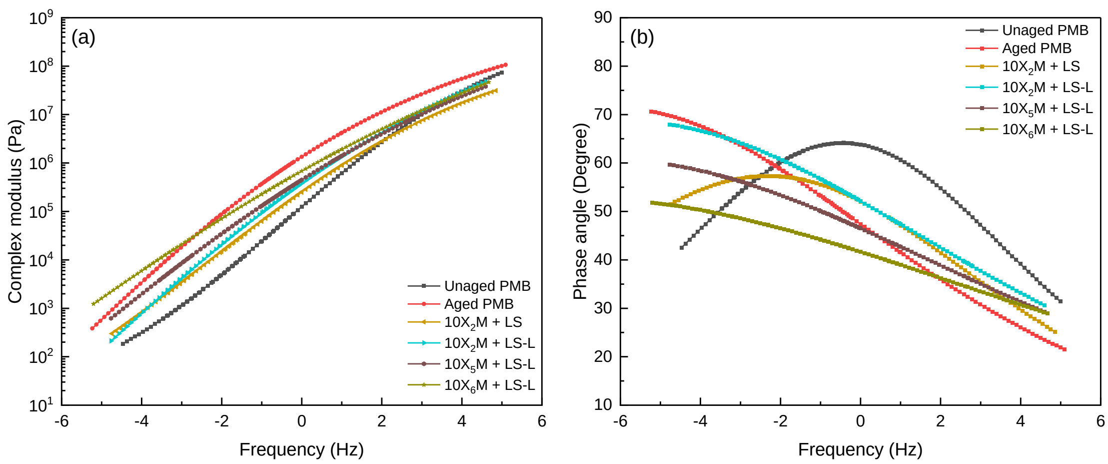

Figure 4-2. Complex modulus and phase angle master curves of rejuvenated bitumen by chemo-oil rejuvenator and chemical rejuvenators.

For chemical rejuvenators, the complex modulus of rejuvenated bitumen is largely influenced by the additional ratio of the chemical compound M. At the X_2 addition ratio level, the complex modulus of rejuvenated bitumen with the chemical rejuvenator is comparable to that with the chemo-oil rejuvenator, and the small difference can be concluded by the extra SBS polymer contained in the chemical rejuvenator. However, as the chemical compound addition ratio increases, the complex modulus of rejuvenated bitumen increases as well, and this increased range is particularly significant at the low frequency range. The phase angle master curves of rejuvenated bitumen with chemical rejuvenators exhibit a similar shape but differ in the phase angle level. The higher the ratio of the chemical compound M, the lower the phase angle master curve. Nevertheless, all three chemical rejuvenators have the ability to enhance the elasticity of rejuvenated bitumen at low frequencies while preserving a good viscosity at high frequencies.

In general, this chemical compound M has a great potential for enhancing the elasticity of rejuvenated bitumen, which is particularly beneficial for its high temperature performance. Meanwhile, it is necessary to control the addition ratio of this chemical compound M and combine use with oil contained components to improve the viscosity of rejuvenated bitumen at the mid to low frequencies to get a better low temperature cracking resistance and fatigue life performance.

4.2. High Temperature Properties Based on MSCR Results

As presented in **Figure 4-3**, pure oil and physical rejuvenators are not able to improve the average percent recovery value R. In contrast, their presence reduces the R-value, which is connected to the fact that the oil components in them make the bitumen more viscous. The phase angle master curves result in **Section 4.1** also support this phenomenon. The pure chemical compound can significantly improve the average percent recovery value R even beyond the unaged PMB due to the extraordinary elasticity recovery ability. Rejuvenated bitumen with the chemo-oil rejuvenator has almost the same R-value as the aged PMB. The chemo-oil rejuvenator contains both oil and chemical components, which have opposite effects on the elasticity recovery of rejuvenated bitumen. The oil component reduces the elasticity, while the chemical component increases it. At this level of chemical compound addition ratio, the oil component counteracts the chemical component, resulting in no significant change in the R-value compared to the aged PMB. As for the chemical rejuvenators, the recovery value of rejuvenated bitumen increases with the addition ratio of the chemical compound M, also proved by the phase angle master curves in the previous section. This confirms that the use of the chemical compound contributes to the high temperature performance of rejuvenated bitumen.

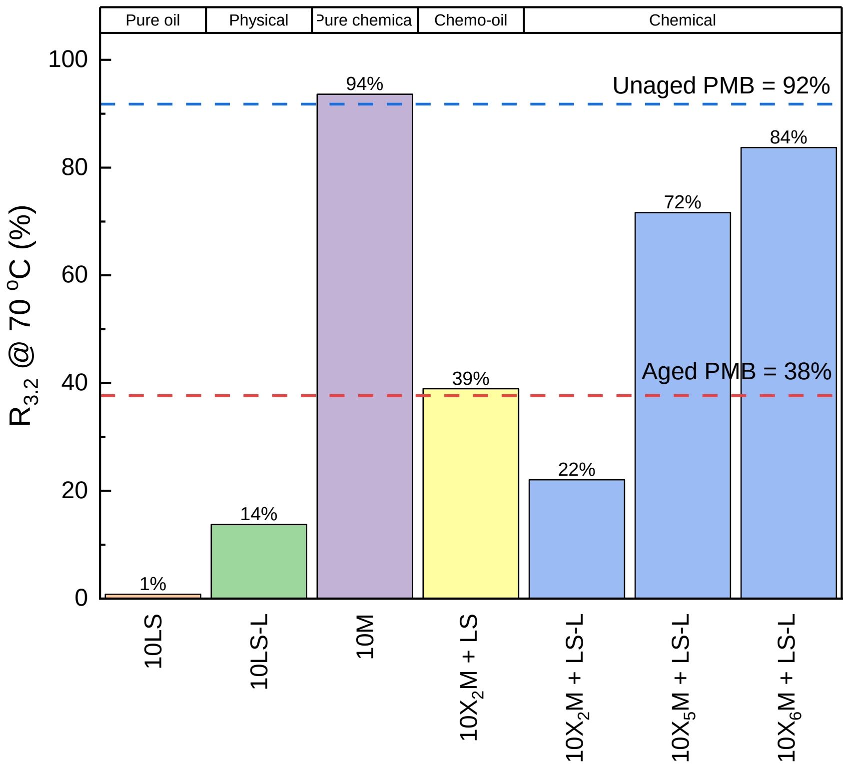

Figure 4-3. 70°C MSCR results of rejuvenated bitumen by pure oil rejuvenator, physical rejuvenator, pure chemical compound, chemo-oil rejuvenator, and chemical rejuvenators.

4.3. Low Temperature Properties Based on Creep-Relaxation Results

Figure 4-4 presents the maximum shear stress of different rejuvenated bitumen in the creep-relaxation tests. As demonstrated in this figure, the pure oil rejuvenator can effectively soften the aged PMB and lower the maximum shear stress even below the unaged PMB. The physical rejuvenator produced the same result, but its reduced range was smaller than that of the pure oil rejuvenator, possibly as a result of the additional SBS polymer that the physical rejuvenator contained. The maximal shear stress will be greatly increased when using the pure chemical compound, as predicted in the master curves analysis in **Section 4.1**. The results of using chemo-oil and chemical rejuvenators were comparable to those of using the pure oil rejuvenator and the physical rejuvenator, proving that adding additional chemical compounds will not exacerbate the softening effect or raise the maximum shear stress.

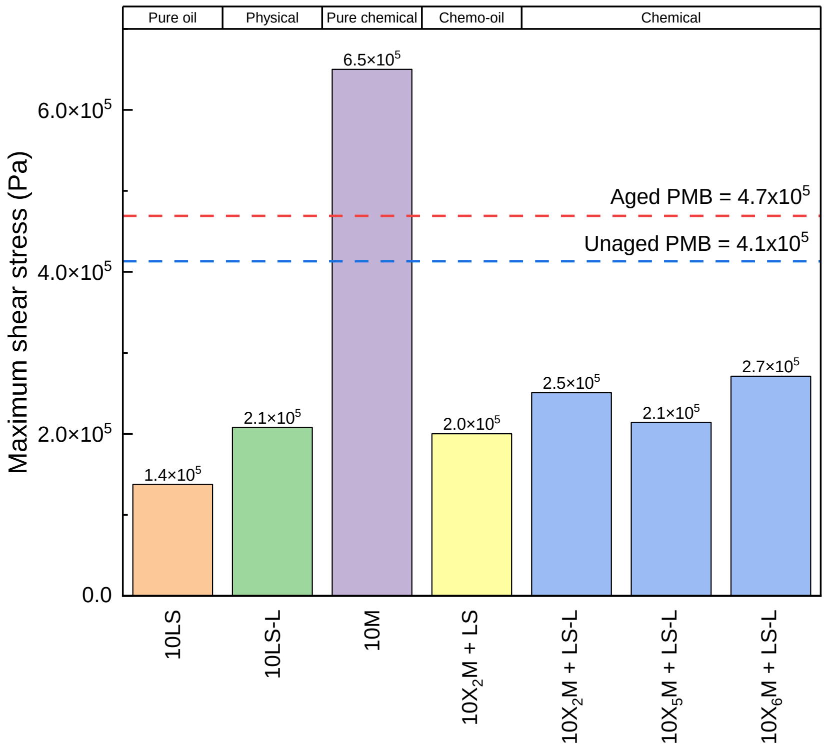

Figure 4-4. Maximum shear stress of rejuvenated bitumen by pure oil rejuvenator, physical rejuvenator, pure chemical compound, chemo-oil rejuvenator, and chemical rejuvenators in creep-relaxation tests.

Figure 4-5 demonstrates the time for stress reduced 50% and 90% from the maximum of different rejuvenated bitumen samples in the creep-relaxation tests. Similar to the results of maximum shear stress, the pure oil rejuvenator and the physical rejuvenator can reduce this time by a significant amount below the aged PMB. The additional SBS polymer in the physical rejuvenator has nearly no impact on the time difference between the physical rejuvenator and the pure oil rejuvenator. The introduction of the pure chemical compound will dramatically extend the needed time, cause the rejuvenated bitumen to accrue more stress and increase the vulnerability to cracking at low temperatures. The chemo-oil rejuvenator can let the rejuvenated bitumen at the same level as unaged PMB in terms of time for stress reduced 50% from the maximum, as shown in **Figure 4-5(a)**. Chemical rejuvenators can also shorten this period of time, though the results are not as effective as chemo-oil rejuvenators. For stress reduced 90% from the maximum results (**Figure 4-5(b)**), the chemo-oil rejuvenator has considerably superior results to chemical rejuvenators, maybe as a result of the extra SBS polymer in the chemical rejuvenator making the rejuvenated bitumen stiffer than with chemo-oil rejuvenated bitumen. Nevertheless, the two varieties of rejuvenator rejuvenated bitumen still perform significantly better than aged bitumen, and the time results are comparable to those of their base rejuvenators (pure oil rejuvenators and physical rejuvenators), suggesting that the additional chemical compound will not have a considerable detrimental impact.

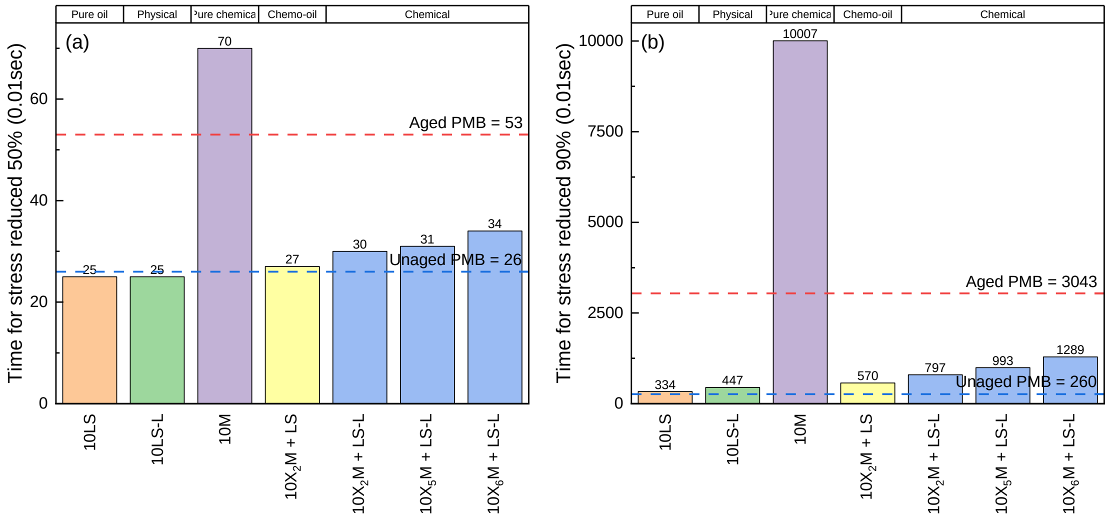

Figure 4-5. (a) time for stress reduced 50% from the maximum and (b) time for stress reduced 90% from the maximum of rejuvenated bitumen samples by pure oil rejuvenator, physical rejuvenator, pure chemical compound, chemo-oil rejuvenator, and chemical rejuvenators in creep-relaxation tests.

4.4. Fatigue Life Performance

Figure 4-6 shows the fatigue life of rejuvenated bitumen samples under 2.5% applied strain and 5% applied strain, respectively. It can be seen that the fatigue life can be greatly improved by the pure oil rejuvenator and the physical rejuvenator under both strain levels, far exceeding that of the unaged PMB. However, at a higher strain level, the fatigue life of rejuvenated bitumen with the physical rejuvenator is shorter than that of the pure oil rejuvenator, which might be due to the presence of extra SBS polymer in the physical rejuvenator. The pure chemical compound rejuvenated bitumen have an excellent fatigue life at lower strain levels, but the performance is subpar at higher strain levels, which is probably because the rejuvenated bitumen is exceptionally stiff at low strain levels but behaves brittle at high strain levels. Rejuvenated bitumen with the chemo-oil rejuvenator generally performs well in fatigue life tests and outperforms unaged PMB at both strain levels. As a combined effect of polymers and chemical compounds, chemical rejuvenators have limited effects in enhancing fatigue life. Nevertheless, the rejuvenated bitumen with chemical rejuvenators has higher fatigue than the aged PMB, and at a low strain level, it even surpasses the unaged PMB.

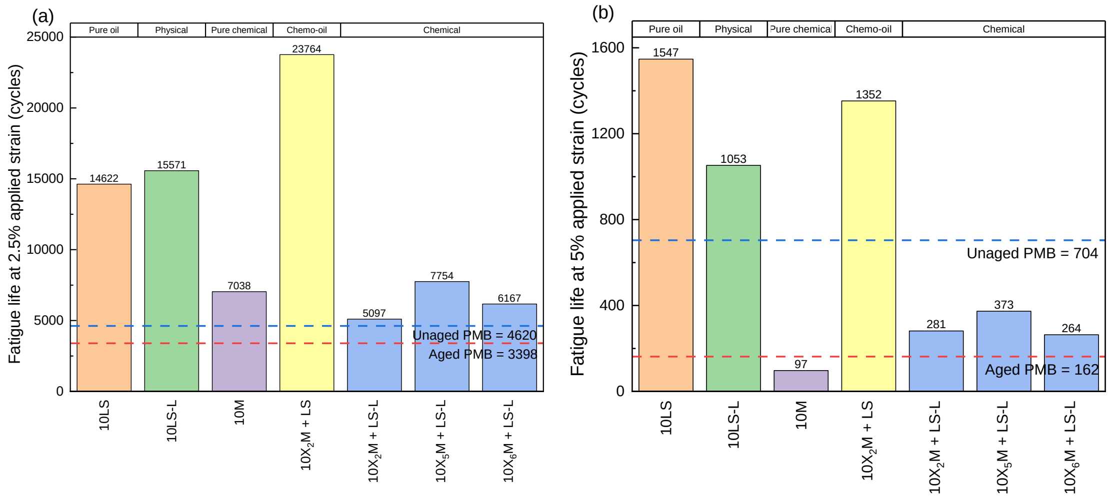

Figure 4-6. (a) fatigue life N_f at 2.5% applied strain and (b) fatigue life N_f at 5% applied strain of rejuvenated bitumen samples by pure oil rejuvenator, physical rejuvenator, pure chemical compound, chemo-oil rejuvenator, and chemical rejuvenators.

4.5. Chemical Properties Based on FTIR Results

This section presents a comparative analysis of the chemical properties of rejuvenated bitumen samples with different types of rejuvenators, based on the FTIR results. Moreover, a polybutadiene group index I_{PB} is computed for each sample to evaluate the recovery of polymer content by various rejuvenators.

Figure 4-7 demonstrates the FTIR spectrum of aged and rejuvenated bitumen samples with the pure oil rejuvenator (10LS) and the physical rejuvenator (10LS-L). The high absorption peaks at 1460 cm^{-1} and 1376 cm^{-1} are from the bending vibration of methylene ($-CH_2-$) and methyl ($-CH_3$) groups in the bitumen, respectively [64]. The 1600 cm^{-1} peak next to them corresponds to the aromatic C=C stretching vibration [65]. As illustrated in **Figure 4-7**, for bio-oil based rejuvenators including LS oil, the absorption peaks at 1746 cm^{-1} and 1163 cm^{-1} can be selected as the characteristic peaks, they are represent the triglycerides ester carbonyl function group and stretching vibration of the C=O ester groups, respectively [66]. The absorption peak at 966 cm^{-1} is associated with the bending vibration of the carbon-hydrogen bond on the carbon-carbon double bond in the butadiene group, which can be selected as the reference characteristic peak for the SBS polymer modifier [67]. The FTIR spectra in **Figure 4-7** show that this 966 cm^{-1} peak intensity of the rejuvenated bitumen sample with the physical rejuvenator is higher than that of the sample with the pure oil rejuvenator, due to the extra SBS polymer introduced by the physical rejuvenator.

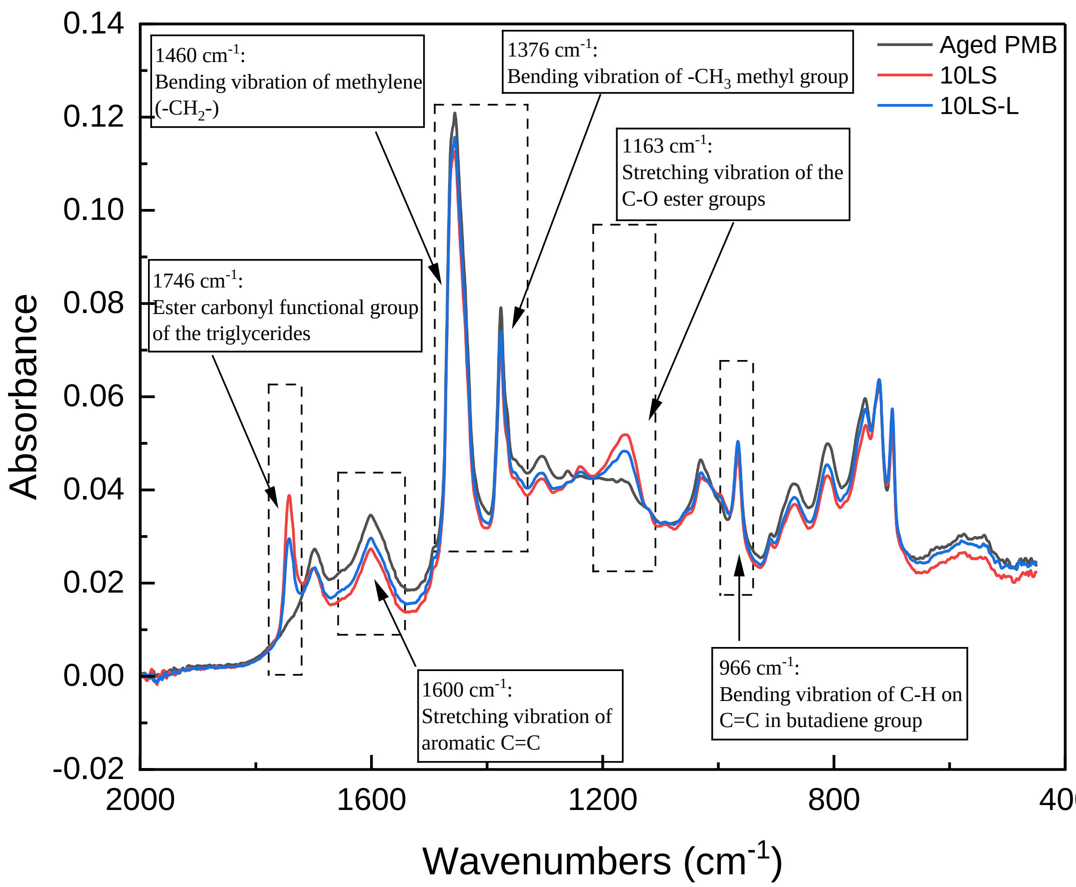

Figure 4-7. FTIR spectrum of aged and rejuvenated bitumen with pure oil rejuvenator and physical rejuvenator.

Figure 4-8 depicts the FTIR spectra of rejuvenated bitumen samples with the pure chemical compound and chemical rejuvenators. In addition to the absorption peaks discussed previously, some new peaks are observed in these samples, indicating the presence of new functional groups. The peak at 2270 cm^{-1} corresponds to the isocyanate group (-NCO) in the chemical compound, which can be used as a characteristic peak for this types of chemical compounds [12]. The peak at 1526 cm^{-1} is associated with the bending vibration of the N-H bond from the amide bond [47]. The rest two absorption peaks at 1311 and 1219 cm^{-1} are corresponding to the stretching vibration of the C-N bond from the amide bond [47]. More importantly, as demonstrated in **Figure 4-8**, the appearance of these three absorption peaks confirmed the chemical reactions between the chemical compound M and the degraded SBS polymer [47].

