**CIE5050-09 Additional Graduation Work, Research Project**

# Effects of Novel Rejuvenators on Chemical and Rheological Properties of Aged SBS Modified Bitumen

**Final Report**

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**September 2022**

# Summary

Bitumen is extensively used in numerous industries today, particularly in the field of road construction. With economic growth, the requirements for road quality are constantly improving, and SBS modified bitumen is popularly utilized due to its outstanding performance and competitive pricing. However, SBS modified bitumen, like normal bitumen, will be aged by oxygen, ultraviolet (UV), and heat, resulting in asphalt pavement distress and the necessity for maintenance, causing a significant amount of wasted modified asphalt. It is essential to recycle waste asphalt in order to reduce road construction and maintenance costs, save original resources, and protect the environment. Since many bitumen rejuvenators only rejuvenate the aged bitumen, and the excellent performance of SBS modified bitumen is largely attributable to the SBS polymer and polymer network structure in it. As a necessary consequence, during rejuvenation, it is important to consider the simultaneous rejuvenation of both aged bitumen and degraded SBS polymer.

In this research project, SBS modified bitumen was aged with thin-film oven test (TFOT), followed by pressure aging vessel (PAV), and various contents and proportions of reference rejuvenators, physical rejuvenators, and chemical rejuvenators were applied to the aged bitumen. Dynamic shear rheometer (DSR) tests and Fourier transform infrared (FTIR) tests were conducted on the aged and rejuvenated bitumen samples to study the rejuvenation effects with different types of oil, SBS content, and chemical compounds by comparing the rheological and chemical properties. The main research outcomes are as follows:

- The rejuvenation effects of pure oil based rejuvenators are intimately connected to environmental temperature and oil molecular weight. Rejuvenated bitumen with high molecular weight oil, such as aromatic oil, has better rutting resistance in high temperatures. Rejuvenated bitumen with low molecular weight oil, such as rapeseed oil and RP1000, has better cracking and fatigue resistance at low temperatures.

- Compared to the reference and physical rejuvenators used in this project, rejuvenated bitumen with chemical rejuvenators performed admirably at high temperatures. The low temperature performance of rejuvenated bitumen with chemical rejuvenators is generally undesirable, with poor cracking and fatigue resistance at most evaluation indexes, as the chemical rejuvenators harden the rejuvenated bitumen excessively.

- Increasing the SBS content in physical rejuvenators makes the rejuvenated bitumen more elastic and improves rutting resistance at high temperatures. At low temperatures, higher SBS content reduces the cracking resistance but

partially improves the fatigue resistance of the rejuvenated bitumen under some evaluation indexes.

- The effects of different oil types and proportions for physical rejuvenators at high temperatures are a little complicated. Increasing the rejuvenator proportion of physical rejuvenators with low or medium SBS content reduces high temperature performance, indicating that the oil is now dominant. Raising the rejuvenator proportion of physical rejuvenators with high SBS content improves high temperature performance, implying that SBS is currently playing the lead role. In physical rejuvenators containing rapeseed oil and a high SBS content, rising the rejuvenator proportion has little effect on high temperature performance, possibly because the high viscosity of rapeseed oil has diminished the effect of the high SBS content. For the low temperature performance, rejuvenated bitumen with aromatic oil containing physical rejuvenators has the worst performance than tall oil and rapeseed oil, which is consistent with the effect pattern of pure oil based rejuvenators. Furthermore, increasing the proportion of physical rejuvenators improves the cracking and fatigue resistance of rejuvenated bitumen in most evaluation indexes.

- In terms of FTIR analysis, the polybutadiene group index $I_{PB}$ of rejuvenated bitumen with physical rejuvenators increases significantly when compared to the aged bitumen, and the index continues to rise as the proportion of the rejuvenator or the content of SBS in the rejuvenators increases. Moreover, the $I_{PB}$ index increases for rejuvenated bitumen with chemical rejuvenators, and a group of new absorption peaks in the spectrum demonstrated that MDI has chemical reactions with degraded SBS polymer and has successfully connected the fracture SBS polymer segment.

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# 1. Introduction

## 1.1. Research Background

Bitumen, a hydrocarbon found naturally or obtained through petroleum distillation, has been used by people for over 5,000 years (Read and Whiteoak, 2003). Nowadays, bitumen is used extensively in a variety of industries, including agriculture, construction, and manufacturing (Read and Whiteoak, 2003). In the field of pavement, asphalt concrete is widely praised for its characteristics like ease maintenance and driving comfort, as an indispensable component of asphalt concrete, the importance of bitumen is self-evident (Xu *et al.*, 2018). As a result of this, the quantity of bitumen used in pavement construction is substantial. According to Read and Whiteoak (2003), in 1960 the UK's annual bitumen consumption was one million tons, and with the start of the highway construction program in the 1960s, by 1970 the UK's annual bitumen consumption had doubled compared to a decade earlier, and reached an annual consumption peak of 2.4 million tons by 1973. It should be noted, however, that the original properties of bitumen are highly influenced by the production and processing processes, and are also directly related to the quality of crude oil (Porto *et al.*, 2019). Although bitumen performance can be improved by using high-quality crude oil and a proper distillation process, the fact is that the bitumen industry has been forced to look for other ways to improve bitumen performance due to a lack of petroleum resources to produce high-quality bitumen and the inability to fully guarantee effective control measures in the refining process (Porto *et al.*, 2019; Zhu, Birgisson and Kringos, 2014). Furthermore, rapid economic growth in recent decades has resulted in a rise in traffic volume, a rise in traffic load, and pavement problems like cracking and rutting caused by a dearth of maintenance (Zhu, Birgisson and Kringos, 2014). As a consequence, all of these put greater expectations on the performance of bitumen. In light of this, it is critical to understand how to improve the performance of bitumen.