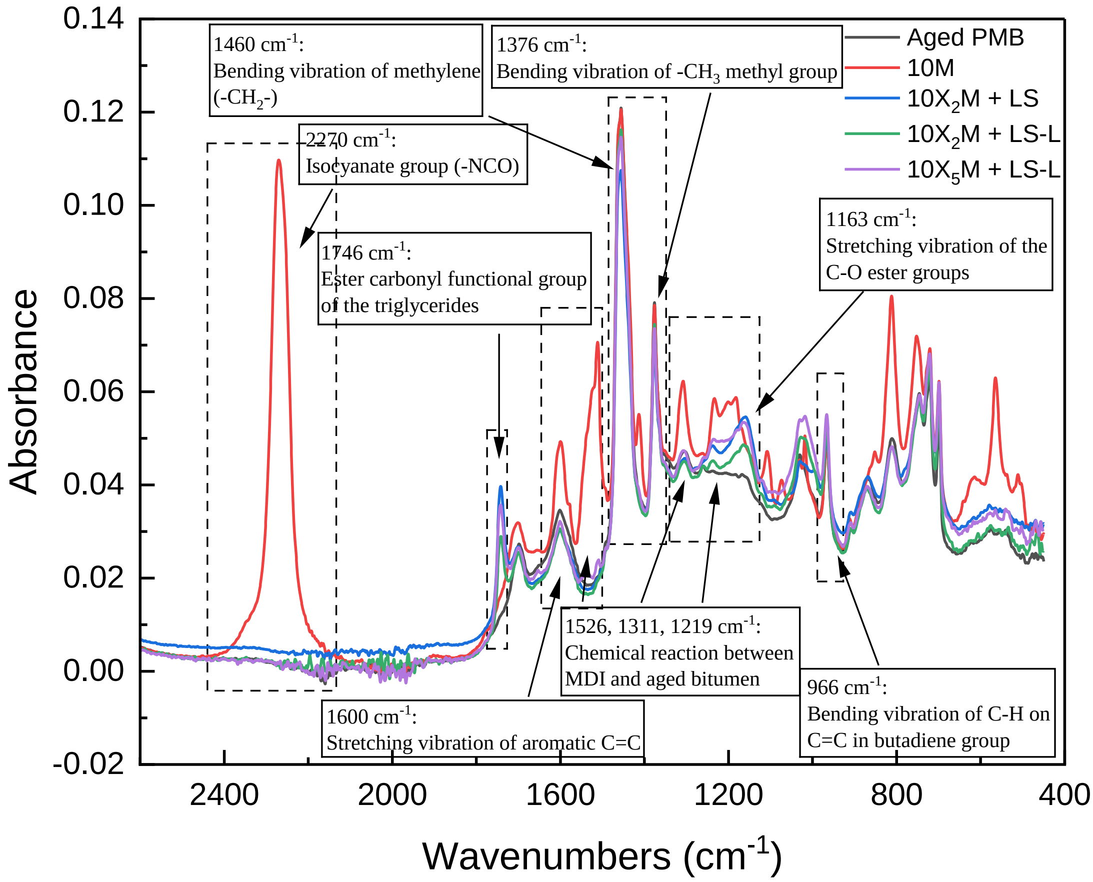

Figure 4-8. FTIR spectrum of aged and rejuvenated bitumen with pure chemical compound and chemical rejuvenators.

For a more precise and intuitive understanding of the SBS polymer content in the sample, the ratio of absorbance values was used to eliminate errors caused by sample preparation, thickness, and other factors [66]. In order to do that, the summarized area of the high absorption peaks at 1460 cm^{-1} and 1376 cm^{-1} were used as a standard reference value, and with the area of the polybutadiene group peak at 966 cm^{-1} to get the polybutadiene group index I_{PB}, as calculated through the following equation.

$$I_{PB} = \frac{A_{966}}{A_{1460} + A_{1376}} \tag{10}$$

The I_{PB} results of aged and rejuvenated bitumen samples with various rejuvenators are presented in

Figure 4-9. The I_{PB} index, which indicates the carbon-carbon double bond content in the polybutadiene group, decreased by 2.3% due to aging. This corroborated the aging mechanism of SBS polymer as demonstrated in **Figure 1-1**, namely the cleavage of carbon-carbon double bonds and the formation of oxygen-containing groups. In addition, as discussed in **Section 1.4**, the pure oil rejuvenator cannot restore the degraded SBS polymer and leads to further dilution of the existing polymers, which is also evidenced by the reduction in I_{PB} index of rejuvenated bitumen with pure oil rejuvenator. The I_{PB} index of the bitumen rejuvenated with the physical rejuvenator presents a slight increase, which is attributed to the additional SBS polymer contained in the rejuvenator. The rejuvenated bitumen with the pure chemical compound M showed a significant increase in the I_{PB} index, reaching the level of unaged PMB. This indicates that M can effectively reconnect the broken PB segments by reacting with the active oxygen-containing groups in the degraded polymer. The FTIR spectra confirmed this by showing the absorption peaks at 1526, 1311, and 1219 cm^{-1}, as illustrated in **Figure 4-8**. The I_{PB} index of the rejuvenated bitumen with the chemo-oil rejuvenator ($10X_2M$ + LS) was higher than that of the rejuvenated bitumen with the pure oil rejuvenator (10LS). This further confirmed that the additional chemical compound M contributed to the recovery of the degraded SBS polymer. The rejuvenated bitumen with chemical rejuvenators also exhibited an increased I_{PB} index, which was positively correlated with the amount of the chemical compound added.

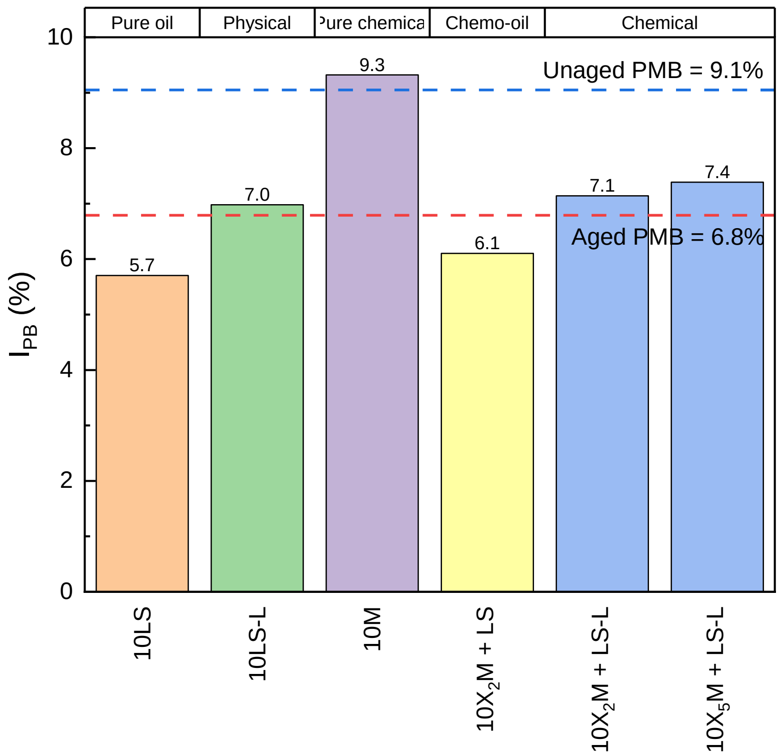

Figure 4-9. Polybutadiene group index I_{PB} of aged and rejuvenated bitumen.

4.6. Rejuvenators' Comparative Analysis Summary

This Chapter presented a comparative analysis of the rejuvenation effects of different types of rejuvenators on aged SBS modified bitumen. The analysis was based on the complex modulus and phase angle master curves, high temperature elasticity, low temperature cracking resistance, fatigue life performance, and chemical properties of the rejuvenated bitumen as measured by FTIR.

The results indicate that the pure oil rejuvenator can effectively replenish the light components and soften the aged bitumen, thereby enhancing the low temperature cracking resistance and fatigue life performance of the rejuvenated bitumen. However, the high temperature elasticity of the rejuvenated bitumen deteriorates due to the increased viscosity caused by the oil. Moreover, the FTIR spectra and the I_{PB} index reveal that the pure oil rejuvenator cannot restore the degraded SBS polymer and will further dilute the existing polymers. The physical rejuvenator, at the same dosage, provides fewer light components than the pure oil rejuvenator due to the presence of the SBS polymer in its composition. Consequently, the bitumen rejuvenated with the physical rejuvenator exhibits inferior low temperature cracking resistance and fatigue life performance than the bitumen rejuvenated with the pure oil rejuvenator. Moreover, the existing SBS polymer in the physical rejuvenator further compromises these two properties. However, the elasticity of the bitumen rejuvenated with the physical rejuvenator is enhanced by the additional SBS polymer and the degraded SBS polymer network structure is partially restored. The FTIR spectra and the I_{PB} index confirm that the polymer content in the rejuvenated bitumen is increased to some extent. The pure chemical compound significantly enhances the elasticity of the rejuvenated bitumen. As evidenced by the FTIR spectra and the I_{PB} index, the chemical compound reacts with the degraded SBS polymer and reconnects the broken PB segments. However, the bitumen rejuvenated with the pure chemical compound suffers from poor low temperature cracking resistance and fatigue life performance due to the lack of light components in its composition, and these properties are even worse than that of the aged PMB. In contrast, chemical rejuvenators combine the advantages of both the physical rejuvenator and the chemical compound. They can replenish the light components and soften the aged bitumen, thereby improving the low temperature cracking resistance and fatigue life performance of the rejuvenated bitumen. They can also provide fresh SBS polymer and reactivate the existing SBS polymer by the chemical compound to restore the degraded SBS polymer and reconstruct the polymer network structure.

Figure 4-10 demonstrates the summary of the rejuvenation effects and mechanisms of different types of rejuvenators. As discussed above, the pure oil rejuvenator can effectively provide light components, but it cannot restore the polymer network. Therefore, the pure oil rejuvenator is positioned at the bottom right corner of the quadrant. The physical rejuvenator can partially restore the polymer network with the fresh SBS polymer it contains, but it provides fewer light components than the pure oil rejuvenator. The pure chemical compound can dramatically recover the polymer network, but it lacks the oil part and cannot provide light components. Therefore, the pure chemical compound is located at the top left corner of the quadrant. The chemical rejuvenators can provide light components and significantly restore the polymer network simultaneously, thus they are positioned at the top right part of the quadrant.

One of the objectives of the present master thesis is to optimize the chemical rejuvenators toward the top left corner to further enhance their abilities on light components composition and polymer network recovery.

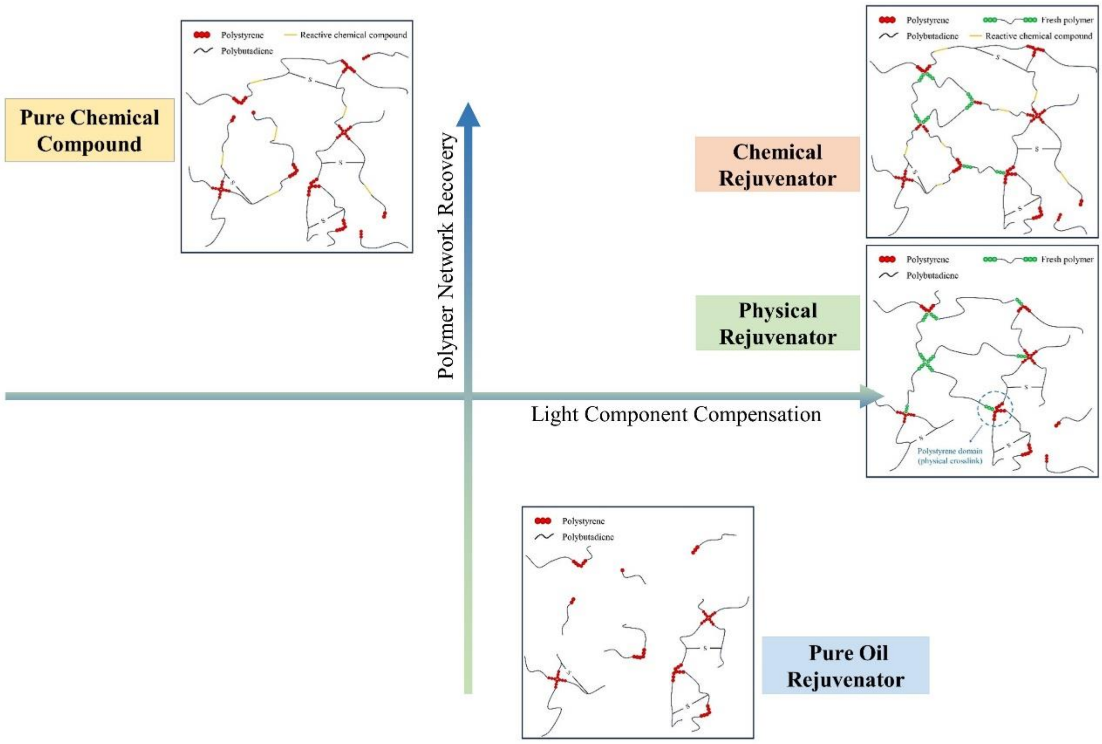

Figure 4-10. Summarized effects and mechanisms of different types of rejuvenators.

Chapter 5. Rejuvenation Mechanism and Optimization of Chemical Rejuvenators

5.1. Rejuvenation Mechanism of Chemical Compound M

As already demonstrated in **Chapter 4**, adding a small amount of chemical compounds can greatly improve the high temperature performance of aged bitumen without significantly reducing its low temperature performance or fatigue life. It has been discovered, however, that this chemical compound M predominantly reacts with polar groups that include hydrogen atoms in asphaltenes, resins, and even aromatics in bitumen [68–70]. Therefore, in order to determine whether or not the degraded polymer network structure was restored, it was necessary to show that this chemical compound M did interact with the fractured SBS polymer.

Figure 5-1 presents the complex modulus and phase angle master curves of base bitumen (base-bit, unmodified Total 70/100) added with chemical compound M and polymer modified bitumen (PMB) added with chemical compound M. Each bitumen has unaged and aged samples before being mixed with this chemical compound to observe the effect of bitumen aging on the chemical reaction of this compound. **Figure 5-1(a, b)** shows the complex modulus and phase angle master curves of unaged base-bit and PMB added with chemical compound M. The complex modulus master curves demonstrate no variation between the original samples and the chemical compound added samples. The phase angle master curves for base-bit samples have not changed much as well. It is clear that for unaged PMB, the addition of chemical compound M will lower the plateau area level and slightly increase the downward trend. It is clear that for unaged PMB, the addition of chemical compound M will lower the plateau area level and slightly increase the downward trend. The findings show that this chemical component M will only have limited interactions with the chemicals in unaged bitumen. The addition of chemical compound M will, to variable degrees, increase the complex modulus of aged bitumen (**Figure 5-1(c)**). When it comes the phase angle, chemical compound M will visibly reduce it for base-bit at low frequencies but drastically reduce it for PMB. As the only difference between aged base-bit and aged PMB is that aged PMB contains degraded SBS polymers, the only explanation for the difference in the reducing magnitude of the phase angle curves after the addition of the compounds between the two is that the compounds react with the degraded SBS polymers.

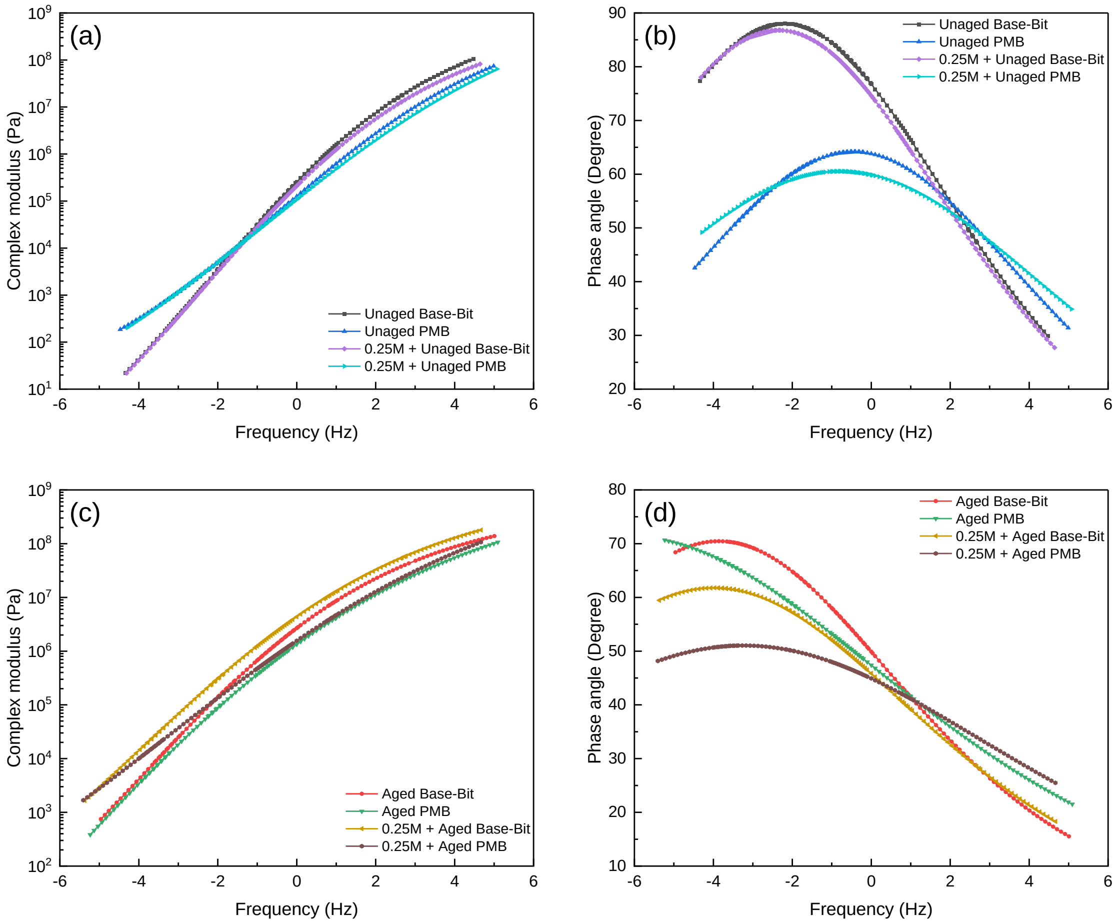

Figure 5-1. Complex modulus and phase angle master curves of (a, b) unaged base bitumen and unaged PMB added with chemical compound M and (c, d) aged base bitumen and aged PMB added with chemical compound M.

5.2. Chemical Rejuvenator Components Optimization

As pre-described, chemical rejuvenators consist of three components: oil, SBS polymer, and chemical compound. Different types of oil, SBS polymer proportions, and chemical compound addition ratios will inevitably have an impact on the rejuvenation effect. Therefore, in this section, the influence of each component on the rejuvenation effect will be investigated.

5.2.1. Oil selection

Figure 5-2 presents the complex modulus and phase angle master curves of rejuvenated bitumen samples with three chemical rejuvenators that are made of three different oils, including Aro oil, Rap oil, and LS oil. Three chemical rejuvenators rejuvenated bitumen have a very closed complex modulus when the chemical compound M addition is X_4%. When the chemical compound ratio was reduced to X_2%, the rejuvenator with LS oil showed the best softening effect, especially at the low frequency range. Rejuvenated bitumen shows nearly identical phase angle master curves for rejuvenators with high chemical compound proportions. Rejuvenated bitumen with Rap oil included rejuvenator had a greater elasticity at the low frequency range for rejuvenators with low chemical compound percentage, followed by rejuvenators with LS oil and Aro oil.

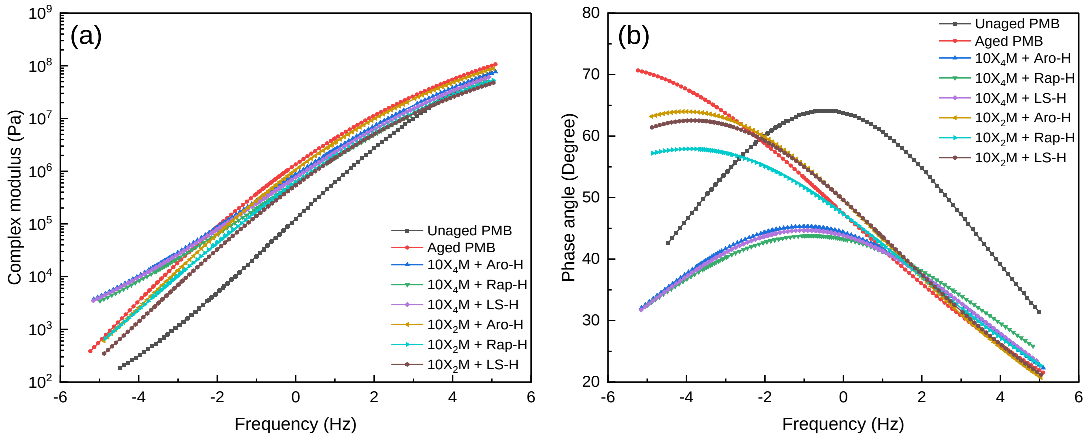

Figure 5-2. Complex modulus and phase angle master curves of rejuvenated bitumen with rejuvenators containing different oil.

For impacts of oil types on high temperature rejuvenation effects, **Figure 5-3** demonstrates the average percent recovery value R at 70 degrees from the MSCR tests. When the chemical compound content is high, the R-value for the three rejuvenated bitumen samples is nearly identical. Bitumen with Rap oil based chemical rejuvenator demonstrated greater recovery rates when the chemical compound level was low, which was also supported by the phase angle master curves findings. It is also consistent with the complex modulus data, where LS oil demonstrated the strongest softening effect, that the rejuvenated bitumen utilizing LS oil contained rejuvenator had the lowest recovery rate.

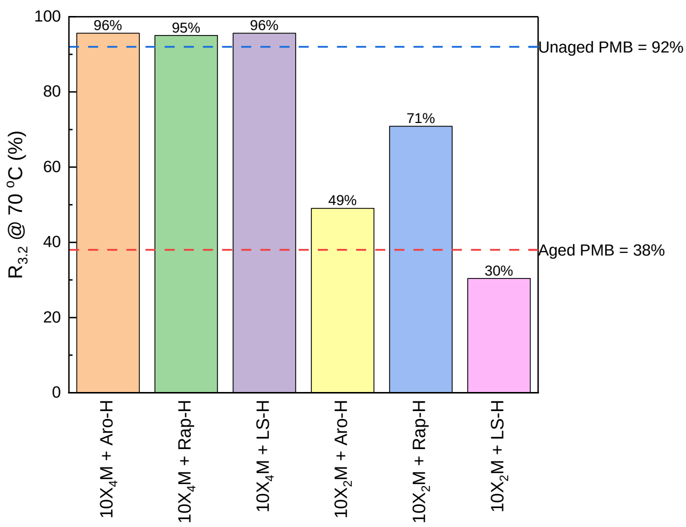

Figure 5-3. 70°C MSCR results of rejuvenated bitumen with rejuvenators containing different oil.

The maximal shear stress of rejuvenated bitumen with rejuvenators containing various oils is shown in **Figure 5-4** for low temperature characteristics. The figure illustrates that rejuvenated bitumen with Rap oil in the rejuvenator has the best reduced maximum stress when the chemical compound level is high. While two rejuvenators containing LS oil and Rap oil have nearly the same effect when the chemical content is lowered.

The results of time for stress reduced 50% and 90% from the maximum are identical to the maximum shear stress results, as presented in **Figure 5-5**. The rejuvenated bitumen using the rejuvenator containing Rap oil had the lowest needed time for stress to reduce when the chemical compound level was high. However, the rejuvenator with LS oil outperformed the rejuvenators containing the other two types of oil when the chemical compound content was low, showing a good low temperature cracking resistance.

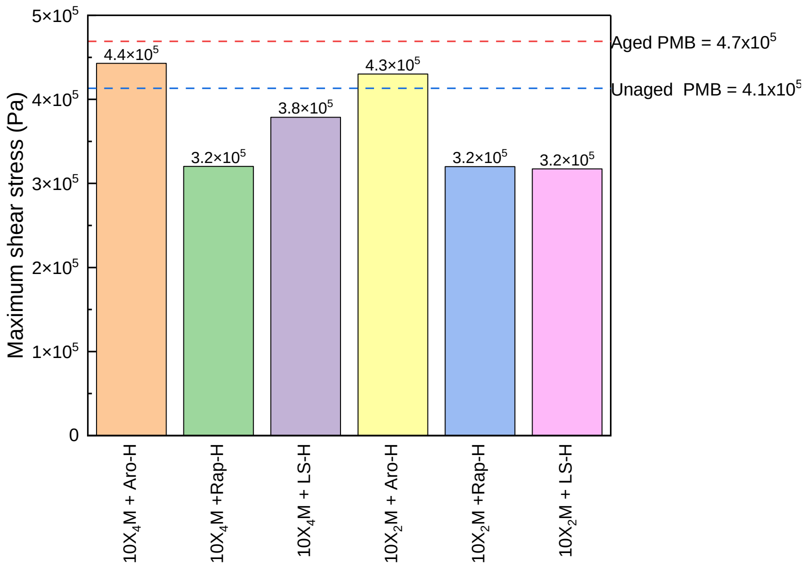

Figure 5-4. Maximum shear stress of rejuvenated bitumen with rejuvenators containing different oil in creep-relaxation tests.

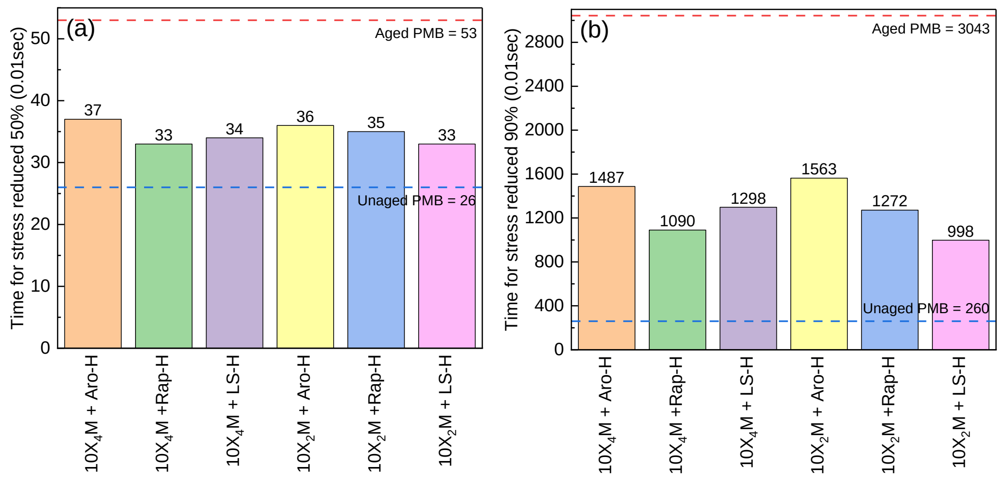

Figure 5-5. (a) time for stress reduced 50% from the maximum and (b) time for stress reduced 90% from the maximum of rejuvenated bitumen samples with rejuvenators containing different oil in creep-relaxation tests.

Figure 5-6 demonstrates the fatigue life of rejuvenated bitumen which using rejuvenators containing different oils under 2.5% and 5% applied strain, respectively. It can be seen that rejuvenated bitumen employing the rejuvenator incorporating LS oil has an unequivocal advantage in fatigue life under both applied strain conditions, regardless of whether the chemical compound concentration is high or low. This conclusion is consistent with the findings in **Section 4.3**, which is rejuvenators consisting of LS oil have the best rejuvenation effects on fatigue life, no matter which type of rejuvenators it is.

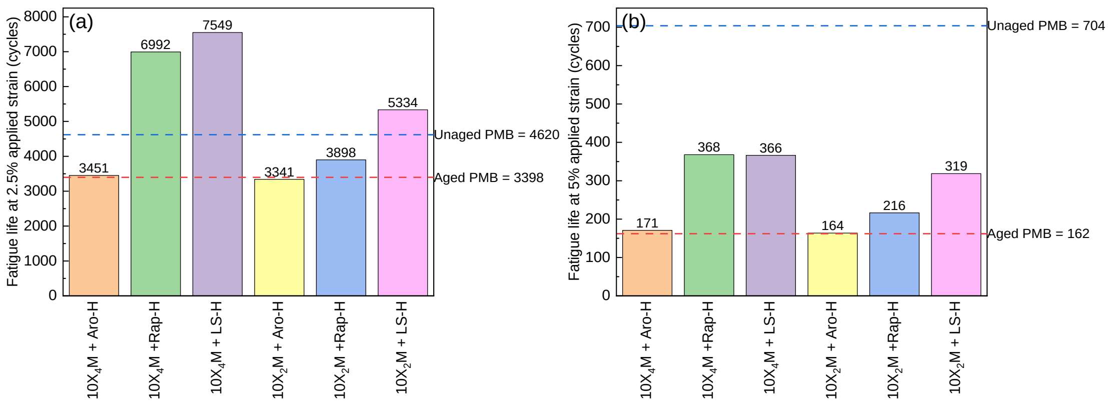

Figure 5-6. (a) fatigue life N_f at 2.5% applied strain and (b) fatigue life N_f at 5% applied strain of rejuvenated bitumen samples with rejuvenators containing different oil.

Following a comprehensive analysis, LS oil was determined to be the oil employed in the upcoming chemical rejuvenator research. The reason for this is that the oil component in the chemical rejuvenator is primarily responsible for replenishing the lost light components in the bitumen phase due to aging and softening the aged bitumen. As can be seen from the findings displayed above, rejuvenated bitumen performed best in terms of low temperature cracking resistance and fatigue life with the usage of rejuvenators containing LS oil. Even though LS oil contained rejuvenators function less well at high temperatures, the problem can be solved by changing the chemical compound proportion, as the chemical compound is mostly responsible for the high temperature performance.

5.2.2. SBS polymer proportions determination

Figure 5-7 demonstrates the complex modulus and phase angle master curves of rejuvenated bitumen samples with three chemical rejuvenators that SBS polymer content varying from low to high. It is obvious that the rejuvenator with low polymer content has the best softening effect, while rejuvenated bitumen with medium and high polymer content rejuvenators have almost the same complex modulus curve. The phase angle results are nearly identical for rejuvenated bitumen with medium and high polymer content rejuvenators, while the rejuvenated bitumen with low polymer content rejuvenator has higher phase angles, predicting potentially better low temperature cracking resistance and fatigue life but not as good high temperature performance as the other two.

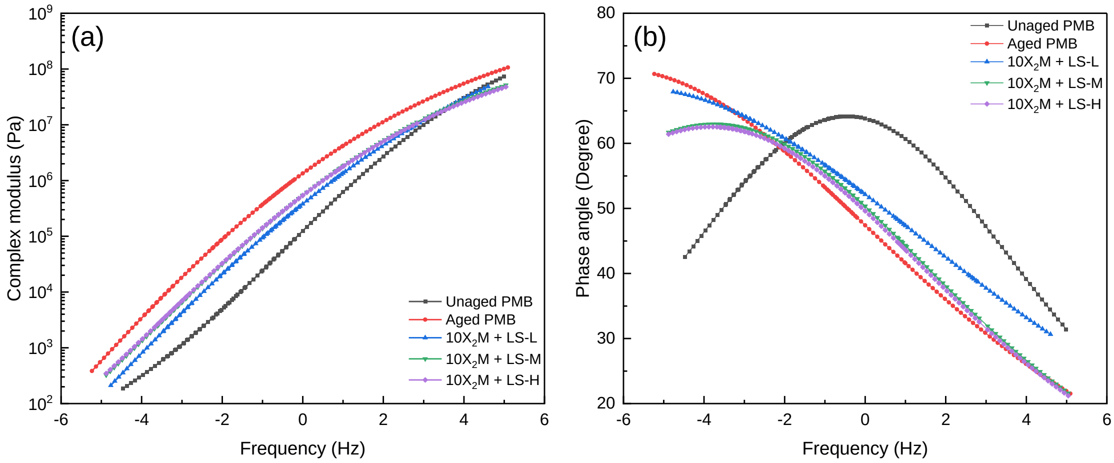

Figure 5-7. Complex modulus and phase angle master curves of rejuvenated bitumen with rejuvenators containing different SBS polymer proportion.

As anticipated by the master curve results, bitumen with medium and high polymer content rejuvenators had a higher average percent recovery value R, and the numbers were about the same for both. However, none of the three recovery rates exceeded the aged bitumen, indicating the necessity to re-adjust the chemical compound proportion regardless of the polymer content of the rejuvenator used.

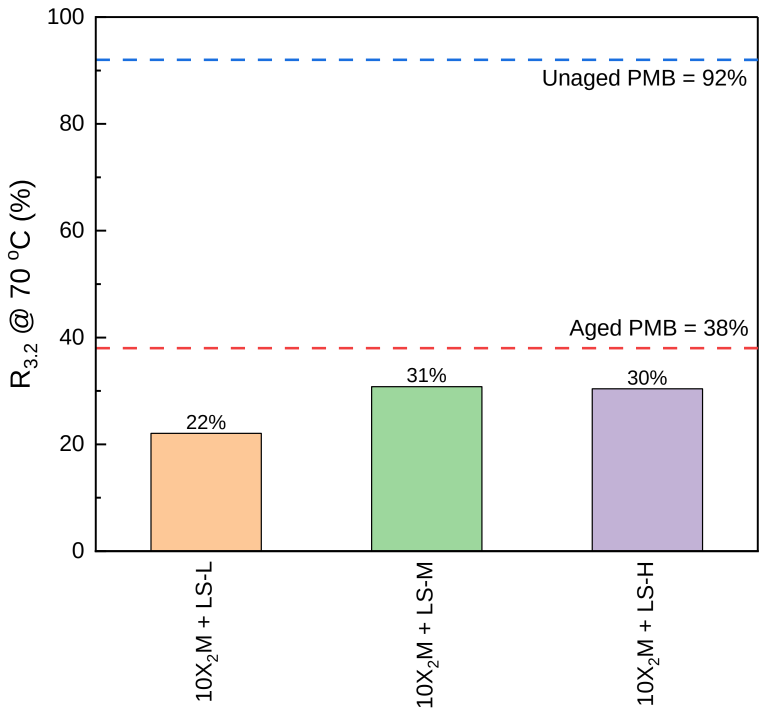

Figure 5-8. 70°C MSCR results of rejuvenated bitumen with rejuvenators containing different SBS polymer proportion.

For low temperature performance, the maximal shear stress of rejuvenated bitumen with rejuvenators containing different SBS polymer content is shown in **Figure 5-9**. It can be seen that the bitumen with a low polymer content rejuvenator has a significantly low maximum shear stress. The same pattern can be seen in the results of stress reductions of 50% and 90% from the maximum, as shown in **Figure 5-10**. The rejuvenated bitumen with the lowest polymer content rejuvenator required the least amount of time to reduce stress.

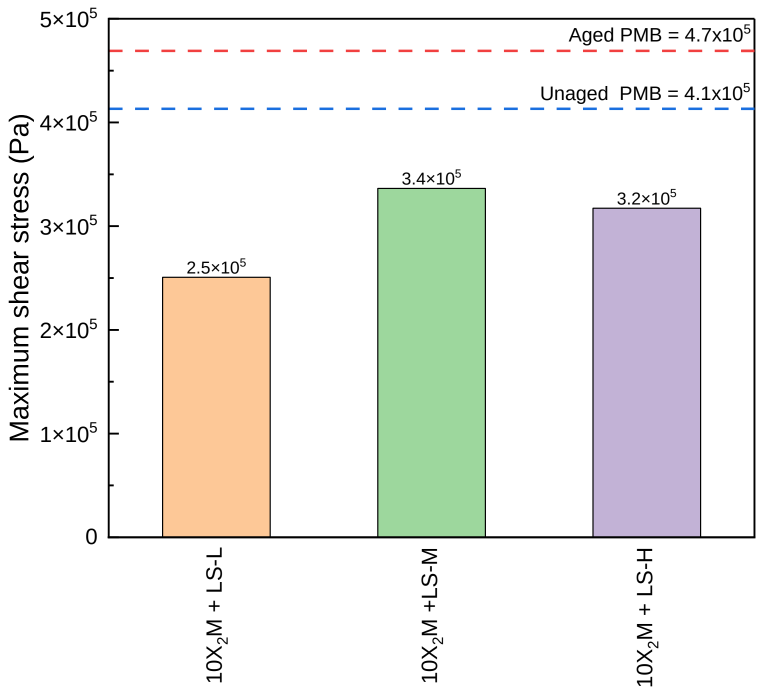

Figure 5-9. Maximum shear stress of rejuvenated bitumen with rejuvenators containing different SBS polymer proportion in creep-relaxation tests.

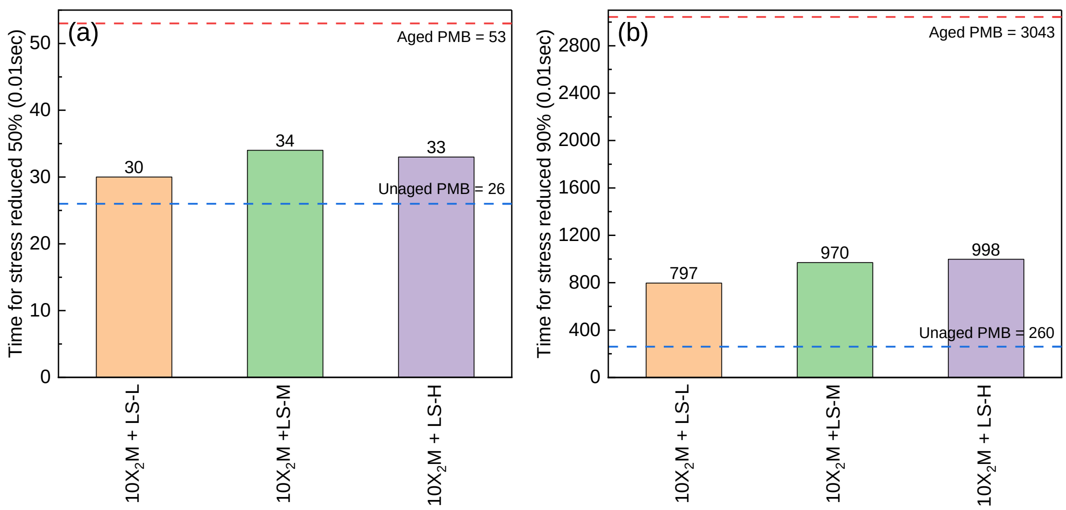

Figure 5-10. (a) time for stress reduced 50% from the maximum and (b) time for stress reduced 90% from the maximum of rejuvenated bitumen samples with rejuvenators containing different SBS polymer proportion in creep-relaxation tests.

Figure 5-11 presents the fatigue life of rejuvenated bitumen which using rejuvenators containing different SBS polymer content and tested under 2.5% and 5% applied strain, respectively. It can be seen that the rejuvenator with low polymer content has a medium rejuvenated bitumen fatigue life at low strains and a comparatively short fatigue life as the strain increases. It should be noted that at low strains rejuvenated bitumen with three different polymer content rejuvenators even had higher fatigue life than unaged bitumen, whereas at high strains the rejuvenated bitumen with low polymer content rejuvenator had nearly twice the fatigue life of aged bitumen, despite performing 12% worse than the other two.

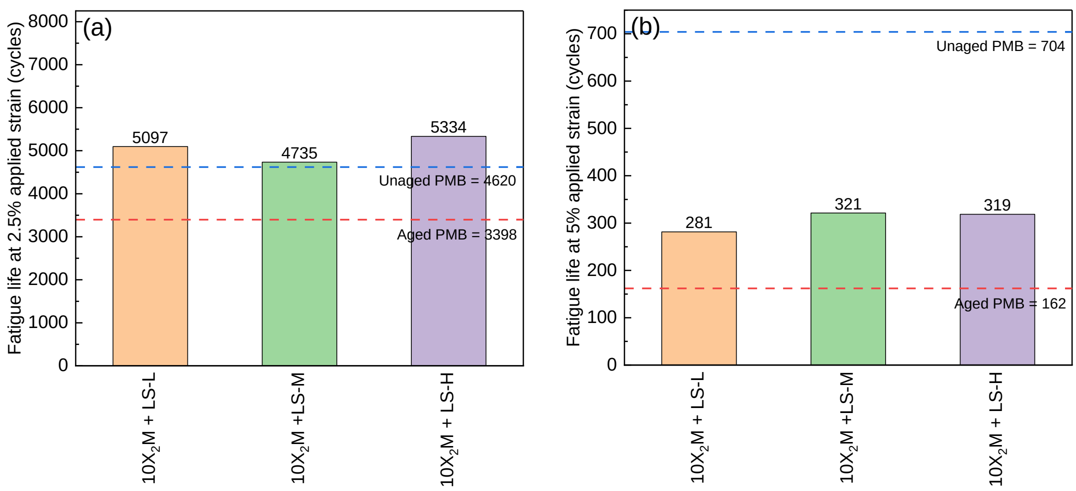

Figure 5-11. (a) fatigue life N_f at 2.5% applied strain and (b) fatigue life N_f at 5% applied strain of rejuvenated bitumen samples with rejuvenators containing different SBS polymer proportion.

Although the three chemical rejuvenators with three different polymer contents performed admirably overall, it was decided to employ a rejuvenator with a low polymer content in future research. High temperature elastic recovery was not well improved by any of the three rejuvenators, however as previously mentioned, this problem can be resolved by altering the chemical compound proportion. On the other hand, the rejuvenator with low polymer content had unquestionably the best performance at low temperatures. For fatigue life results, though the low polymer content rejuvenator performed less well than the other two at large strain levels, it was only 12% behind and outperformed aged bitumen by almost twice as much in terms of fatigue life.

5.2.3. Chemical compound addition ratios determination

The complex modulus and phase angle master curves of rejuvenated bitumen with rejuvenators containing different chemical compound addition ratios are shown in **Figure 5-12**. In the high frequency region, the complex modulus of rejuvenated bitumen with rejuvenators comprising different chemical compound content are similar, but as the frequency decreases, the corresponding variations begin to appear. The complex modulus master curves of rejuvenated bitumen can be roughly divided into three groups as the chemical compound content increases. A low chemical compound content group (X_1% - X_2%) with the lowest modulus, a medium chemical compound content group (X_3% - X_5%) with a medium modulus, and a high chemical compound content group (X_6%) with the highest modulus, which may even be high than that of aged bitumen. Just like the complex modulus master curves, the phase angle master curves likewise fall into three groups and, in general, decrease as the proportion of compounds added increases. If the addition ratio is X_2% or below, the chemical compound seems to be ineffectual, while an addition ratio of X_6% may have a negative impact on the low temperature performance and fatigue life of rejuvenated bitumen.

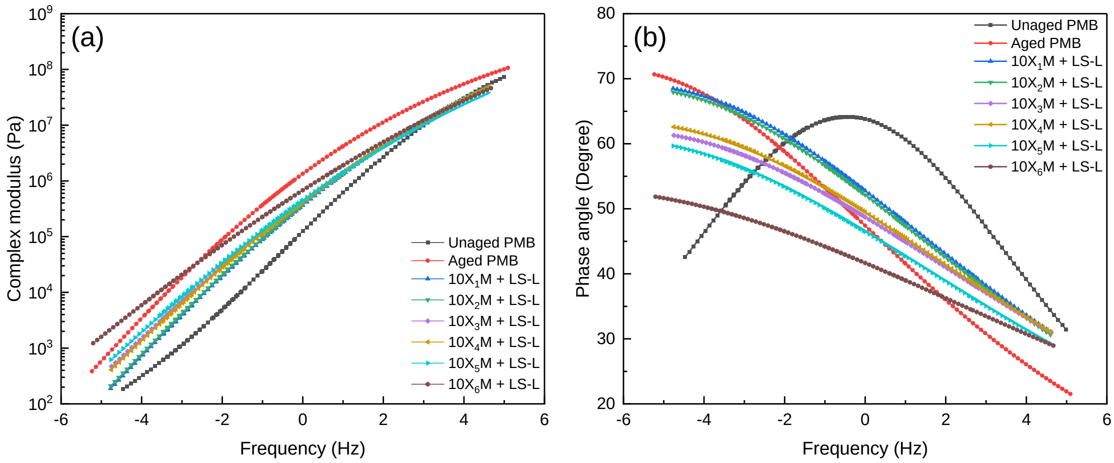

Figure 5-12. Complex modulus and phase angle master curves of rejuvenated bitumen with rejuvenators containing different chemical compound addition ratios.

Figure 5-13 presents the average percent recover value R of rejuvenated bitumen with rejuvenators containing different chemical compound additional ratios. The outcome is clear. The oil component of the rejuvenator exerts a dominant influence when the chemical compound proportion is less than X_3%, softening the aged bitumen excessively and lowering the R-value. The impact of each component balances out at X_3% chemical compound content, preventing the recovery rate from rising or falling too much from that of aged bitumen. After that, the R-value started to progressively rise as the chemical compound content increased, showing that the compound that was added at this point played a dominant role.

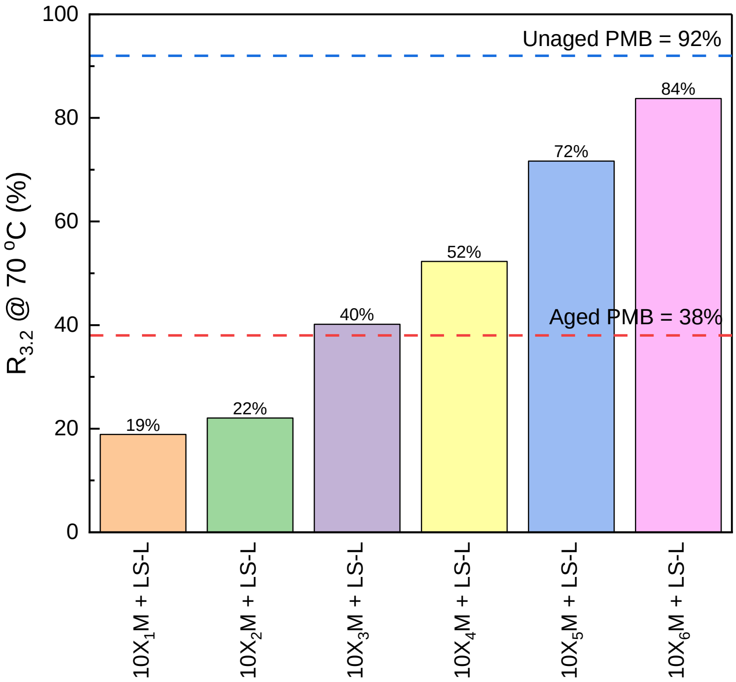

Figure 5-13. 70°C MSCR results of rejuvenated bitumen with rejuvenators containing different chemical compound addition ratios.