Various additives and modifiers, including polymers, oxidants and antioxidants, hydrocarbons, and chemical modifiers, are introduced to bitumen to improve its performance (Porto *et al.*, 2019). Among all of these additives and modifiers, polymer modification has been one of the most popular methods, and among all the widely known bitumen modification polymers like polypropylene (PP), ethylene butyl acrylate (EBA), and styrene-isoprene-styrene (SIS), styrene-butadiene-styrene (SBS) has attracted widespread interest due to not only its comparatively good dispersibility in bitumen but also the relatively excellent performance and reasonable price of the SBS modified bitumen (Zhu, Birgisson and Kringos, 2014). Unfortunately, SBS and SBS modified bitumen, like base bitumen, also suffer from aging due to environmental factors including oxygen, ultraviolet (UV), and heat, which can furthermore lead to pavement problems such as cracking, rutting and raveling (Han *et al.*, 2022). As a result, after a long period of use, the asphalt pavement will need to be reconstructed, leading to a huge amount of asphalt waste (Zhu *et al.*, 2019). In order to reduce road construction and maintenance costs, save original resources and protect the environment, it is necessary to recycle these asphalt wastes (Zhu *et al.*, 2019). However, since recycled bitumen waste inevitably deteriorates over time, many transportation authorities and departments limit the proportion of recycled bitumen added to the asphalt mixture to avoid affecting overall pavement performance (Leng *et al.*, 2018). In response to this issue, rejuvenators can be used to aged bitumen to improve their viscoelastic and rheological properties (Behnood, 2019).

In light of this, this study will focus on the rejuvenation of aged SBS modified bitumen and aim to summarize the rules by comparing the effects of various rejuvenators on the chemical and rheological properties of the aged SBS modified bitumen.

## 1.2. Current Aging Research on SBS Modified Bitumen

The aging mechanism of SBS modified asphalt is complex, but it can be roughly categorized into two parts: aging of the base bitumen and degradation of the SBS modifier (Xing, Liu and Li, 2020).

Bitumen aging is influenced by a variety of mechanisms, including physical hardening, volatile component loss, photooxidation, and thermal oxidation (Lu, Talon and Redelius, 2008). Among all the aging effects, hardening is the most noteworthy one since it reduces the crack resistance of the asphalt mixture, making it more prone to cracking in low temperature environments. Furthermore, the hardening of bitumen can be divided into reversible hardening and irreversible hardening. Reversible hardening or physical hardening is caused by molecular reorganization of bitumen or crystallization of wax, and it is usually reversible by raising the bitumen temperature (Frolov *et al.*, 2016; Camargo *et al.*, 2020). Irreversible hardening is typically caused by oxidation, exudation of oil components, and evaporation of light components (Read and Whiteoak, 2003; Camargo *et al.*, 2020). In the oxidation process of bitumen, compounds such as sulfoxide and ketone are formed, and the formation of ketone is related to the viscosity and asphaltenes increasing of the bitumen (Camargo *et al.*, 2020). With that said, because of the stiffness it can dramatically increase and make the bitumen more prone to cracking, thermal oxidation has become one of the recognized key aging mechanisms of bitumen (Jing *et al.*, 2020).

At the SBS polymer level, while some cross-linking reaction occurs, aging mainly degrades the polymer into small molecules (Sun, Wang and Zhang, 2014). In addition, Chen *et al.* (2020) point out that the unsaturated carbon-carbon double bonds (C=C) in the polybutadiene (PB) segment of SBS can easily become the targets of oxygen and degrade under the action of ultraviolet (UV) and heat, making the chain scission reaction of the PB segment play a major role in the degradation of SBS. Moreover, Xu *et al.* (2017) found out that the content of C=C decreased during the aging process of SBS polymers, and a significant amount of active oxygen-containing groups such as -OH, -COOH and C=O were produced. A figure shown below has illustrated the SBS aging mechanism and process.