Figure 5-14 and **Figure 5-15** demonstrate the low temperature cracking resistance of rejuvenated bitumen with rejuvenators containing different chemical compound addition ratios from the creep-relaxation results. In general, rejuvenated bitumen performs worse at low temperatures as the chemical compound content increases, which is connected to the fact that the chemical compound causes the bitumen to become harder. For chemical component addition ratios less than or equal to X_4%, each rejuvenated bitumen performed substantially identically at low temperatures. However, the time needed for rejuvenated bitumen to reduce 90% stress rose noticeably as the compound content grew to X_5% and above. In comparison to the X_4% chemical compound addition ratio, doubling the chemical compound content lengthens the stress relaxation time by more than 50%, which makes the rejuvenated bitumen more prone to cracking at low temperatures.

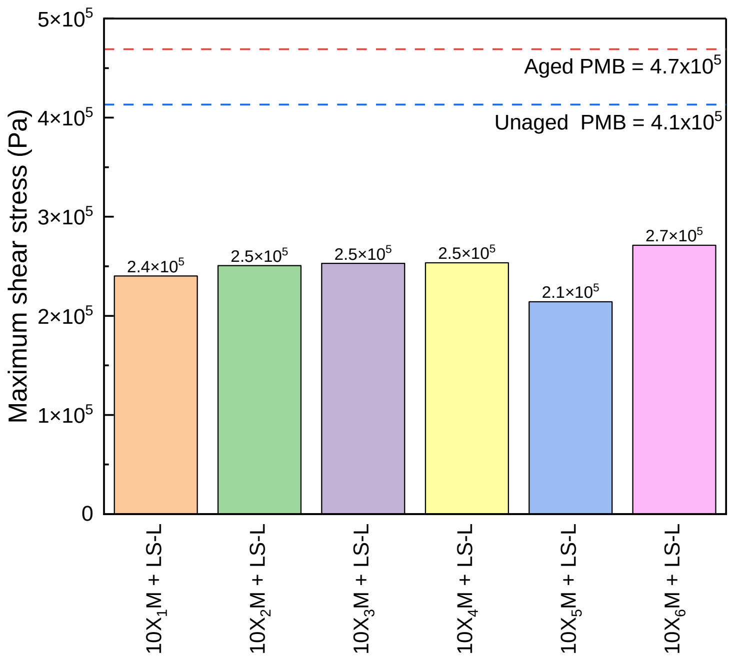

Figure 5-14. Maximum shear stress of rejuvenated bitumen with rejuvenators containing different chemical compound addition ratios in creep-relaxation tests.

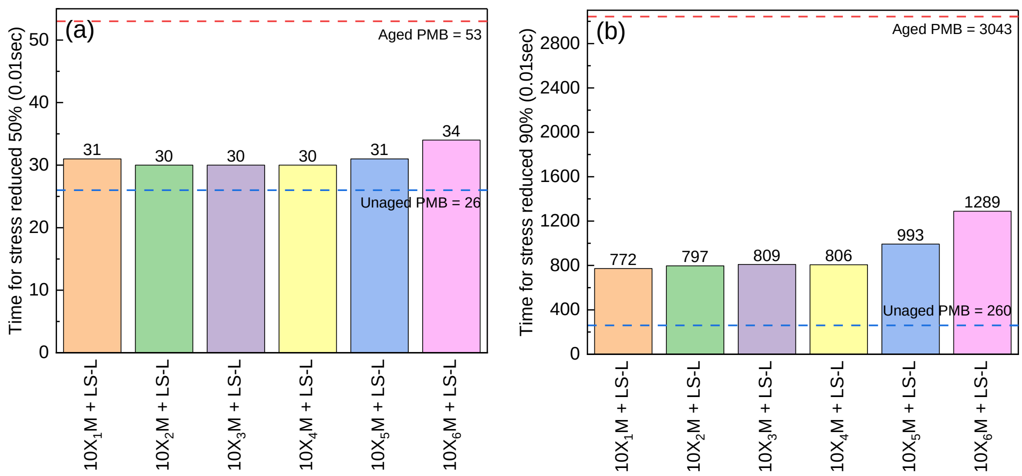

Figure 5-15. (a) time for stress reduced 50% from the maximum and (b) time for stress reduced 90% from the maximum of rejuvenated bitumen samples with rejuvenators containing different chemical compound addition ratios in creep-relaxation tests.

As the addition ratios of the chemical compound in the rejuvenator grow, the fatigue life of rejuvenated bitumen first decreases then increases, and finally decreases once more.

It can be seen that at low strains, all rejuvenator chemical compound variables can provide rejuvenated bitumen with a fatigue life that is longer than that of unaged bitumen. Although the performance of each rejuvenated bitumen is not as good as that of unaged bitumen as the strain increases, there is at least a 60% improvement over aged bitumen.

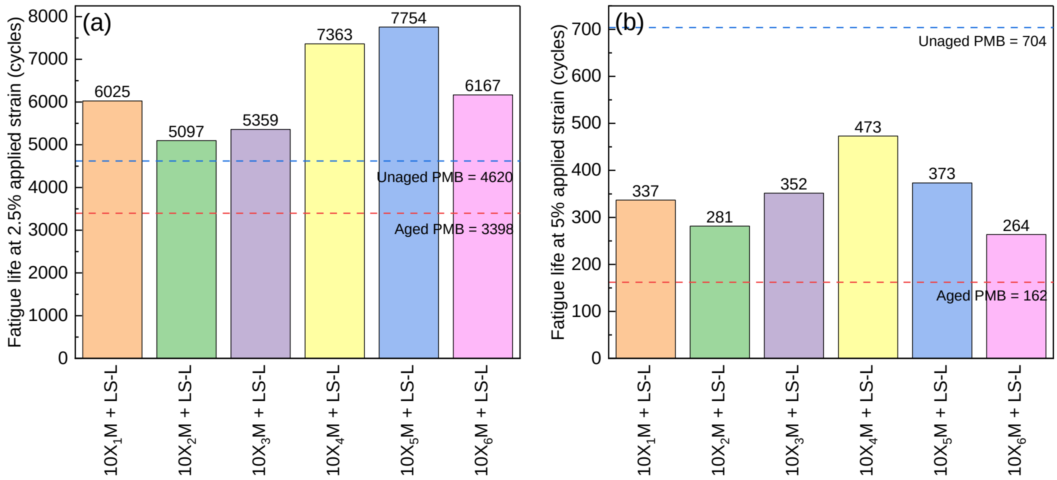

Figure 5-16. (a) fatigue life N_f at 2.5% applied strain and (b) fatigue life N_f at 5% applied strain of rejuvenated bitumen samples with rejuvenators containing different chemical compound addition ratios.

Figure 5-17 presents the fatigue life of rejuvenated bitumen samples with rejuvenators containing different chemical compound addition ratios under applied strains ranging from 0.1% to 50%. As can be seen, bitumen that has been rejuvenated by adding either high (X_5% - X_6%) or low (X_1% - X_2%) content chemical compound at low strains has a high fatigue life. On the other hand, bitumen that has been rejuvenated by rejuvenators that use medium (X_3% - X_4%) content compound has a relatively low fatigue life, but one that is still significantly higher than that of unaged bitumen. Rejuvenators with medium chemical compound contents start to demonstrate the benefit of having a longer fatigue life than rejuvenators with other chemical compound contents at high strains.

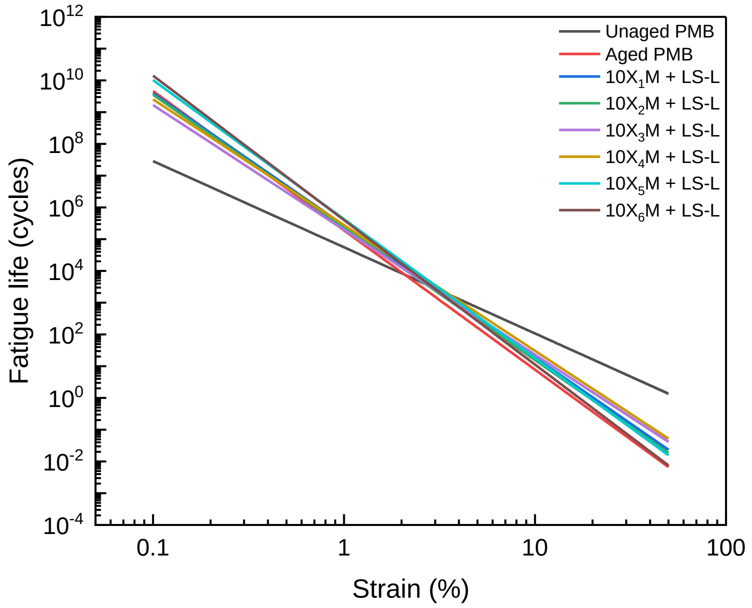

Figure 5-17. Fatigue life at various applied strains of rejuvenated bitumen with rejuvenators containing different chemical compound addition ratios.

With all factors taken into account, a chemical compound addition ratio between X_4% - X_5% in the aged bitumen may be the best option, balancing the performance of rejuvenated bitumen in both high and low temperatures as well as fatigue life. Higher chemical compound content rejuvenated bitumen performs better at high temperature ravelling resistance but performs averagely at low temperatures and has a shorter fatigue life. Rejuvenated bitumen with a chemical compound content below the recommended range does not perform as well as rejuvenated bitumen that has a chemical compound content within the range among high temperatures, low temperatures, and fatigue life.

5.2.4. Components optimization summary

In this section on chemical rejuvenator components optimization, the effects of Aro oil, Rap oil, and LS oil on rejuvenation were first compared. As previously mentioned, oil is primarily utilized in rejuvenators to soften aged bitumen and replenish lost light components. LS oil was chosen as the base oil for the following rejuvenation studies because the rejuvenated bitumen employing it had good low temperature cracking resistance and fatigue life. Though LS oil contained rejuvenators function unfavourably at high temperatures, the problem can be solved by adjusting the percentage of the chemical compound, as the chemical compound is mostly responsible for the high temperature performance. The effect of different rejuvenator polymer contents on rejuvenation has also been studied and it was decided to use a rejuvenator with a low polymer content in future research. Rejuvenators with low polymer content have the best low temperature performance and fatigue life well beyond that of aged bitumen, although it does not perform well at high temperatures, as previously stated, this problem can be improved by adjusting the chemical compound content. The optimal chemical compound addition ratio for balancing high and low temperature performance as well as fatigue life was found to be between X_4% and X_5%. While a chemical compound content that is too high enhances high temperature performance but decreases fatigue life, one that is too low performs badly in every aspect.

Chapter 6. Compatibility and Durability Investigation

A few selected rejuvenated bitumen samples with pure oil rejuvenators, physical rejuvenators, and chemical rejuvenators were aged again with TFOT and PAV to study their aging resistance and durability.

Figure 6-1 presents the complex modulus and phase angle master curves of rejuvenated bitumen and re-aged rejuvenated bitumen with pure oil rejuvenators. As can be observed from the curves, when the aged bitumen is aged again, its complex modulus considerably increases and the phase angle significantly reduces, which is particularly apparent in the low frequency range. In comparison to the other two oils, re-aged rejuvenated bitumen with Aro oil has a higher complex modulus and a lower phase angle, indicating an unfavourable re-aging resistance. In the medium to high frequency range, the phase angle of the re-aged bitumen with Rap oil is slightly higher than that of the re-aged bitumen with LS oil, and as the frequency decreases, the phase angle level of the two re-aged bitumen swapped.

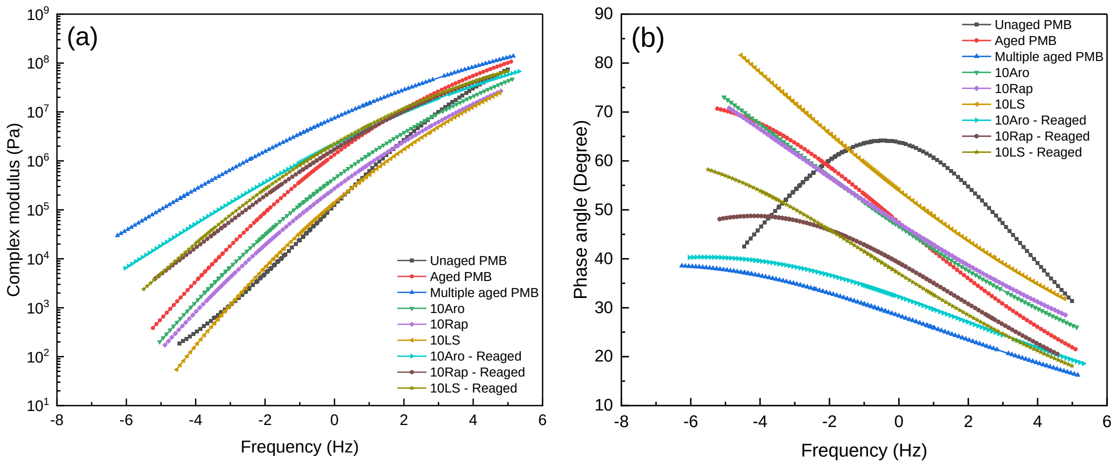

Figure 6-1. Complex modulus and phase angle master curves of rejuvenated bitumen and re-aged rejuvenated bitumen with pure oil rejuvenators.

In contrast to the other three re-aged bitumen using physical rejuvenators, 10LS-L - Reaged, a re-aged bitumen with LS oil and low polymer content, has the lowest complex modulus. In the mid to high frequency range, the bitumen with Rap oil has a relatively low complex modulus for re-aged bitumen with physical rejuvenators that have a high polymer content. Similar to the complex modulus master curves, 10LS-L - Reaged has the highest phase angle level among the re-aged bitumen. However, the one employing Aro oil currently has a larger phase angle for re-aged bitumen using physical rejuvenators that contain a high polymer content.

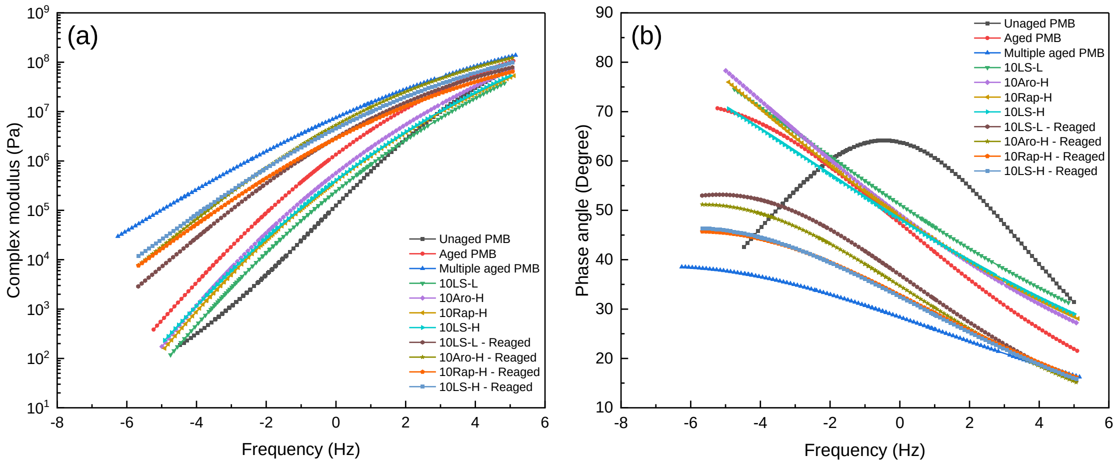

Figure 6-2. Complex modulus and phase angle master curves of rejuvenated bitumen and re-aged rejuvenated bitumen with physical rejuvenators.

As for the chemical rejuvenators, re-aged bitumen with a low polymer content chemical rejuvenator has the lowest complex modulus and the highest phase angle curve, followed by the chemical rejuvenator with high polymer content and Rap oil. Chemical rejuvenator with high polymer content and Aro oil or LS oil has nearly the same highest complex modulus. For phase angle result, the rejuvenator containing Aro oil performs slightly better than with LS oil.

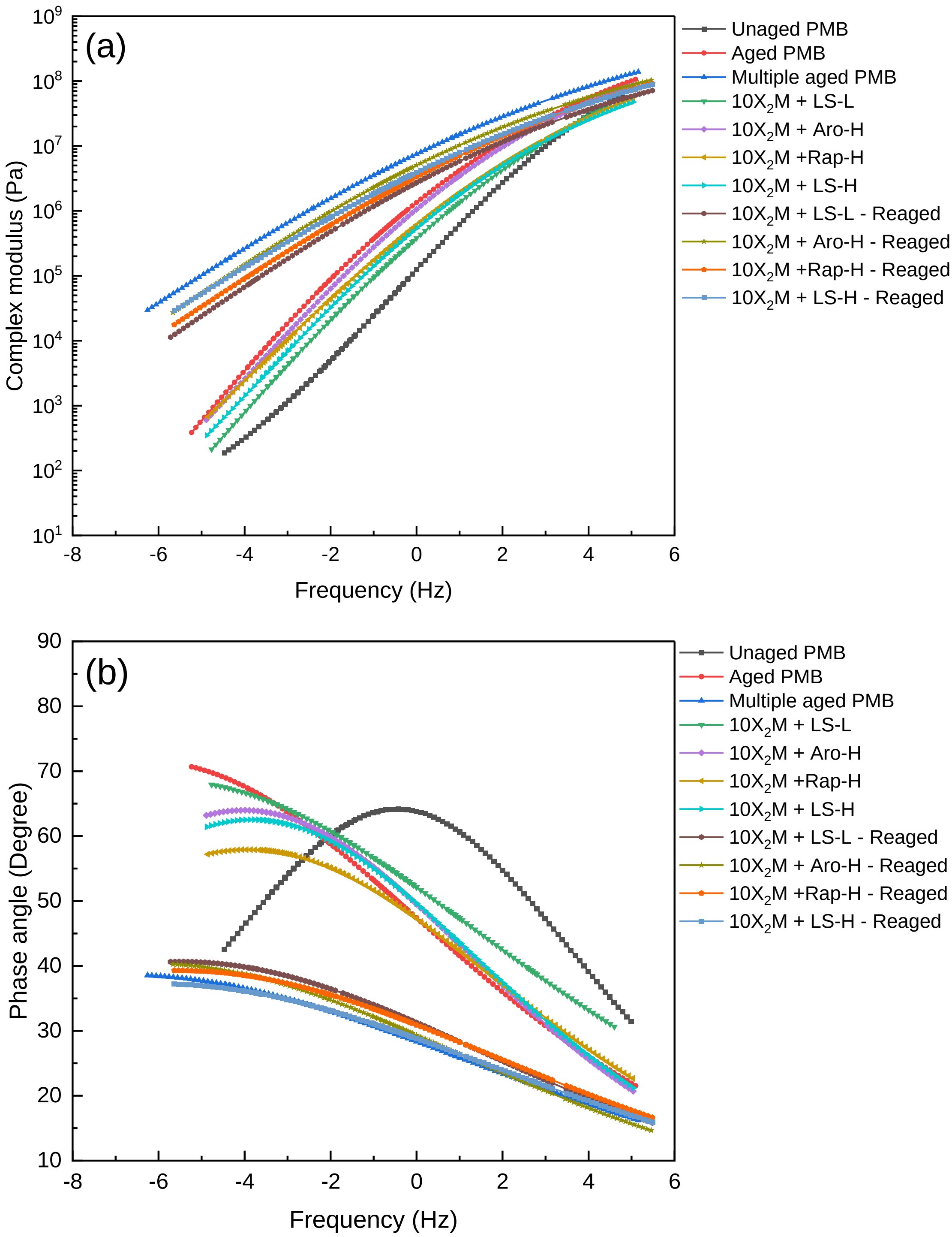

Figure 6-3. Complex modulus and phase angle master curves of rejuvenated bitumen and re-aged rejuvenated bitumen with chemical rejuvenators.

Figure 6-4 demonstrates the average percent recovery value R from the 70°C MSCR tests. It can be seen that the R-value of multiple aged bitumen rises to a level that is nearly equal to unaged bitumen after re-aging. However, the high recovery rate of re-aged bitumen is due to its extreme hardness rather than its elasticity like unaged bitumen, therefore having a higher recovery rate after re-aging is not necessarily an advantage. In addition, the recovery rate of rejuvenated bitumen after re-aging is also increased to different degrees. Re-aged rejuvenated bitumen with chemical rejuvenators has the highest recovery rate, followed by re-aged bitumen with physical rejuvenators, and finally by bitumen with pure oil rejuvenators. Furthermore, no matter what type of rejuvenator is used on rejuvenated bitumen, as long as it contains Rap oil, this bitumen will have the highest recovery rate of any bitumen with the same type of rejuvenator when it is re-aged. Additionally, if the polymer content in the same type of rejuvenator is low, the bitumen will have a slightly lower recovery rate after re-aging.