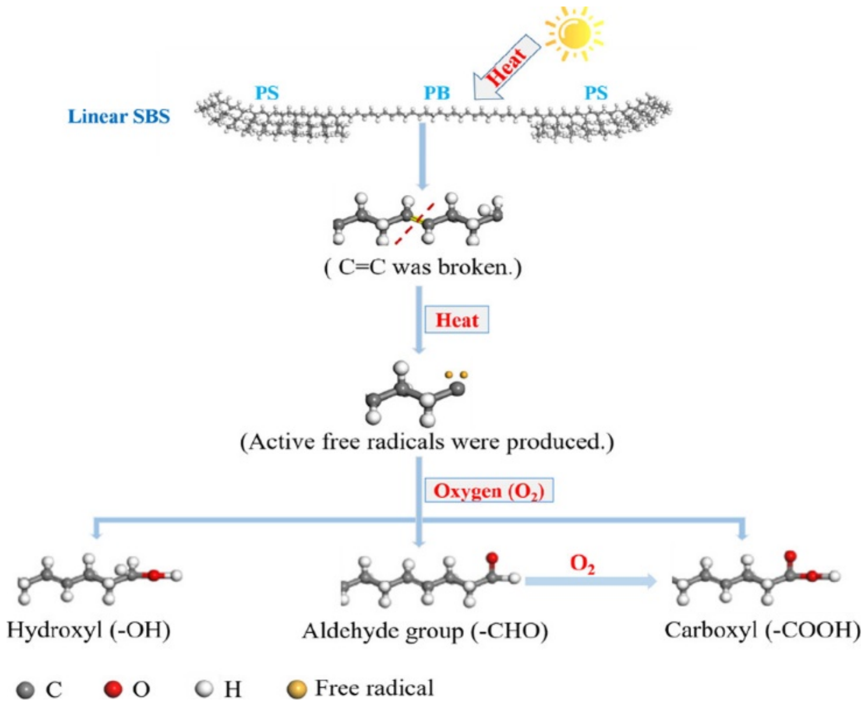


Figure 1. SBS aging mechanism and process (Han *et al.*, 2021).

However, in the aging process of the modified bitumen, in addition to the aging of the base bitumen and the degradation of the SBS polymer, the existence of SBS also makes the aging process of the modified bitumen different from that of the base bitumen (Wei, Zhang and Duan, 2020). For example, the decrease in permeability value of aged SBS polymer indicates that the aged polymer imparts less viscoelasticity to the modified bitumen than the base bitumen (Wang *et al.*, 2020). Furthermore, the rheological properties of aged modified bitumen are influenced by the combined effects of base bitumen aging and polymer degradation (Wei, Zhang and Duan, 2020). In light of this, when studying and using rejuvenators based on the aged SBS modified bitumen, it is necessary to consider the co-rejuvenation on both base bitumen and SBS polymer.

## 1.3. Current Rejuvenation Research on Aged SBS Modified Bitumen

As previously stated, when rejuvenating the SBS modified bitumen, consideration should be given to both the aged base bitumen and the degraded SBS polymer. In general, base bitumen rejuvenation technology is relatively mature, and the most commonly used rejuvenation methods include adding rejuvenators, adding modifiers, and mixing fresh asphalt, with adding rejuvenators being the most effective way (Su and Schlangen, 2012).

Lin *et al.* (2021) added three rejuvenators to the aged SBS modified bitumen, and the results indicated that the low viscosity rejuvenator rich in saturated components can significantly reduce the complex modulus and increase the phase angle of the aged bitumen, whereas rejuvenator full with aromatic component is less effective at improving fatigue performance after linear amplitude sweep (LAS) experiments. Cao *et al.* (2019) chose corn oil, cashew shell oil, waste engine oil, and vacuum steam oil to rejuvenate the aged SBS modified bitumen, and according to their findings, aged bitumen rejuvenated from cashew shell oil has the best anti-aging performance, since the cashew shell oil has the best softening effect on aged bitumen because it is rich in aromatic derivatives. The study on waste cooking oil (WCO) by Azahar *et al.* (2016) discovered that waste cooking oil after chemical modified acid reduction treatment could increase the rutting resistance of aged bitumen and decrease the temperature sensitivity. Another study on waste edible vegetable oil (WEVO) by Chen *et al.* (2014) illustrated that WEVO can effectively soften and enhance the physical and rheological properties of aged bitumen, but it could not change the colloidal structure, and the thermal stability, elasticity, and low temperature flexibility of the regenerated aged bitumen should be expanded. Cai *et al.* (2019) studied bio-rejuvenators and revealed that the rejuvenation process of bio-rejuvenators is entirely a physical behaviour, with no chemical functional groups changed, implying that bio-rejuvenators cannot repair the broken SBS chains and restore the cross-linked structure in aged SBS modified bitumen. According to a research conducted by Cong *et al.* (2015), the best physical and rheological properties of rejuvenated bitumen are obtained when the mixing ratio of aged bitumen and fresh bitumen is 35:65 and the content of rejuvenator is 5-10 wt.%.

Aside from the traditional rejuvenators mentioned above, rejuvenating with chemical compounds is becoming increasingly popular. Xu, Yu, Xue, Zhang, He, *et al.* (2017), for example, used 1, 4-butanediol diglycidyl ether (BUDGE) and trimethylolpropane triglycidyl ether (TMPGE) as rejuvenators for SBS modified bitumen respectively, and the results showed that both rejuvenators could improve the low-temperature ductility and crack resistance of aged bitumen, with BUDGE performed better. Another research conducted by Han *et al.* (2021) found that the effect of reactive rejuvenators made from TDI (toluene-2, 4-diisocyanate) or HDI (hexamethylene diisocyanate) and polyethylene glycol is superior to simply using TDI or HDI with aromatic hydrocarbon oil. According to their study, the rejuvenated bitumen with the new rejuvenators added with polyethylene glycol outperforms the rejuvenated bitumen with only TDI or HDI and aromatic hydrocarbon oil in terms of rutting resistance and cracking resistance (Han *et al.*, 2021).

Understanding the various rejuvenators shown above, however, reveals that most of the rejuvenators improve the performance of aged bitumen by adding aromatic compounds, light components, or by rebalancing the components in the aged bitumen. The vast majority of these processes are physical behaviours. They can effectively improve the performance of aged bitumen, but they are unable to rebuild the SBS broken chain and restore the cross-linked structure, which is the primary source of SBS modified bitumen's excellent performance, meaning that the utilization rate of wasted SBS modified bitumen cannot be increased effectively (Cai *et al.*, 2019; Han *et al.*, 2021).

## 1.4. Methodology of This Research Project

As described in previous sections, most rejuvenators in development today are physically acting on unmodified bitumen or the aged bitumen phase of modified bitumen, and while they may significantly improve the performance of the aged bitumen, they have no effect on the SBS polymers that were degraded by aging. Not to mention that some rejuvenators improve the low temperature performance of aged bitumen while deteriorating the high temperature performance (Han *et al.*, 2022). Furthermore, the excellent performance of SBS modified bitumen is largely attributable to the SBS segment and the polymer network structure formed by it (Cai *et al.*, 2019). Therefore, if the rejuvenator is incapable of effectively restore the SBS content and reconstruct the polymer network structure, the waste SBS modified bitumen will not be fully utilized (Han *et al.*, 2021).

In light of this, this research project will simulate the long-term aging of SBS modified bitumen under natural conditions by using the pressure aging vessel (PAV), and then rejuvenate the aged bitumen with different types and proportions of rejuvenators. By comparatively studying the chemical and rheological properties of the fresh bitumen, aged bitumen, and different rejuvenated bitumen through analysing the results from the Fourier transform infrared (FTIR) tests and the dynamic shear rheometer (DSR) tests, the pattern of the rejuvenation effect for different types and proportions of rejuvenators can be summarized to make the wasted aged SBS modified bitumen being utilized in a more efficient way.

The complete structure of this research project was summarized in the figure below.

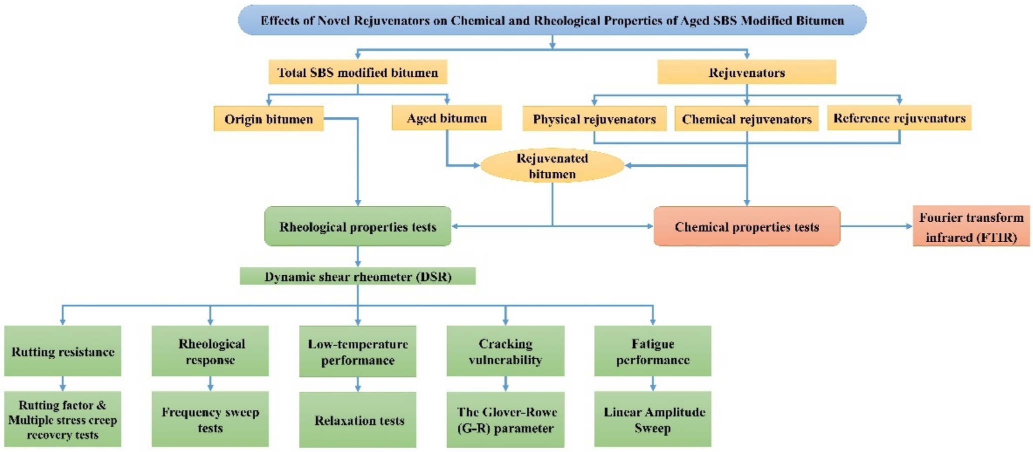



Figure 2. Complete structure of this research project.

# 2. Materials and Sample Preparation

## 2.1. Bitumen Aging

The SBS modified bitumen used in this project is provided by TotalEnergies SE. In order to simulate the short-term aging of bitumen, thin-film oven test (TFOT) was conducted on the fresh bitumen at 163 °C for 5 hours. For long-term aging simulation, pressure aging vessel (PAV) was used on the short-term aged bitumen at 100 °C for 80 hours.

## 2.2. Rejuvenators Preparation

The rejuvenators used in this project can be categorized into three groups – reference rejuvenators, physical rejuvenators, and chemical rejuvenators.

Reference rejuvenators include pure oil based rejuvenators such as rapeseed oil, aromatic oil, RP1000, and epoxidized soybean oil, commercial rejuvenators such as Latexfalt R20 and Anova, also previously laboratory made rejuvenators like HCP and HCP-2. The usage of reference rejuvenators is intended to study the rejuvenation effects of various types of oil, as well as to compare the rejuvenation effects with physical and chemical rejuvenators made in this project.