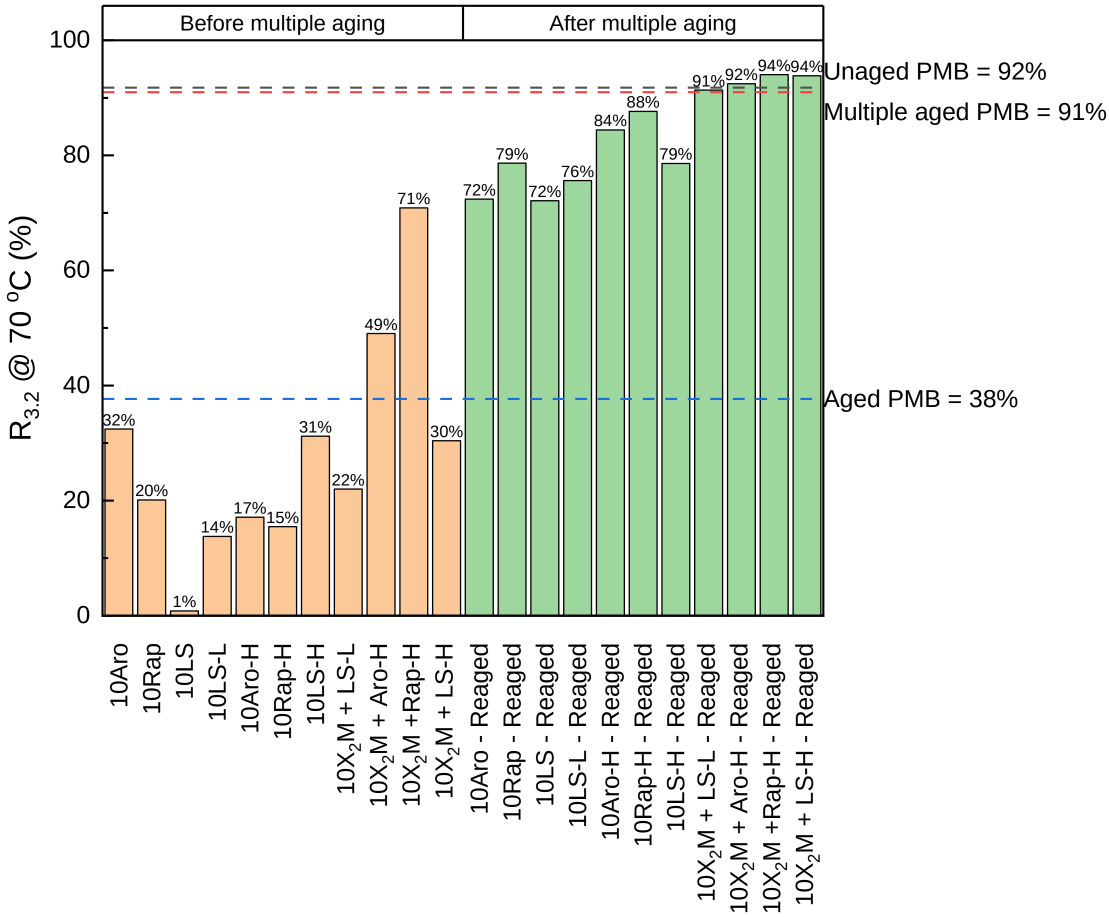

Figure 6-4. 70°C MSCR results of rejuvenated bitumen and re-aged rejuvenated bitumen.

Figure 6-5 and **Figure 6-6** present the maximum shear stress and 50% stress reduction time of rejuvenated bitumen and re-aged rejuvenated bitumen from the creep-relaxation tests. The lack of 90% stress reduction time results was due to the fact that the re-aged bitumen was too hard to allow for a 90% stress reduction within the 100-second time constraint of this creep-relaxation experiment. Surprisingly for maximum shear stress results, rejuvenated bitumen with physical rejuvenators demonstrated the highest maximum shear stresses following re-aging, after which came re-aged bitumen with chemical rejuvenators and bitumen with pure oil rejuvenators. In addition, contrary to the recovery rate results, regardless of the type of rejuvenator, as long as it contained Rap oil, the re-aged rejuvenated bitumen with this rejuvenator had the lowest maximum shear stress and stress reduction time of any rejuvenated bitumen employing this type rejuvenator.

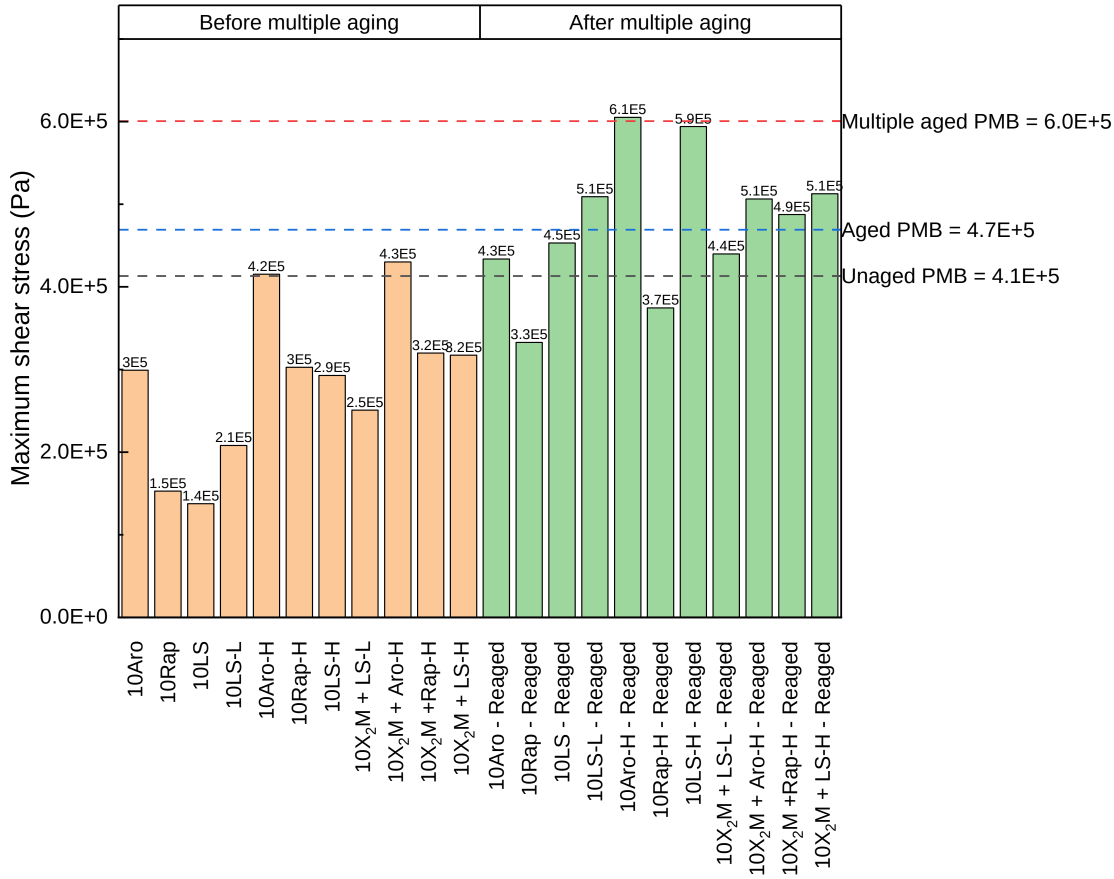

Figure 6-5. Maximum shear stress of rejuvenated bitumen and re-aged rejuvenated bitumen in creep-relaxation tests.

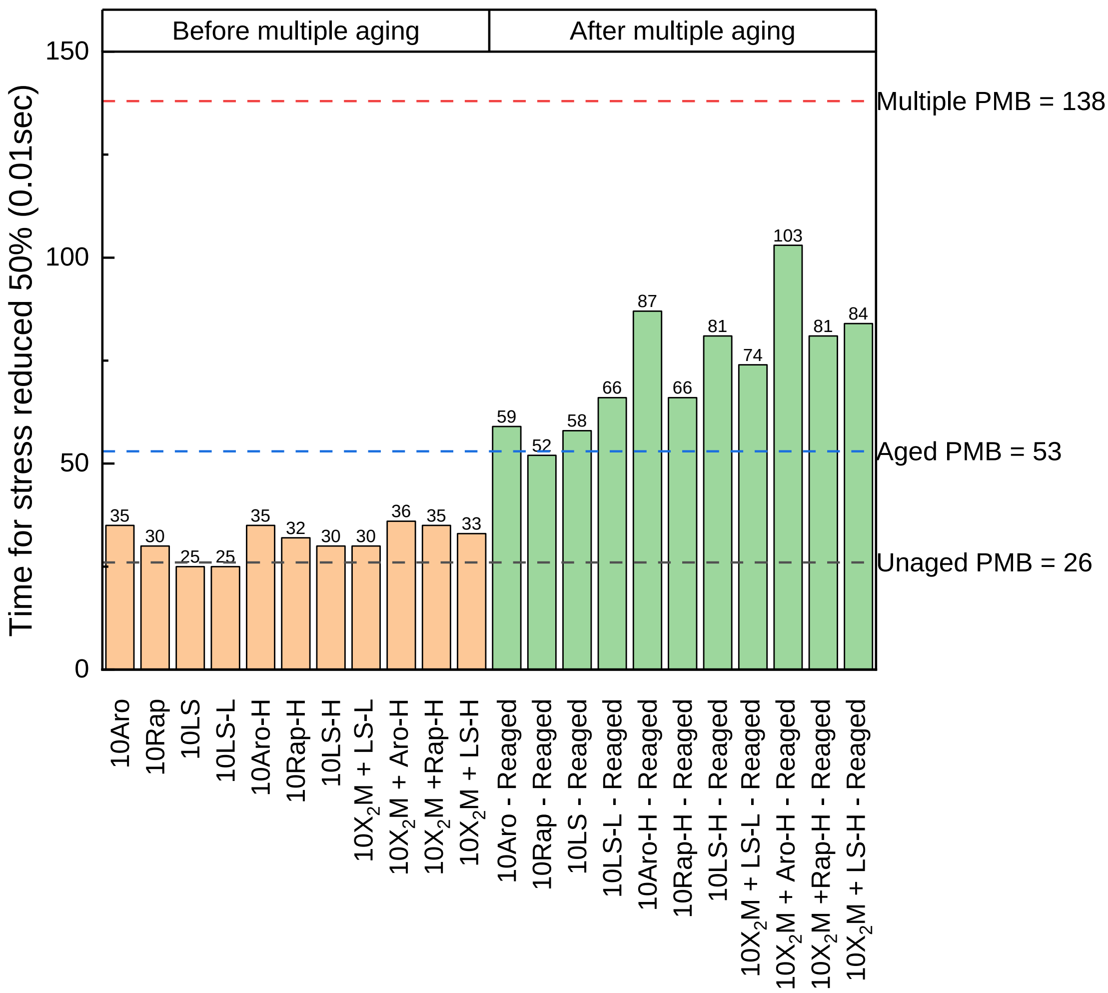

Figure 6-6. Time for stress reduced 50% from the maximum of rejuvenated bitumen and re-aged rejuvenated bitumen in creep-relaxation tests.

The fatigue life of re-aged rejuvenated bitumen compared with rejuvenated bitumen under 2.5% and 5% applied strain is shown in **Figure 6-7** and **Figure 6-8**. As can be seen from the higher fatigue life of multiple aged bitumen, the increase in hardness associated with aging may allow re-aged bitumen to have a higher fatigue life, especially at low strains. In addition, re-aged bitumen with chemical rejuvenators has the highest fatigue life under both strain conditions. Furthermore, rejuvenated bitumen with the rejuvenator including Rap oil continues to function effectively, particularly the re-aged rejuvenated bitumen with pure Rap oil, which has the second-highest fatigue life in both strain situations after chemical rejuvenators.

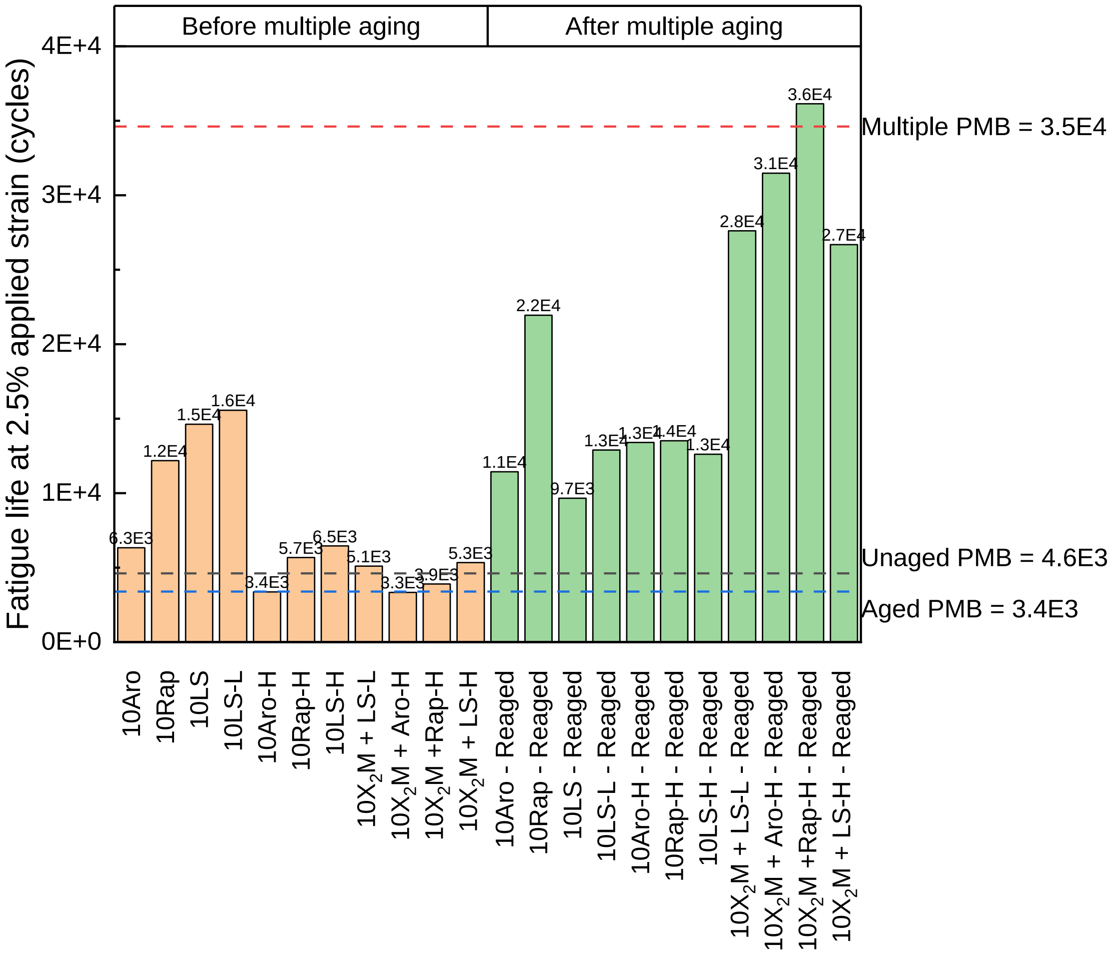

Figure 6-7. Fatigue life N_f at 2.5% applied strain of rejuvenated bitumen and re-aged rejuvenated bitumen.

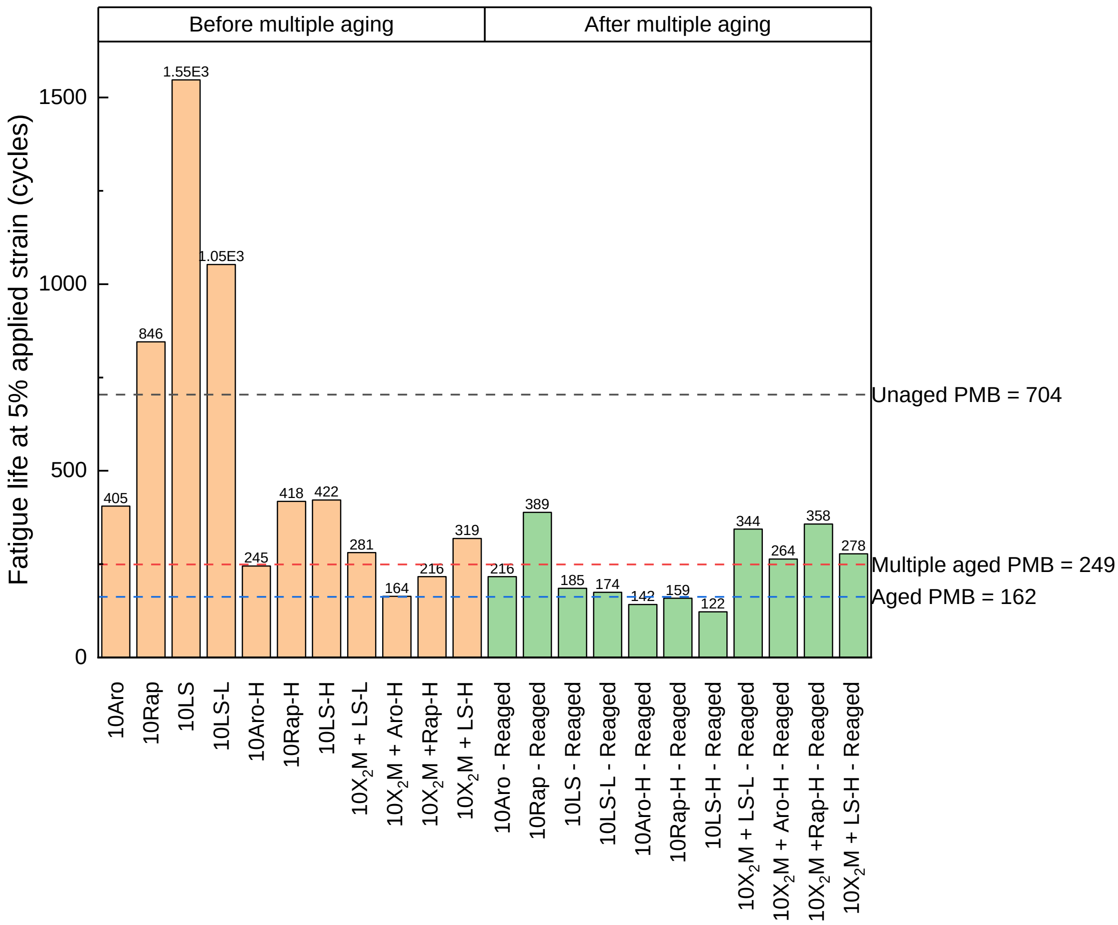

Figure 6-8. Fatigue life N_f at 5% applied strain of rejuvenated bitumen and re-aged rejuvenated bitumen.

Overall, the increased hardness associated with multiple ageing may account for the outstanding performance of re-aged bitumen in some aspects, such as recovery rates in high temperatures. However, it is also obvious that there is a clear difference between re-aged rejuvenated bitumen and multiple aged bitumen, particularly at low temperatures and fatigue life. The better low temperature performance and fatigue life of the re-aged rejuvenated bitumen suggest that the rejuvenators in the rejuvenated bitumen provide an effective anti-ageing effect. In particular, the chemical rejuvenator with low polymer content has excellent high temperature and fatigue life performance as well as not bad low temperature performance.

Chapter 7. Rejuvenator Addition Ratio Determination

The previous research has been based on a 10% rejuvenator addition ratio. In this section, the impacts of increasing the percentage of rejuvenator addition on rejuvenation effects will be investigated. Four rejuvenators will be added to aged bitumen at a 20% ratio by weight and the rejuvenation effects will be compared to the three rejuvenators that performed best in **Section 5.2.3** which were added in a 10% ratio by weight.

7.1. Bitumen Binder Rheological Properties Results

Figure 7-1 presents the complex modulus and phase angle master curves of rejuvenated bitumen with four different rejuvenators added in a 20% ratio by weight, and compares the curves of three rejuvenated bitumen that performed best in **Section 5.2.3** which rejuvenators were added in a 10% ratio by weight. In the high frequency region, four rejuvenated bitumen with a 20% rejuvenator addition ratio had a lower modulus than rejuvenated bitumen with a 10% rejuvenator addition ratio, even lower than that of unaged bitumen. The two rejuvenated bitumen with lower chemical compound content and 20% rejuvenator addition ratio have the lowest modulus over all frequencies. In addition, even the rejuvenated bitumen with a higher chemical compound content (X_6% - X_7%) does not have a higher complex modulus after increasing the rejuvenator addition ratio, which is also lower than the complex modulus of the rejuvenated bitumen with the highest chemical compound content (X_6%) in the 10% rejuvenator addition ratio. For the phase angle master curves of rejuvenated bitumen with 20% rejuvenator additive, rejuvenated bitumen with a low chemical compound content (X_2% - X_4%) has a higher curve and rejuvenated bitumen with a high chemical compound content (X_7%) has the lowest curve.

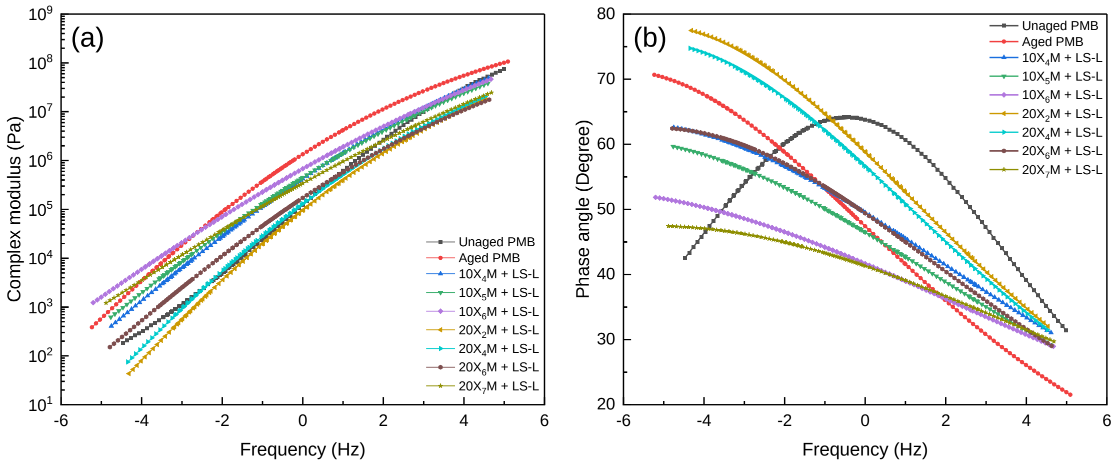

Figure 7-1. Complex modulus and phase angle master curves of rejuvenated bitumen with rejuvenators added in 20% and compared with three best rejuvenators in previous section which added in 10%.

For the average percent recovery value R in high temperatures, as demonstrated in **Figure 7-2**, the R-value increases as the chemical compound content grows. However, when the chemical compound content is too low, the recovery rate of rejuvenated bitumen is approximated to 0. Even at X_6% compound content, the R-value is still less than aged bitumen by more than a third. The recovery rate of rejuvenated bitumen, however, soars to the same level as unaged bitumen as the chemical compound content increases to X_7%, greatly outpacing that of rejuvenated bitumen with 10% rejuvenator content.