The physical rejuvenators indicate that the rejuvenation process of this rejuvenator in aged bitumen is a physical behaviour. Ingredients for this type of rejuvenators include aromatic oil, tall oil, rapeseed oil, and polymer. Kraton linear SBS 1101 polymer was used in this project for physical rejuvenators. When producing the physical rejuvenators, the mixing temperature was set to 150 °C and the polymer was added into the oil at a small quantity in high frequency, the high shear mixer was used to ensure that the various components in the rejuvenators were evenly mixed.

The chemical rejuvenator means that the components in the rejuvenator will have reaction with some of the active oxygen-containing groups in the aged SBS modified bitumen during the rejuvenation process to achieve the effect of improving performance. The materials used to produce the chemical rejuvenators include aromatic oil, rapeseed oil, and methylene diphenyl diisocyanate (MDI). Beyond this, hydroxyl terminated polybutadiene (HTPB) was used to react with MDI to produce a new chemical component called M-HTPB.

## 2.3. Rejuvenated Bitumen Preparation

The aged bitumen was first redistributed into small cans, and then the rejuvenators were added to the small cans at the set target proportion, the aged bitumen and the rejuvenators were thoroughly mixed using a small hand-held mixer at the temperature of 170 °C for 15 minutes, and finally the prepared rejuvenated bitumen was poured on silicone paper to make samples for DSR and FTIR analysis.

## 2.4. Summary and Sample Code Names

During this project, 25 rejuvenated bitumen samples were made in total, as shown in the photo below.

Figure 3. Rejuvenators (left part) and rejuvenated bitumen samples (right part) made in this project.

In order to conveniently and intuitively distinguish different rejuvenated bitumen, each sample was given a unique code name based on the different types and proportions of rejuvenators used. The code names and the corresponding rejuvenators used for the rejuvenated bitumen samples were summarized in the following table.

Table 1. Code names and corresponding rejuvenators for rejuvenated bitumen samples.

| | **Code name** | **Rejuvenator and proportion** |
|---|---|---|
| Aged bitumen | 4PAV | 80h PAV aged bitumen |
| Reference rejuvenators | 10% Rap | 10% rapeseed oil |
| | 10% Aro | 10% aromatic oil |
| | 10% RP | 10% RP1000 |
| | 10% Lat | 10% Latexfalt R20 |
| | 10% Anova | 10% Anova |
| | 100% HCPMA | 100% HCPMA |
| | 10% Resin-XH | 10% HCP |
| | 10% Diesel-H | 10% HCP-2 |
| | 10% ESO | 10% epoxidized soybean oil |
| Physical rejuvenators | 10% Tall-L | 10% tall oil with low polymer content |
| | 10% Tall-M | 10% tall oil with medium polymer content |
| | 10% Tall-H | 10% tall oil with high polymer content |
| | 20% Tall-L | 20% tall oil with low polymer content |
| | 20% Tall-M | 20% tall oil with medium polymer content |
| | 20% Tall-H | 20% tall oil with high polymer content |
| | 10% Rap-H | 10% rapeseed oil with high polymer content |
| | 20% Rap-H | 20% rapeseed oil with high polymer content |
| | 10% Aro-H | 10% aromatic oil with high polymer content |
| | 20% Aro-H | 10% aromatic oil with high polymer content |
| Chemical rejuvenators | 10% MDI | 10% MDI |
| | 10% MDI-Rap-M | 10% MDI with medium rapeseed oil content |
| | 10% MDI-Rap-H | 10% MDI with high rapeseed oil content |
| | 10% M-HTPB | 10% M-HTPB with aromatic oil |

# 3. Effects of Rejuvenators on Rheological Properties of Aged SBS Modified Bitumen

## 3.1. Introduction

Rheology is all about studying of the interaction between the stress and strain of a material under specific loading and environmental conditions (Widyatmoko, 2016). While the viscoelastic properties of bitumen are commonly represented in complex modulus and phase angle, it is important to understand how the rheological properties are characterized on bitumen (Widyatmoko, 2016). More importantly, the rheological properties of bitumen are linked to a variety of pavement distresses problems, including cracking and rutting (Ali, Mashaan and Karim, 2013).

In light of this, this chapter will concentrate on the effect of rejuvenators on the rheological properties of aged bitumen, and compare different rejuvenators on the regeneration effect by performing DSR tests on the rejuvenated bitumen samples, as well as multiple stress creep recovery (MSCR) tests, linear amplitude sweep (LAS) tests, and other analyses.

## 3.2. Experimental Method

### 3.2.1. Frequency Sweep Tests

The studying of rheological properties is based on the results of DSR tests, which are conducted on the Anton Paar Modular Compact Rheometer (MCR). In general, DSR tests are divided into two sections – low temperature (between 0 and 30 °C) and high temperature (between 40 and 80 °C). For the low temperature part, a spindle of 8 mm diameter was used and the gap between the parallel plates is 2 mm. For the high temperature part, a spindle of 25 mm diameter was used and the gap between the parallel plates is 1 mm. Furthermore, the frequency sweep test method was chosen for the DSR tests, and it was conducted at the temperature of 0, 15, 30, 40, 60 and 80 °C while the frequency ranged from 0.1 to 10 Hz.