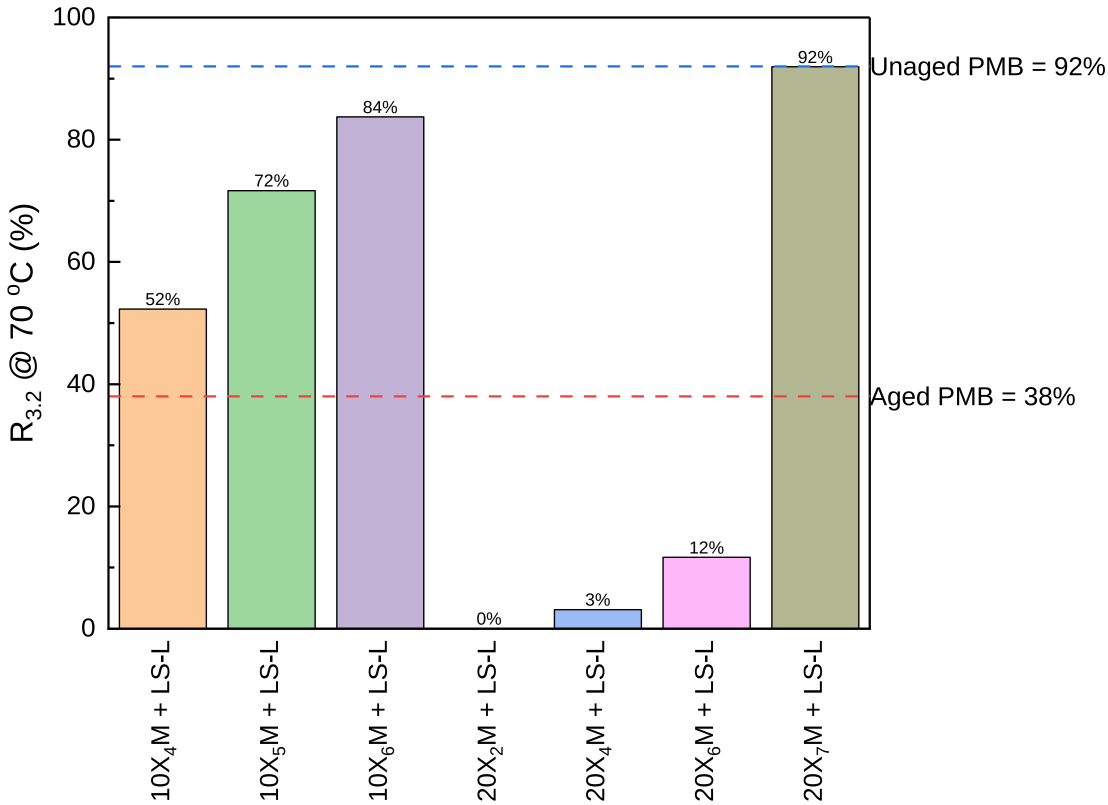

Figure 7-2. 70°C MSCR results of rejuvenated bitumen with rejuvenators added in 20% and compared with three best rejuvenators in previous section which added in 10%.

Figure 7-3 and **Figure 7-4** present the low temperature cracking resistance of rejuvenated bitumen with four different chemical rejuvenators added in 20% from the creep-relaxation results. It can be seen that as the chemical compound content in the rejuvenator increases, so do the maximum shear stress and the time required for stress reduction. It should be noted that for the maximum shear stress, either compound content of the rejuvenator can drastically reduce the stress of aged bitumen, even to a level much lower than that of unaged bitumen. For 50% stress reduction time, even the least effective rejuvenated bitumen with 20% rejuvenator content performs nearly as well as unaged bitumen. While for 90% stress reduction time, rejuvenated bitumen with the highest chemical compound content also has a significantly reduced time compared to aged bitumen, and is also lower than the best performed rejuvenated bitumen with 10% rejuvenator content.

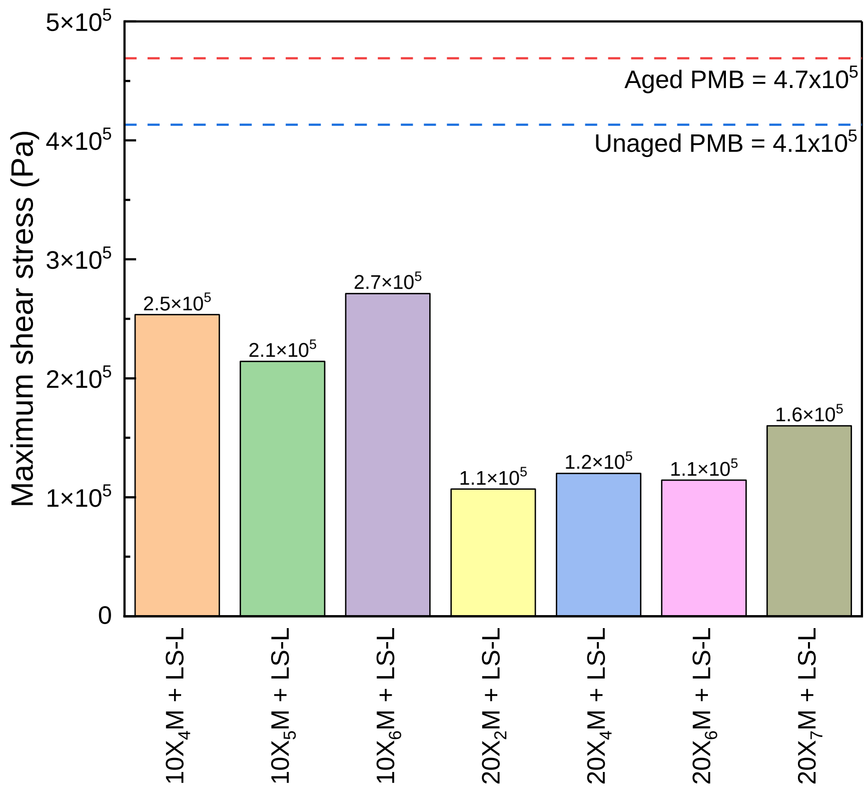

Figure 7-3. Maximum shear stress of rejuvenated bitumen with rejuvenators added in 20% and compared with three best rejuvenators in previous section which added in 10% in creep-relaxation tests.

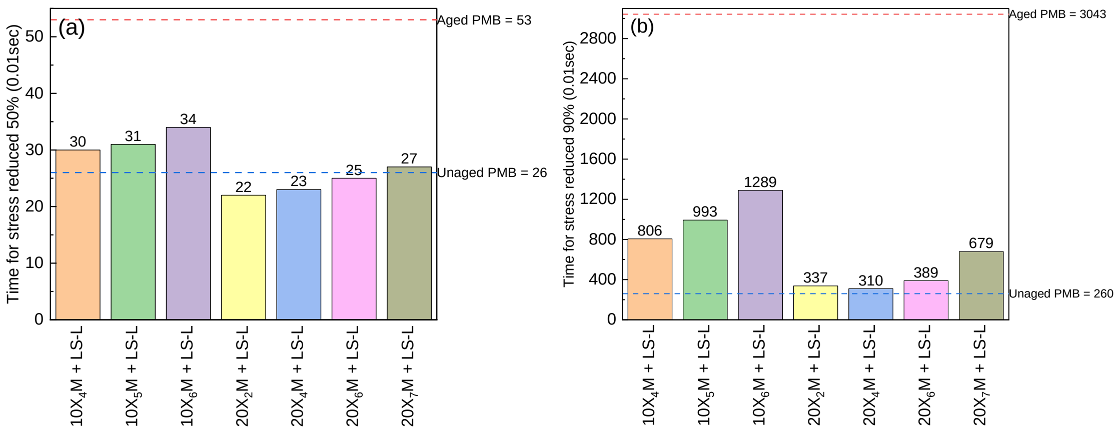

Figure 7-4. (a) time for stress reduced 50% from the maximum and (b) time for stress reduced 90% from the maximum of rejuvenated bitumen samples with rejuvenators added in 20% and compared with three best rejuvenators in previous section which added in 10% in creep-relaxation tests.

Figure 7-5 shows the fatigue life of rejuvenated bitumen samples under 2.5% and 5% applied strain. The results demonstrate that rejuvenated bitumen with a 20% rejuvenator content has a substantially better fatigue life than rejuvenated bitumen with a 10% rejuvenator content, and even outperforms unaged bitumen under all applied strain circumstances.

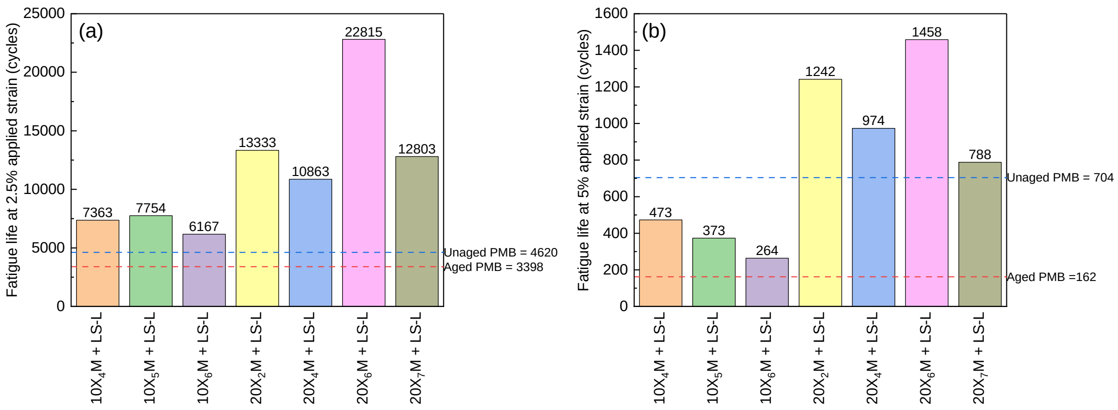

Figure 7-5. (a) fatigue life N_f at 2.5% applied strain and (b) fatigue life N_f at 5% applied strain of rejuvenated bitumen samples with rejuvenators added in 20% and compared with three best rejuvenators in previous section which added in 10%.

Taking into account all the data from this section, using a 20% rejuvenator addition ratio is unquestionably preferable to the use of a 10% addition ratio. For rejuvenated bitumen with 20 X_7M + LS-L, the high temperature elasticity, low temperature cracking resistance, and fatigue life are at the same level or even better than unaged bitumen.

7.2. Mastic Validation

Figure 7-6 presents the complex modulus and phase angle master curves of rejuvenated mastic with different types of rejuvenators. It can be seen that using a pure oil rejuvenator or a physical rejuvenator results in nearly identical complex modulus and phase angle curves. Both reduce the complex modulus of aged mastic and increase elasticity in the low frequencies as well as viscosity in the mid to high frequencies. In contrast, the use of a 10% proportion of chemical rejuvenator will dramatically increase the complex modulus to a level that exceeds the aged mastic, but it will also significantly restore the phase angle plateau region and downward trend. Continuing to increase the proportion of chemical rejuvenator to 20% will substantially reduce the complex modulus and further lower the phase angle.

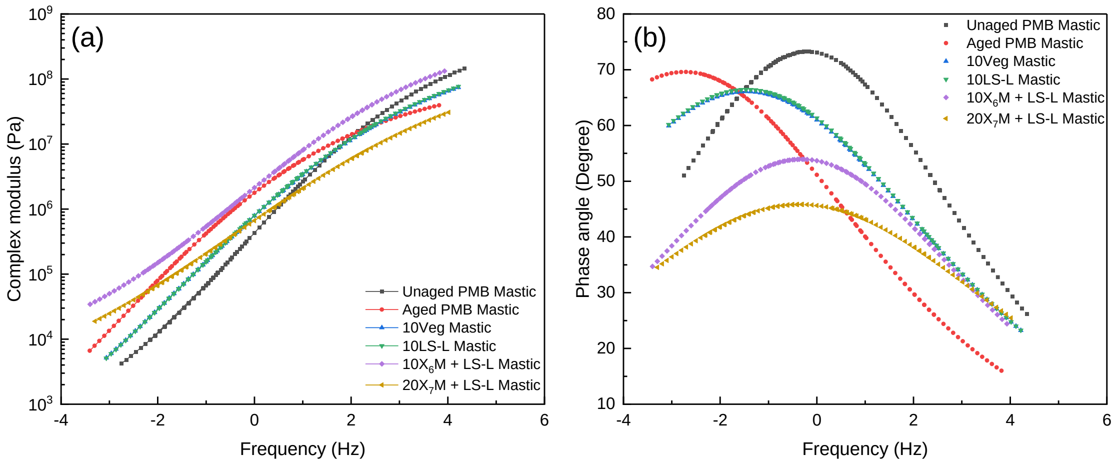

Figure 7-6. Complex modulus and phase angle master curves of rejuvenated mastic with rejuvenators.

Unaged mastic has a significantly lower average percent recovery value R when compared to unaged bitumen binder. This value even became 0 as it aged. In comparison to chemical rejuvenators, the pure oil rejuvenator and the physical rejuvenator are not even able to increase the recovery rate. Instead, a chemical rejuvenator with a 10% addition ratio can readily raise the R-value to about 90%, which is six times higher than unaged mastic. This value can be further enhanced to 95%, which is even higher than that of the unaged bitumen binder, with a 20% chemical rejuvenator.

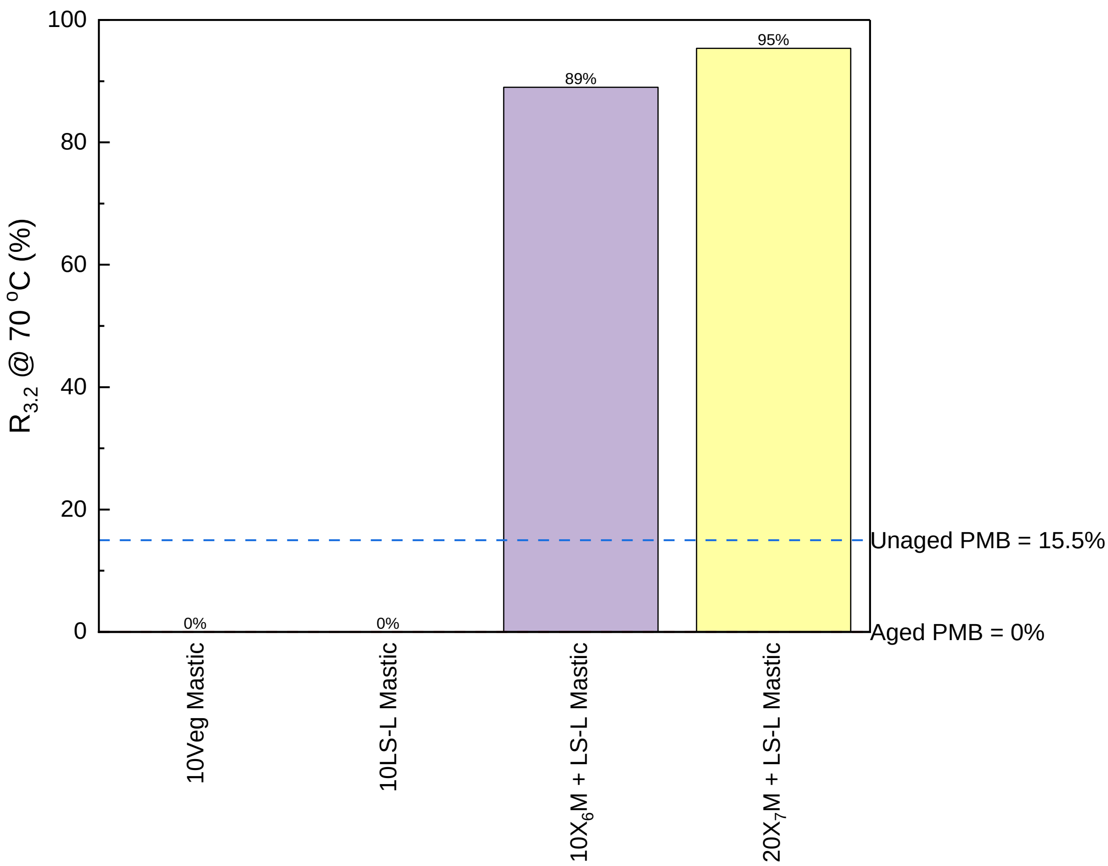

Figure 7-7. 70°C MSCR results of rejuvenated mastic with rejuvenators.

For low temperature performance from the creep-relaxation tests, the use of any rejuvenator will significantly reduce the maximum shear stress, but the stress will slightly increase with the use of a physical rejuvenator and a 10% chemical rejuvenator compared to the use of a pure oil rejuvenator. Moreover, the usage of a 20% chemical rejuvenator results in the lowest maximum shear stress among the others.

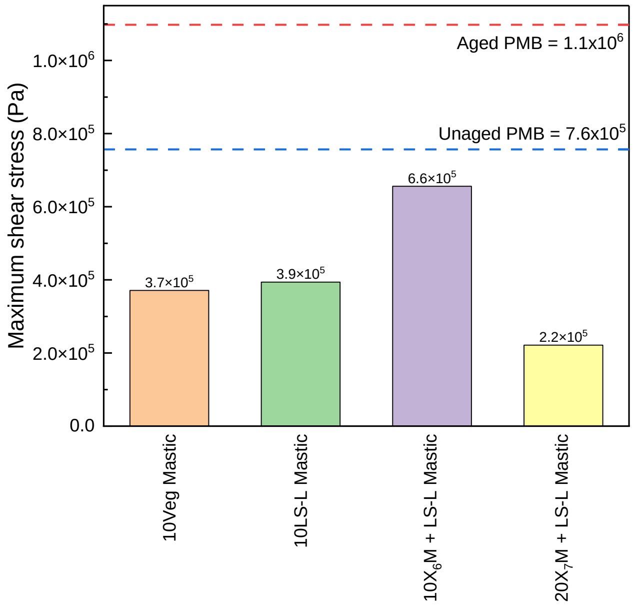

Figure 7-8. Maximum shear stress of rejuvenated mastic with rejuvenators in creep-relaxation tests.

Pure oil rejuvenator, physical rejuvenator, and chemical rejuvenator all produce identical time for stress reduced 50% from the maximum. Still, if the proportion of chemical rejuvenator is further increased, this time will be reduced even more. The use of pure oil rejuvenator, physical rejuvenator, and 20% chemical rejuvenator has a similar effect on the 90% stress reduction time, whereas the use of 10% chemical rejuvenator has the poorest result.

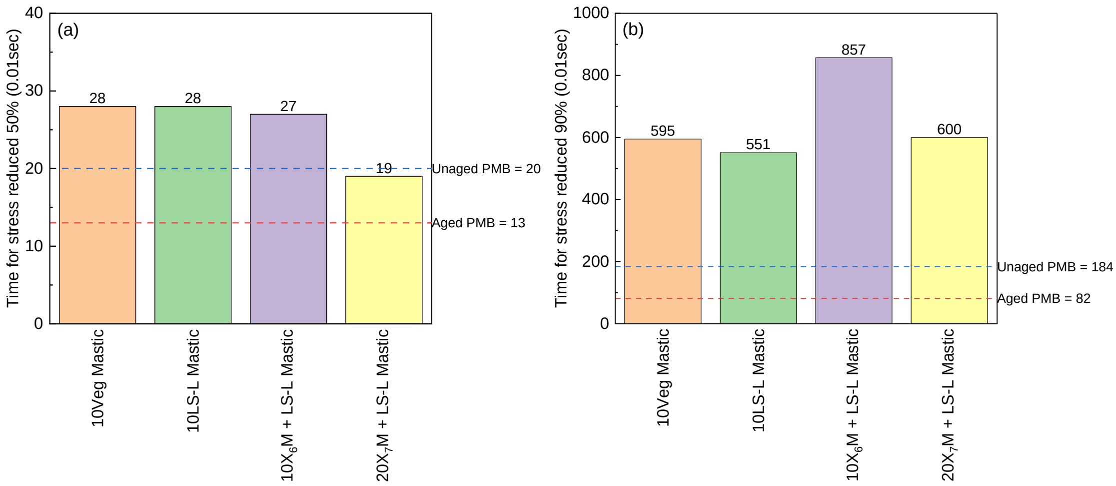

Figure 7-9. (a) time for stress reduced 50% from the maximum and (b) time for stress reduced 90% from the maximum of rejuvenated mastic with rejuvenators in creep-relaxation tests.

In general, pure oil and physical rejuvenators are efficient in increasing viscosity but only mediocre at recovering elasticity. The chemical rejuvenators, on the other hand, significantly improved the elasticity while maintained the viscosity increase and restored the obvious plateau region and downward trend of the aged mastic. As a consequence, only the chemical rejuvenators demonstrated excellent high temperature performance that was dramatically superior to that of unaged mastic, whereas the pure oil and physical rejuvenators did not. The 10% chemical rejuvenator was only moderately effective for low temperature performance, but good results could be obtained by increasing the addition ratio to 20%.

Chapter 8. 50% PMB RAP Recycling

In addition to entirely utilizing rejuvenators to restore the performance of aged bitumen, it can also be improved by introducing fresh bitumen (unaged bitumen) at the same time as the rejuvenator. In this section, the rejuvenated bitumen samples contain 50% aged bitumen and a corresponding percentage of rejuvenator, while the remaining portion will be filled with unaged bitumen.

8.1. Bitumen Binder Rheological Properties Results

Figure 8-1 presents the complex modulus and phase angle master curves of rejuvenated bitumen with rejuvenators and unaged bitumen. As can be observed, employing unaged bitumen and a rejuvenator together can reduce the complex modulus of aged bitumen more effectively. When compared to using a pure oil rejuvenator, the use of a physical rejuvenator slightly increases the complex modulus, while the use of a chemical rejuvenator increases it much more. However, the complex modulus falls and is even lower than the pure oil rejuvenator in the high frequency zone if a chemical rejuvenator is utilized at 20% in relation to the aged bitumen. For phase angle, the additional use of rejuvenators increases the viscosity of rejuvenated bitumen in the high frequency region and increase the elasticity in the low frequency region. The phase angle level decreases with the use of pure oil rejuvenator, physical rejuvenator, 10% chemical rejuvenator, and 20% chemical rejuvenator in that order.

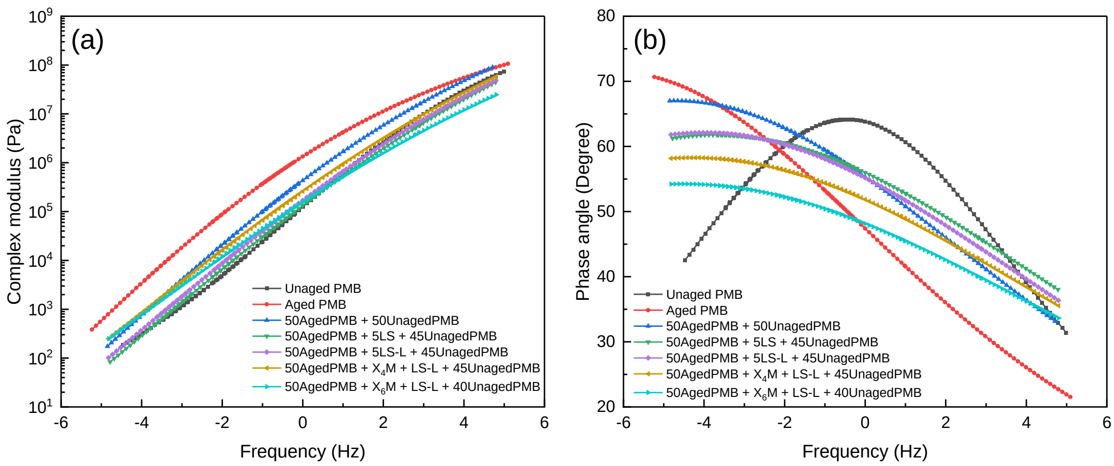

Figure 8-1. Complex modulus and phase angle master curves of rejuvenated bitumen with rejuvenators and unaged bitumen.