The Sigmoidal model developed in the National Cooperative Highway Research Program (NCHRP) Project A-37A was used to construct the complex modulus master curves (Yusoff *et al.*, 2013). The master curves of phase angle were constructed based on the Kramers-Kronig relations (Oshone *et al.*, 2017; Lin *et al.*, 2021). The equations for constructing the master curves of complex modulus and phase angle were shown below.

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

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

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

The reference temperature was set to 30 °C when constructing the master curves for complex modulus and phase angle during the frequency sweep tests.

Moreover, due to the polymer network formed in the bitumen, a downtrend will appear in the low frequency range and a plateau region will form in the phase angle curves for polymer modified bitumen (Asgharzadeh *et al.*, 2013). Inspired by this phenomenon, the area under the phase angle curves at 80 °C was calculated to characterize the high temperature performance of the rejuvenated bitumen, as illustrated in the following figure.

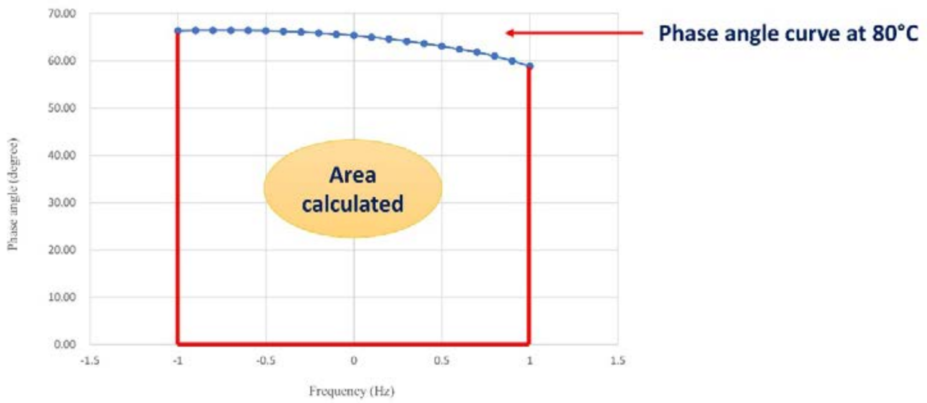



Figure 4. Area calculated under 80 °C phase angle curve.

## 3.2.2. Multiple Stress Creep Recovery (MSCR) Tests

According to AASHTO TP 70-13, the MSCR tests were performed on the DSR equipment with a spindle of 25 mm diameter and 1 mm gap between the parallel plates. During the tests, 0.1 KPa and 3.2 KPa of stresses were applied to the sample respectively and lasted for 1 second before the sample was given 9 seconds to recover.

The tests were repeated 30 times, and the average percent recovery R as well as the nonrecoverable creep compliance $J_{nr}$ were calculated using the specification mentioned above.

### 3.2.3. Creep-Relaxation Tests

The creep-relaxation tests were performed on the DSR equipment using a spindle with 8 mm diameter and parallel plates with a 2 mm gap at the temperature of 0 °C. The samples were subjected to 1% shear strain in a matter of seconds before a 100-second relaxation period. The shear stresses of the samples were recorded during the test, and the frequency data is collected at 100 points per second because the relaxation rate is very fast at the start of the test (Jing *et al.*, 2020).

### 3.2.4. Glover-Rowe Parameter Calculations

The Glover-Rowe parameter can be calculated with the complex modulus and phase angle data measured in the DSR equipment at 15 °C and 0.005 rad/s using the equation

$$GR = \frac{G^* \times (\cos\delta)^2}{\sin\delta} \tag{3}$$

where $G^*$ is the complex modulus (Pa), $\delta$ is the phase angle (degree) (Rowe, King and Anderson, 2014).

### 3.2.5. Linear Amplitude Sweep (LAS) Tests

According to AASHTO TP 101-14, the LAS tests were performed on the DSR equipment using a spindle with 8 mm diameter and parallel plates with a 2 mm gap at the temperature of 20 °C. The tests were split into two parts – frequency sweep and amplitude sweep. During the frequency sweep part, the samples were subjected to 0.1% of strain over a frequency range of 0.2 – 30 Hz to determine the damage analysis parameter $\alpha$. At the amplitude sweep part, the frequency was set to 10 Hz and the applied strain was linearly increased from zero to 30% during the tests. The above-mentioned specification was followed in the calculation of the LAS results.

### 3.2.6. Fracture Index Analysis with LAS Tests

According to Hintz (2012), a fracture based model should be used when analysing the results from the LAS tests, since macro fracture failure occurred during the fatigue tests rather than only microscale damage. Furthermore, the LAS tests should be regarded as a damage tolerance test instead of a fatigue test, because the cracking propagation patterns in the LAS tests differ from those in the true fatigue time sweep test (Hintz, 2012). Therefore, Hintz proposed a new parameter called crack length at failure $a_f$ to characterize the relative damage tolerance of bitumen samples. The crack length $a$ can be calculated with the following equation.

$$a = 4 - 4 \times \left(\frac{T_0/\varphi_0}{T_i/\varphi_i}\right)^{0.25} \tag{4}$$

where $T_0$ and $\varphi_0$ are the initial torque and displacement, $T_i$ and $\varphi_i$ are the corresponding torque and displacement values in cycle $i$ (Nuñez, Leonel and Faxina, 2016).

The physical meaning of the crack length $a$ is demonstrated in Figure 5 below.

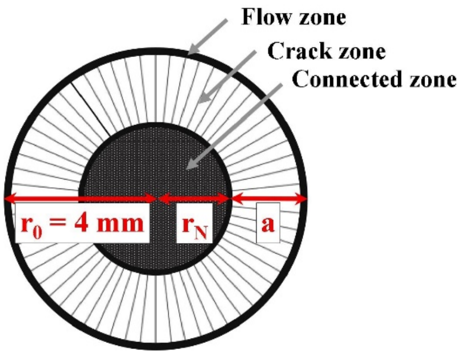



Figure 5. Fracture schematic of bitumen specimen (Asadi, Tabatabaee and Hajj, 2021).

The crack length at failure $a_f$ can be determined by plotting the crack growth rate ($da/dN$) against the crack length $a$, and the failure point is at the local minimum in crack growth rate before the significant increase, as illustrated in the following figure (Hintz, 2012).

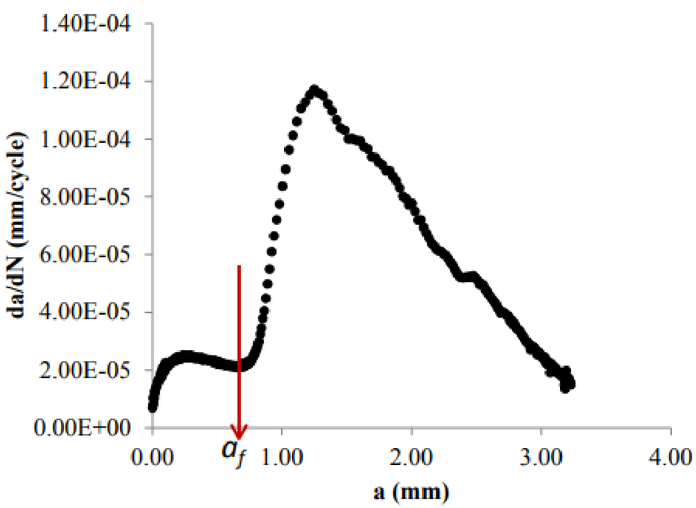



Figure 6. Illustration of crack length at failure $a_f$ (Hintz, 2012).

## 3.3. Results and Discussion

### 3.3.1. Viscoelastic properties analysis

The complex modulus master curves in Figure 7 show that the complex modulus of aged bitumen is greater than that of origin bitumen, indicating that aging causes bitumen to become harder. As presented in Figure 7 (a), the complex modulus of the aged bitumen decreased significantly after adding pure oil based rejuvenators, even lower than that of the origin bitumen, demonstrating that these oils can supplement the reduced light components in the aged bitumen to make it softer (Han *et al.*, 2021). Furthermore, the softening effect of various types of oils can also be seen in Figure 7 (a). For example, RP1000 softens the best, followed by rapeseed oil and, finally, aromatic oil. For the chemical rejuvenators shown in Figure 7 (b), it can be seen that the complex modulus decreased at the high-frequency range but increased in the low-frequency range. High complex modulus at low frequencies, on the other hand, may not be a negative sign because it implies that rutting resistance will be favourable at high temperatures. For physical rejuvenators, higher SBS polymer content in rejuvenators could increase the complex modulus of aged bitumen, as illustrated in Figure 7 (c), but higher rejuvenators proportion added into the aged bitumen would decrease the complex modulus, owing to more oil added into the bitumen, as demonstrated in both Figure 7 (c) and (d). The effects of various oil types used in the physical rejuvenators can be compared in Figure 7 (d). As shown in the figure, physical rejuvenators containing rapeseed oil have the greatest ability to reduce complex modulus, followed by rejuvenators containing tall oil and aromatic oil, respectively.