For high temperature performance, the additional use of pure oil or physical rejuvenators besides unaged bitumen diminishes the average percent recovery value R, which is consistent with the results in **Section 4.2**. Chemical rejuvenators can increase the R-value compared to pure oil and physical rejuvenators, but if applied at a relative addition ratio of 20% to aged bitumen, it can give rejuvenated bitumen the highest recovery rate of these rejuvenators.

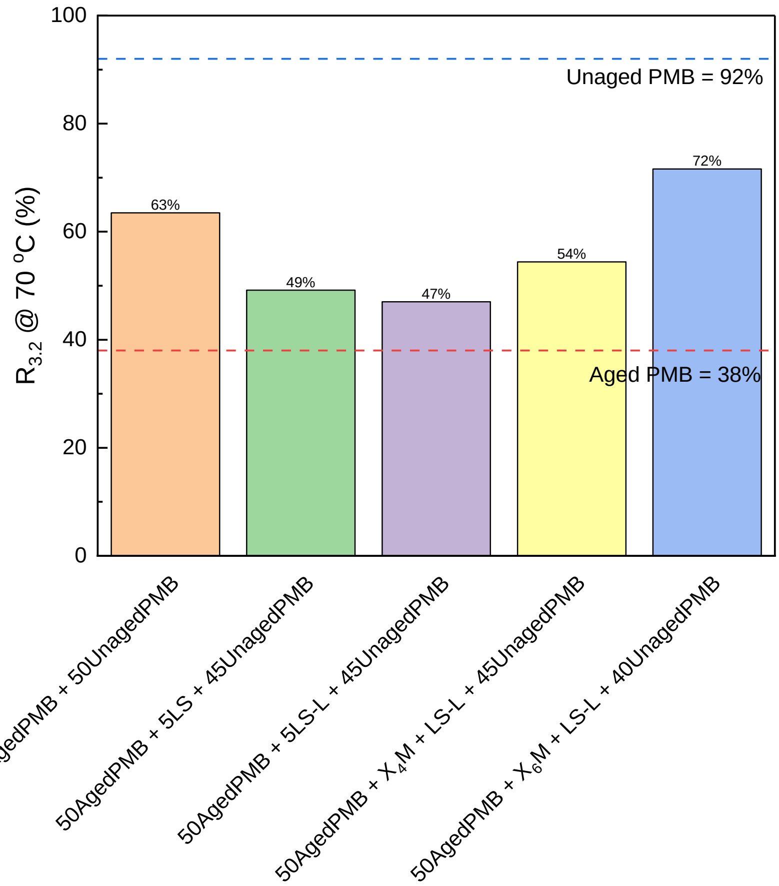

Figure 8-2. 70°C MSCR results of rejuvenated bitumen with rejuvenators and unaged bitumen.

From the low temperature properties demonstrated in **Figure 8-3** and **Figure 8-4**, it can be seen that complete rejuvenation with unaged bitumen results in rejuvenated bitumen having relatively high maximum shear stress and stress reduction times, but they have been greatly decreased compared to aged bitumen. Adding a pure oil rejuvenator in addition to unaged bitumen significantly reduces the maximum shear stress and stress reduction times, whereas adding polymer to a pure oil rejuvenator (physical rejuvenator) and adding polymer as well as chemical compound (chemical rejuvenator) increases the maximum shear stress and stress reduction times in a stepwise manner. However, if the chemical rejuvenator is added at a ratio of 20%, the rejuvenated bitumen has the lowest maximum shear stress, and the stress reduction time is almost at the same level as the unaged bitumen.

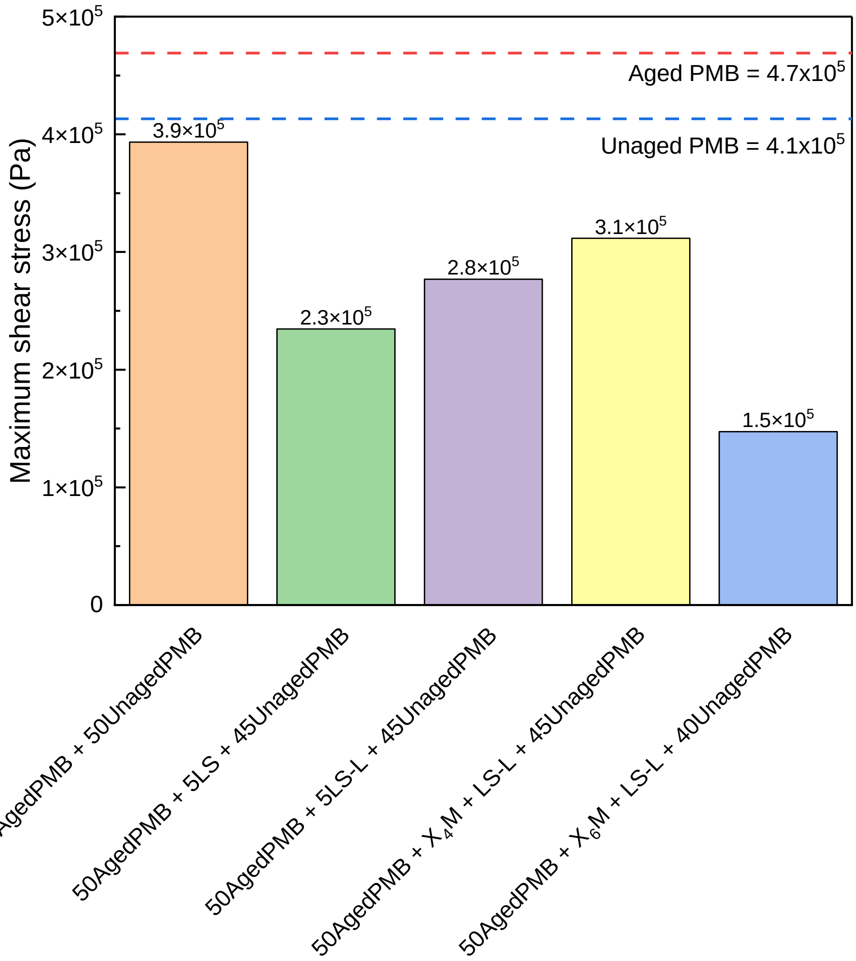

Figure 8-3. Maximum shear stress of rejuvenated bitumen with rejuvenators and unaged bitumen in 10% in creep-relaxation tests.

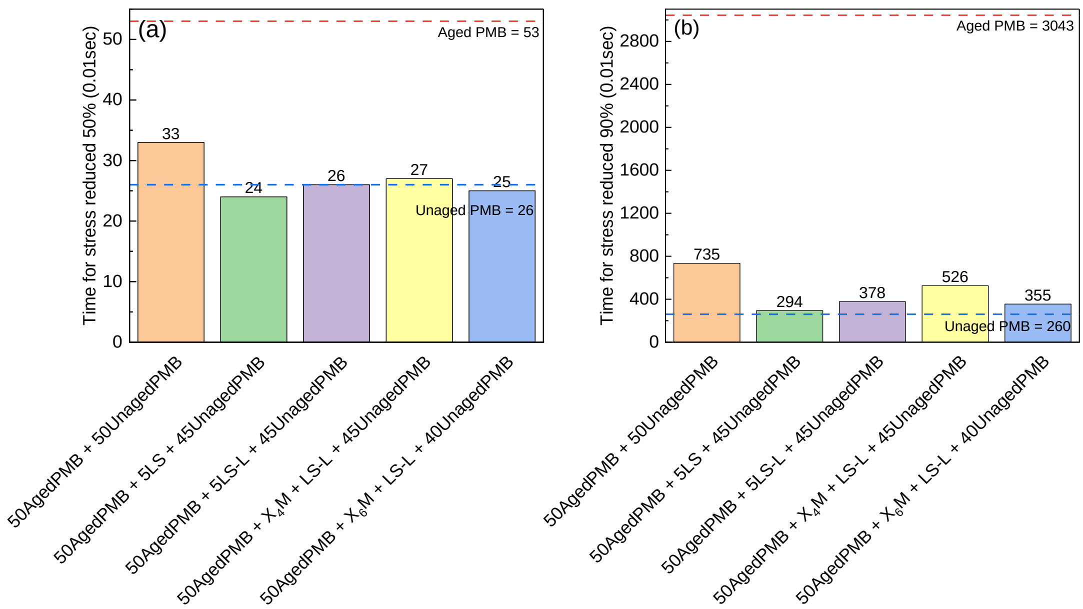

Figure 8-4. (a) time for stress reduced 50% from the maximum and (b) time for stress reduced 90% from the maximum of rejuvenated bitumen samples with rejuvenators and unaged bitumen in creep-relaxation tests.

The fatigue life of rejuvenated bitumen has almost the same pattern as that of low-temperature performance. The lowest fatigue life and potential detrimental impact are associated with the usage of pure unaged bitumen. The additional use of pure oil rejuvenators greatly lengthens fatigue life, while the use of physical rejuvenators and chemical rejuvenators gradually shortens fatigue life, which is also consistent with the low temperature performance results above. The rejuvenated bitumen with a 20% chemical rejuvenator has the highest fatigue life, outlasting unaged bitumen at low strains and coming very close to it at high strains.

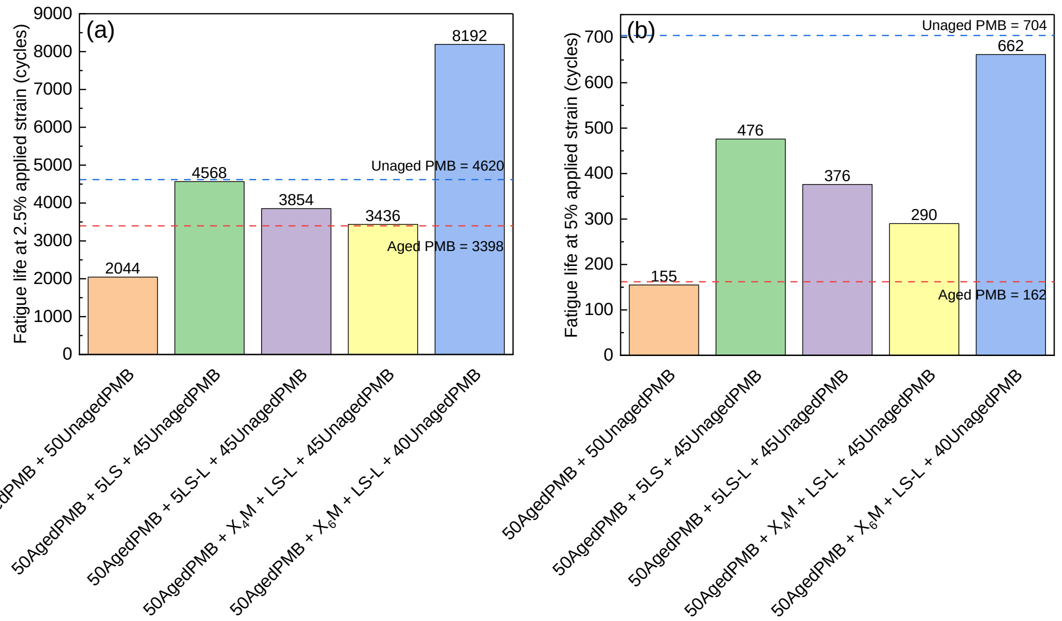

Figure 8-5. (a) fatigue life N_f at 2.5% applied strain and (b) fatigue life N_f at 5% applied strain of rejuvenated bitumen samples with rejuvenators and unaged bitumen.

Furthermore, **Figure 8-6** presents the fatigue life of rejuvenated bitumen under applied strain varying from 0.1% to 50%. It can be seen that rejuvenated bitumen with 20% chemical rejuvenator offers the best fatigue life at the majority of strain levels, outperforming even unaged bitumen at most phases, and is only surpassed by rejuvenated bitumen with pure oil rejuvenator at extremely high strains near 50%.

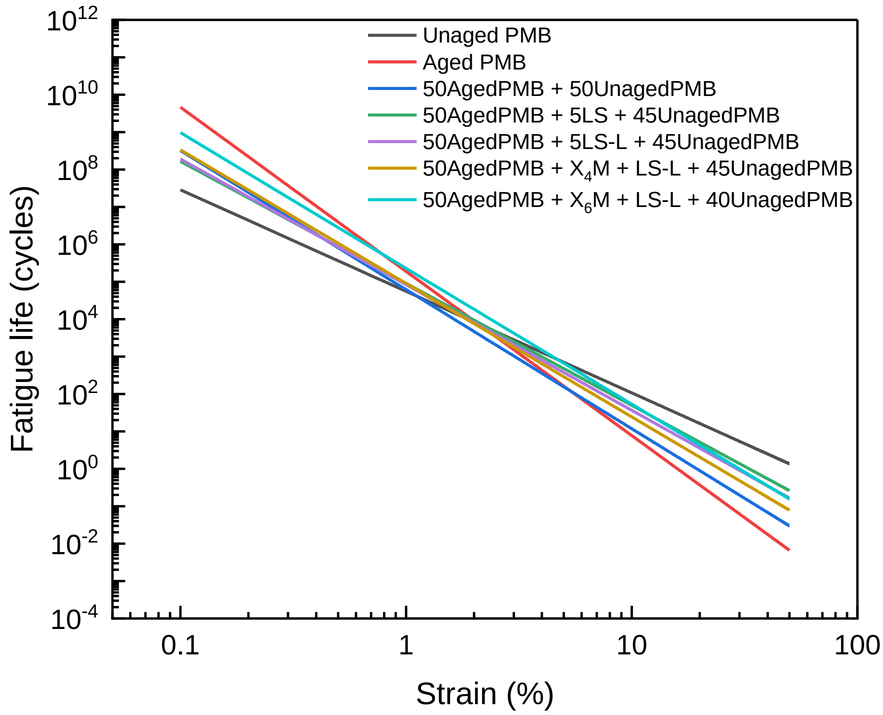

Figure 8-6. Fatigue life at various applied strains of rejuvenated bitumen with rejuvenators and unaged bitumen.

In general, compared to the other samples, rejuvenation with unaged bitumen alone had the worst effects. Pure oil or physical rejuvenators can be applied to achieve good low temperature performance and fatigue life, but high temperature performance is comparatively less favorable. High temperature performance with a 10% chemical rejuvenator was remarkable, but low temperature performance and fatigue life were average. Increasing the chemical rejuvenator addition ratio to 20% resulting in a balanced high and low temperature performance as well as fatigue life, especially performed substantially better in high temperatures and fatigue life compared to the other samples.

8.2. Mastic Validation

Figure 8-7 presents the complex modulus and phase angle master curves of rejuvenated mastics with rejuvenator and unaged bitumen. It is shown that while utilizing unaged bitumen alone can marginally reduce the complex modulus, using rejuvenators in addition results in a significant reduction. Additionally, using a pure oil rejuvenator or a physical rejuvenator will produce nearly identical curves. Comparatively to the other two types of rejuvenators, the use of chemical rejuvenators raises the complex modulus in the low frequency zone and lowers it in the high frequency zone. The findings of the phase angle analysis reveal that the viscosity is greatly increased when rejuvenating with unaged bitumen. A physical rejuvenator used in addition yields similar results, but the effect is greater in the high frequency range. In contrast, using a pure oil rejuvenator in addition results in even higher viscosities. Instead, the use of a chemical rejuvenator restores elasticity substantially, and the use of a chemical rejuvenator with a high additive ratio even improves viscosity in the mid to high frequencies while restoring elasticity in the low frequency zone.

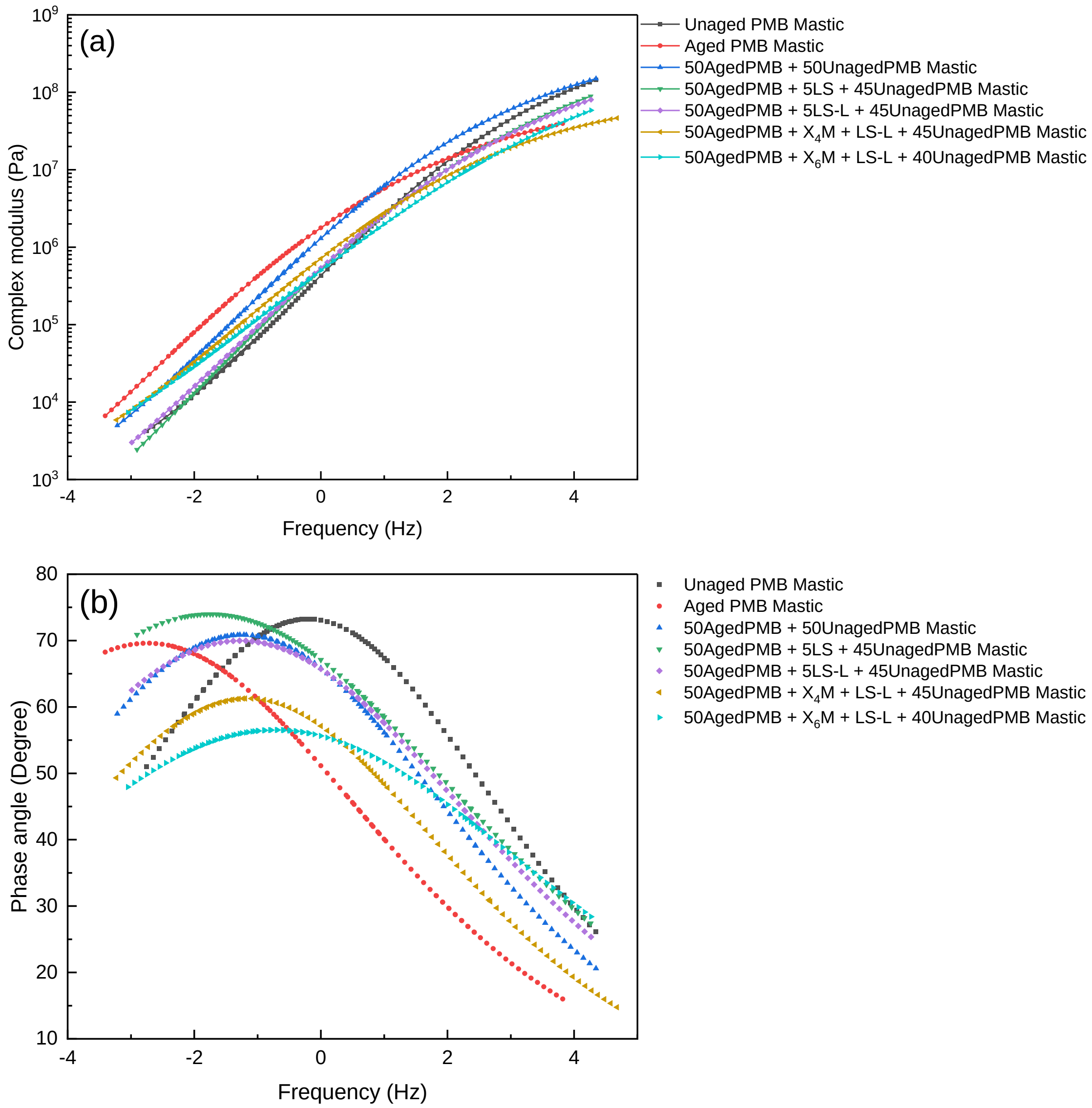

Figure 8-7. Complex modulus and phase angle master curves of rejuvenated mastic with rejuvenator and unaged bitumen.

Figure 8-8 demonstrated the high temperature average percent recovery value R of rejuvenated bitumen with rejuvenator and unaged bitumen from the MSCR tests. It can be seen that rejuvenating using solely unaged bitumen was unable to improve the R-value. Similar to the pure rejuvenator results, the usage of the pure oil rejuvenator and the physical rejuvenator fail to increase the recovery rate as well. However, a chemical rejuvenator with a 10% addition ratio performs less well when applied in combination with unaged bitumen. The R-value is only increased when a 20% chemical rejuvenator is used, and it is then brought back to the same level as the unaged mastic.

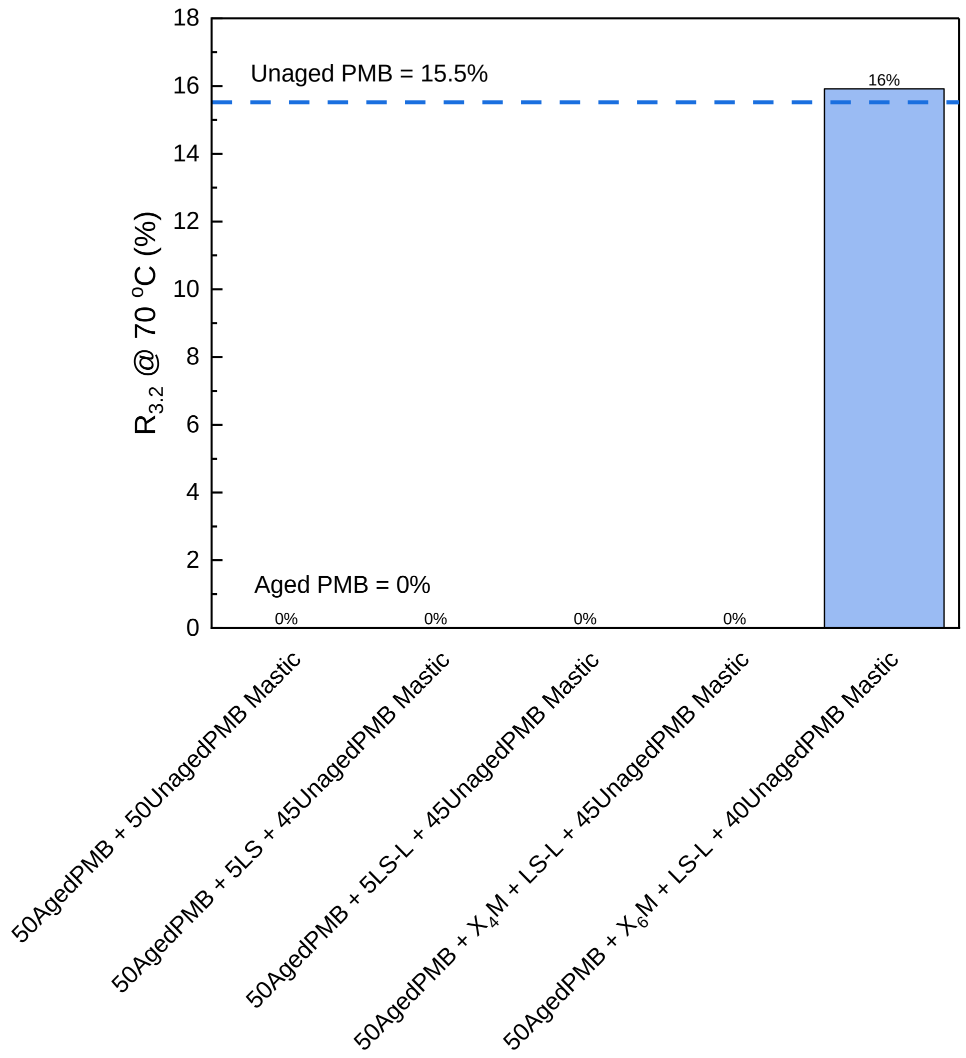

Figure 8-8. 70°C MSCR results of rejuvenated mastic with rejuvenator and unaged bitumen.

The worst outcomes for low temperature performance come from rejuvenating with entirely unaged bitumen. The maximum shear stress and the time required for 50% stress reduction are both greatly decreased by the extra use of rejuvenators. The utilization of pure oil, physical, and 10% chemical rejuvenators have almost the same maximum stress and 50% stress reduction time, while the 90% stress reduction time increases sequentially with the use of the above rejuvenators. The best low temperature performance of any rejuvenated mastic samples is achieved by increasing the chemical rejuvenator addition ratio to 20%.

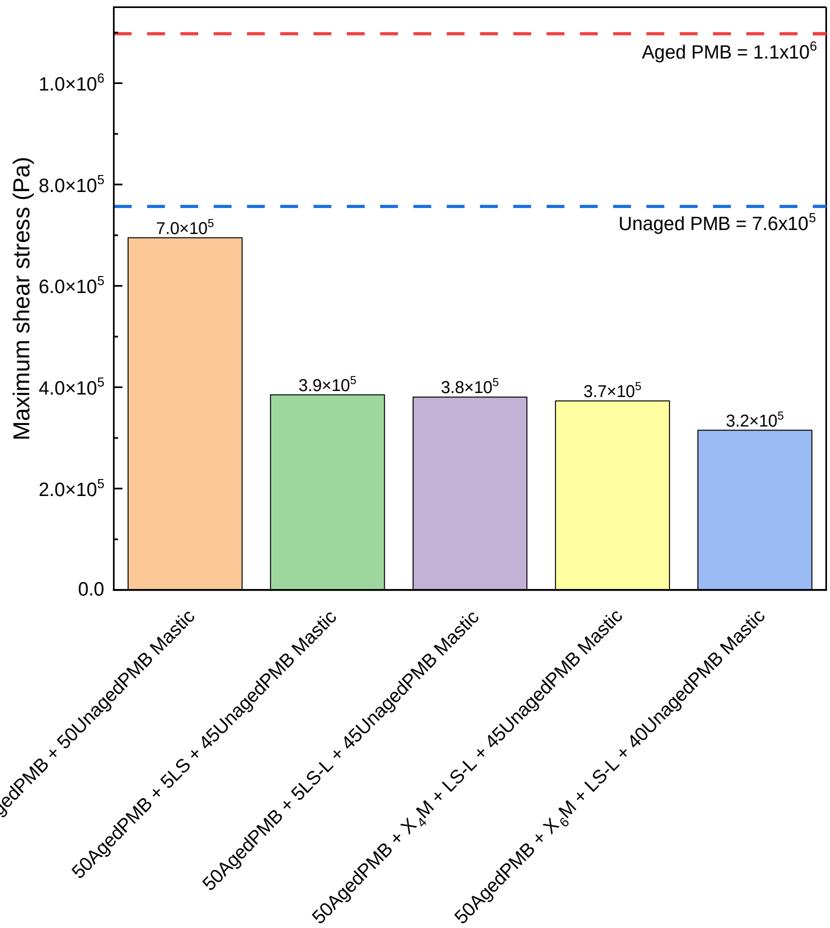

Figure 8-9. Maximum shear stress of rejuvenated mastic with rejuvenator and unaged bitumen in creep-relaxation tests.

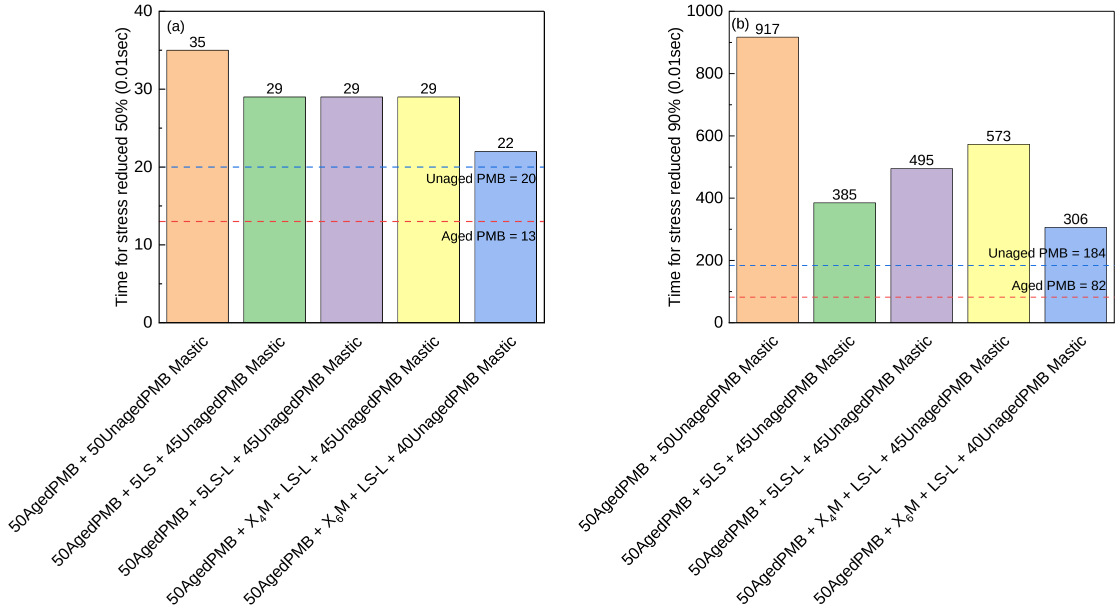

Figure 8-10. (a) time for stress reduced 50% from the maximum and (b) time for stress reduced 90% from the maximum of rejuvenated mastic with rejuvenator and unaged bitumen in creep-relaxation tests.

8.3. Mixtures Validation

8.3.1. Cantabro Tests Results

Figure 8-11 presents the Cantabro loss CL results of different asphalt mixture samples. It can be seen that mixing the RAP only with fresh mixtures leads to the highest Cantabro loss. Adding additional rejuvenators can significantly decrease the CL value to a level even lower than the unaged PMB mixture. The 50% recycled mixture that uses the chemical rejuvenator has the lowest Cantabro loss, which is consistent with the pull-off test results and indicates a good ravelling resistance.

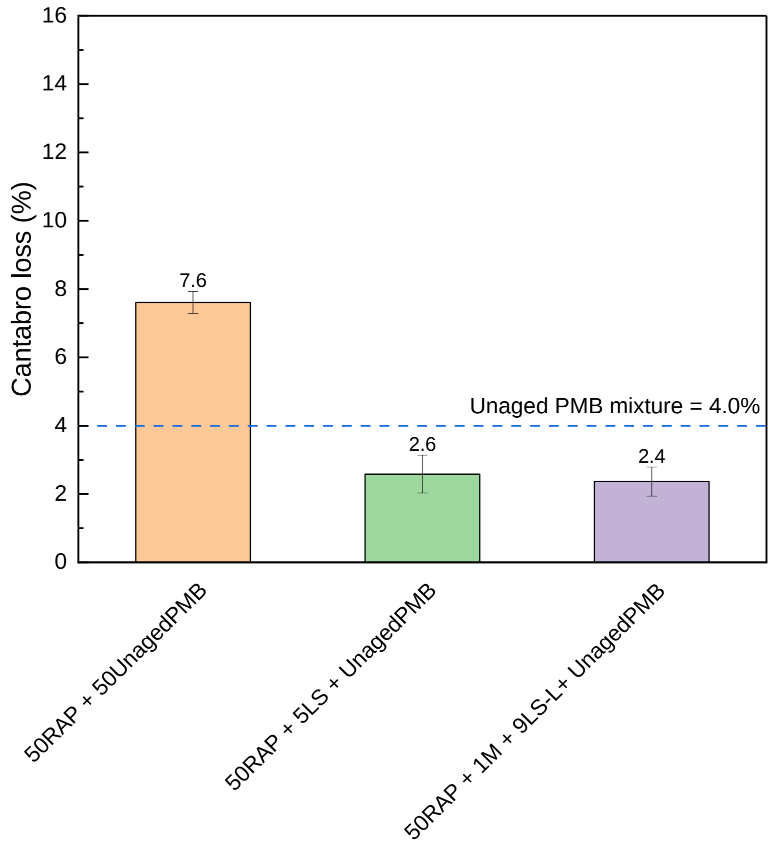

Figure 8-11. Cantabro loss of different asphalt mixture samples.

8.3.2. IDEAL-CT Results

The force versus displacement curves obtained in IDEAL-CT are demonstrated in **Figure 8-12**. A higher peak force occurs when the RAP is only mixed with fresh mixtures, which suggests that it can withstand more force before cracking. Adding additional pure oil or chemical rejuvenator results in a similar peak force, however the descent slope after the peak force becomes flatter, with the mixture employing the chemical rejuvenator having the flattest slope, indicating it can absorb more energy before failing completely.

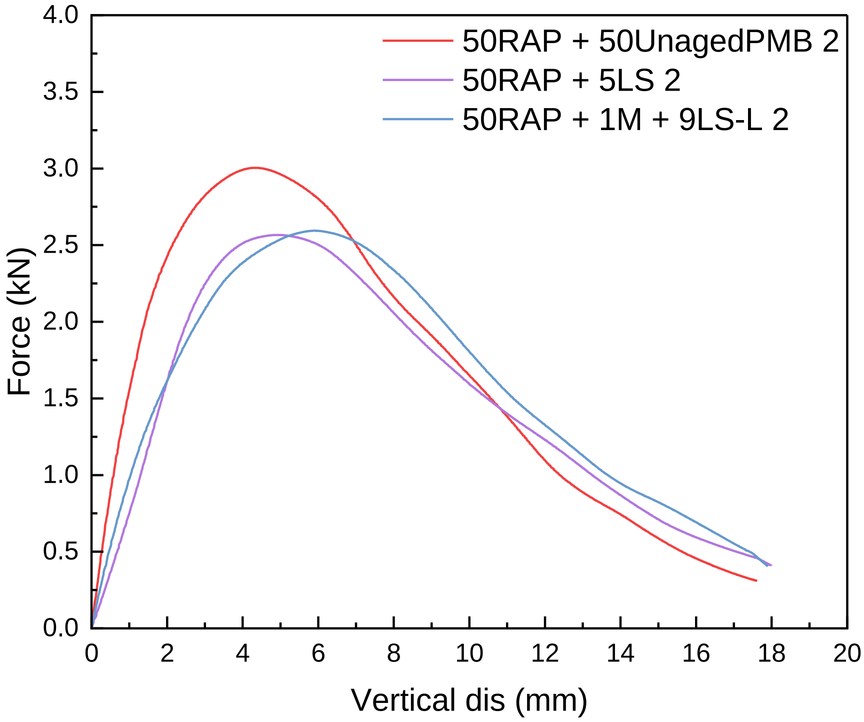

Figure 8-12. Force versus displacement curves from IDEAL-CT.

Figure 8-13 illustrates the failure energy of various asphalt mixture samples which is computed from the area under the force-displacement curve and cross-section area of the mixtures. It can be seen that the RAP that is simply mixed with fresh mixtures has the highest failure energy and that adding extra rejuvenators will lower that failure energy. This may be because the oil component in the rejuvenators makes the rejuvenated mixtures soft. By applying the chemical rejuvenator, the failure energy can be slightly increased. After water damage, the mixture without rejuvenators has an increased failure energy and is the highest among the others, while mixtures with rejuvenators have about the same failure energy prior to water damage.

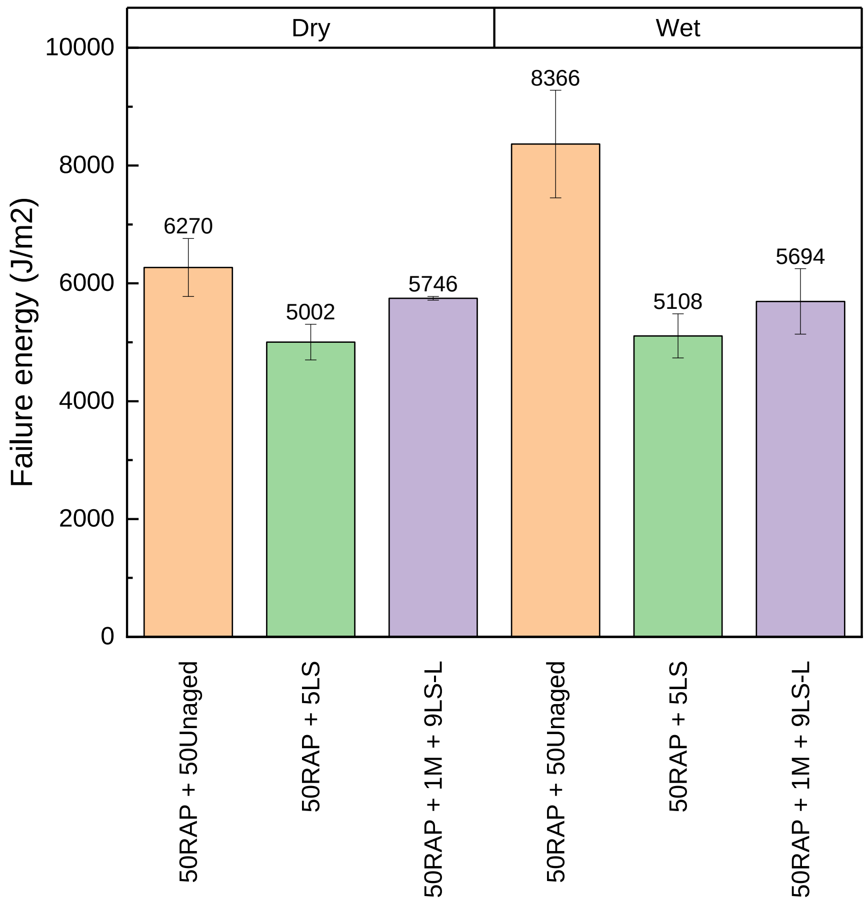

Figure 8-13. Failure energy results from IDEAL-CT.

Combining the failure energy values with the shape of the force-displacement curves, the cracking tolerance index CT_{index} of different asphalt mixture samples can be determined, as shown in **Figure 8-14**. Although the 50% recycled mixture sample containing only RAP and fresh mixture has the highest peak force and failure energy, it has the lowest cracking tolerance index in contrast to the mixture samples employed with additional rejuvenators. This is due to the fact that it has a more abrupt post-peak force decline slope than the other two mixtures with rejuvenators. Besides this, the mixture sample with the chemical rejuvenator demonstrates the highest cracking tolerance index, which is consistent with the effectiveness of the chemical rejuvenator at the binder level.

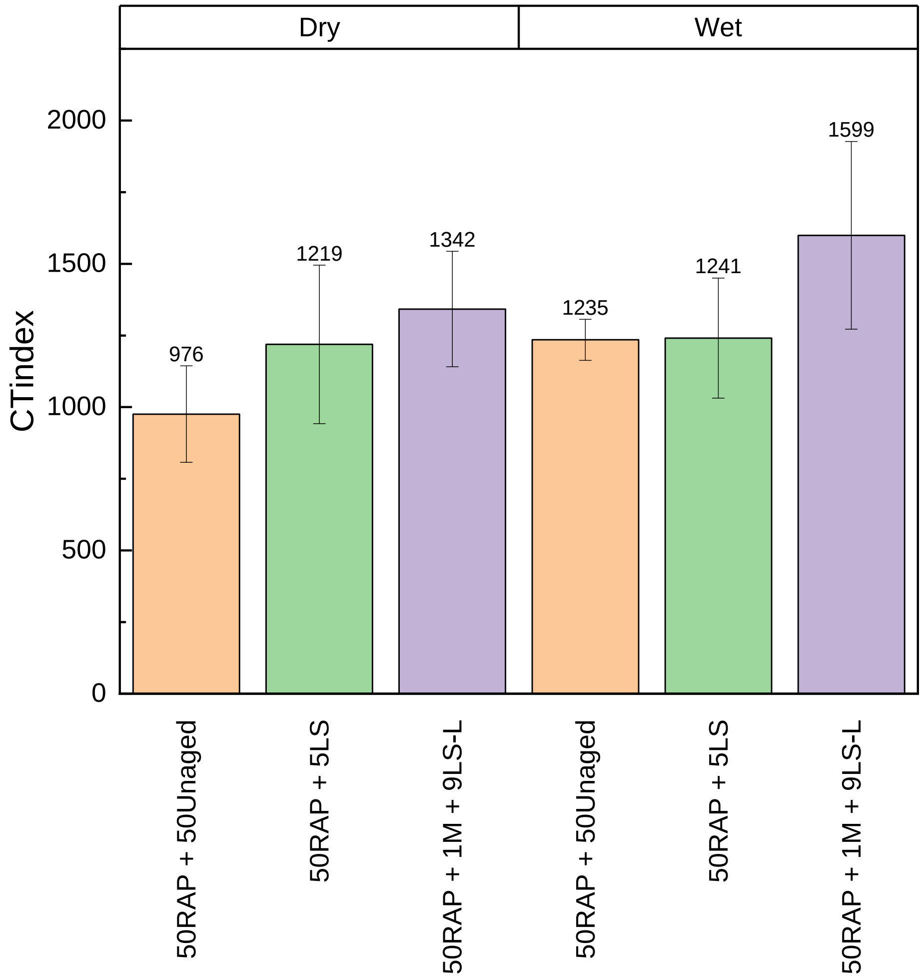

Figure 8-14.Cracking tolerance index of different asphalt mixture samples.

8.3.3. ITSR Results

Figure 8-15 shows the ITSR results of various 50% recycled asphalt mixture samples for moisture resistance evaluation. It can be seen that the ITS increased a little for the recycled mixture sample with only RAP and fresh mixture after water damage. This might be because the short mixing time and low mixing temperature in the mixtures sample preparation step led to insufficient contact between RAP and RAP as well as RAP and fresh mixtures. While the mixture samples were placed into the water bath, the warm environment improved the particle connection therefore increased the strength. The ITSR values are at the same level for 50% recycled mixture samples with additional rejuvenators, and the strength is only marginally reduced after water damage, indicating strong moisture resistance for rejuvenated mixtures with these two rejuvenators.

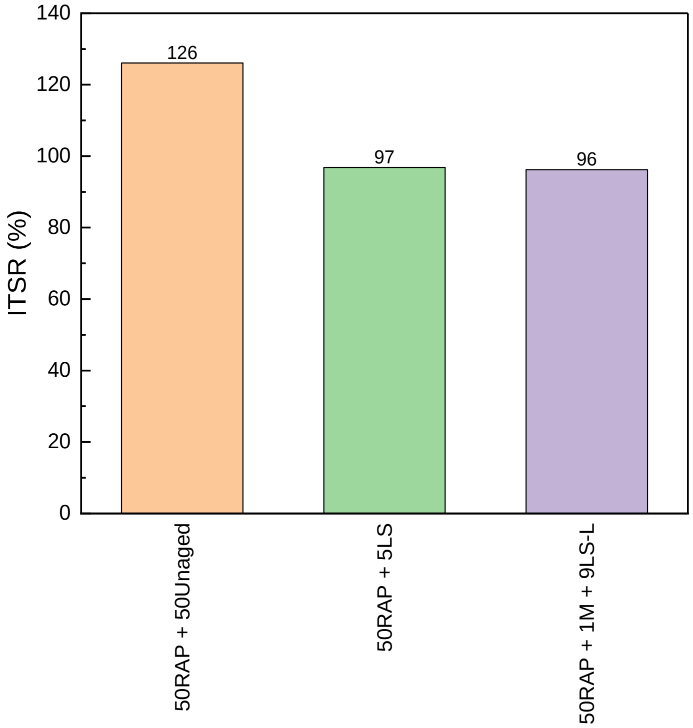

Figure 8-15. ITSR results of 50% recycled asphalt mixture samples.

Chapter 9. Conclusions

The objective of this MSc thesis is to investigate the impacts of various rejuvenator components on the rejuvenation effects and develop a consistent, trustworthy evaluation system. Therefore, a series of experiments was conducted on not only bitumen binder but also mastic and mixtures. Through the research, an evaluation system was constructed and proved to be feasible. Additionally, the impact of different rejuvenation components on the rejuvenation effect has been discovered and a balance between various components has been reached to produce the optimal rejuvenation results.

First, based on the existing evaluation criteria including bitumen binder rheological properties and chemical properties, some novel and significant evaluation methods, such as rejuvenated bitumen binder compatibility and mastic rheology, were proposed and proved to be feasible to complement the evaluation methodology.

In the second section, a comparative analysis of three primary categories of rejuvenators – pure oil rejuvenators, physical rejuvenators, and chemical rejuvenators – has been carried out. It has been shown that chemical rejuvenators have advantages over the other two types of rejuvenators, particularly in the field of elasticity recovery at high temperatures.

Next, the rejuvenation mechanism of the reactive chemical compound M was explained and proved it can repair the broken SBS polymer as well as restore the degraded polymer network structure. Additionally, the possibility of combining the three rejuvenation components – oil, polymer, and reactive chemical compound – was proved. Moreover, the rejuvenator dosage has been studied as well, and found that the best 20% dosage of chemical rejuvenator is capable of making rejuvenated bitumen have the same performance as unaged PMB in both high and low temperatures and fatigue life.

In the last section, the rejuvenators' effectiveness has been validated in the mastic rheological experiments as well as the mixture experiments. The findings of mastic rheological evaluation have shown a strong correlation with the binder results, and it has once again been demonstrated that chemical rejuvenators are more advantageous than the other two types of rejuvenators. The successful performance of chemical rejuvenators has been demonstrated at the mixtures level as well by having the best results among the competition in terms of ravelling resistance and cracking resistance.

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