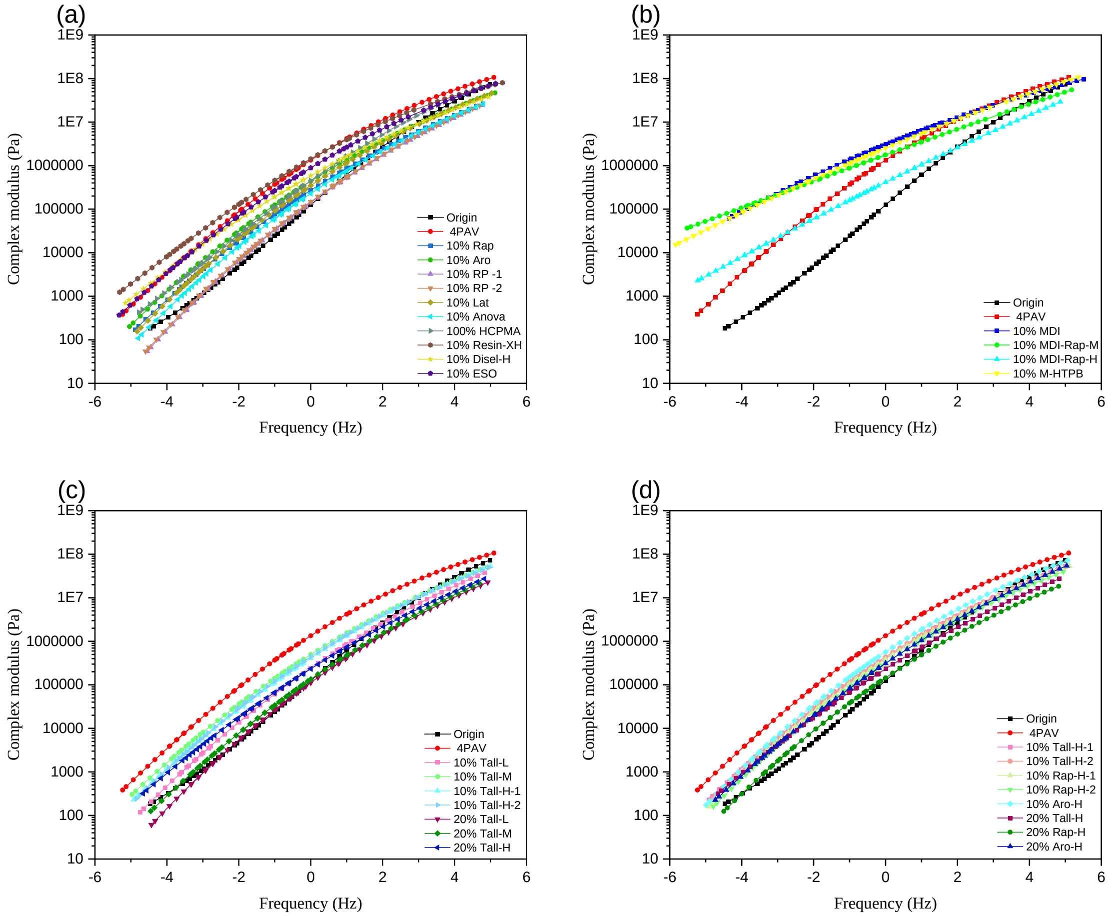



Figure 7. Complex modulus master curves for rejuvenated bitumen samples at a reference temperature of 30 °C, (a) rejuvenated bitumen with reference rejuvenators; (b) rejuvenated bitumen with chemical rejuvenators; (c) rejuvenated bitumen with physical rejuvenators in different SBS content; (d) rejuvenated bitumen with physical rejuvenators in different oil type.

The origin bitumen phase angle master curve exhibits a clear downward trend at the low frequencies and a plateau region at the middle, as illustrated in Figure 8. After aging, the downtrend and plateau region vanished, indicating that the polymer network has degraded during aging (Asgharzadeh *et al.*, 2013; Lin *et al.*, 2021). As demonstrated in Figure 8 (a), the phase angle of the aged bitumen increased markedly after adding pure oil based rejuvenators, with RP1000 increasing the most in terms of phase angle, followed by aromatic oil and rapeseed oil. For the rejuvenated bitumen with HCP (10% Resin-XH) and HCPMA, due to the high SBS polymer content added to the aged bitumen, a downtrend and plateau region have appeared in their phase angle master curves (Figure 8 (a)). Figure 8 (b) shows that all of the rejuvenated bitumen with chemical rejuvenators has a significant decrease in the phase angle master curve. Moreover, when compared to rejuvenated bitumen with 10% MDI, adding a small amount of rapeseed oil (10% MDI-Rap-M) can dramatically reduce the phase angle at low frequencies, implying that high temperature rutting resistance will be improved. For physical rejuvenators, the phase angle has increased for all rejuvenated bitumen, mainly due to the fact that physical rejuvenators contain a high percentage of oil (Figure

8 (c) and (d)). As illustrated in Figure 8 (c), increased SBS content in physical rejuvenators may decrease the phase angle of aged bitumen, particularly at low frequencies, as the polymer network is reconstructed. For different oil types in the physical rejuvenators, rapeseed oil and aromatic oil have a greater effect on increasing the phase angle than tall oil, as presented in Figure 8 (d). The effect of the physical rejuvenators proportion on the phase angle delivers somewhat complicated results. Raising the rejuvenator proportion of physical rejuvenators with low or medium SBS polymer content increases the phase angle, indicating that the oil in the rejuvenators plays a significant role (Figure 8 (c)). In the case of physical rejuvenators with a high SBS polymer content, increasing the rejuvenator proportion reduces the phase angle, revealing that the SBS polymer is currently dominant (Figure 8 (d)). However, for physical rejuvenators containing rapeseed oil and a high SBS polymer content, increasing the rejuvenator proportion has little effect on the phase angle because the high viscosity of rapeseed oil has neutralized the effect of the high SBS polymer content (Figure 8 (d)).

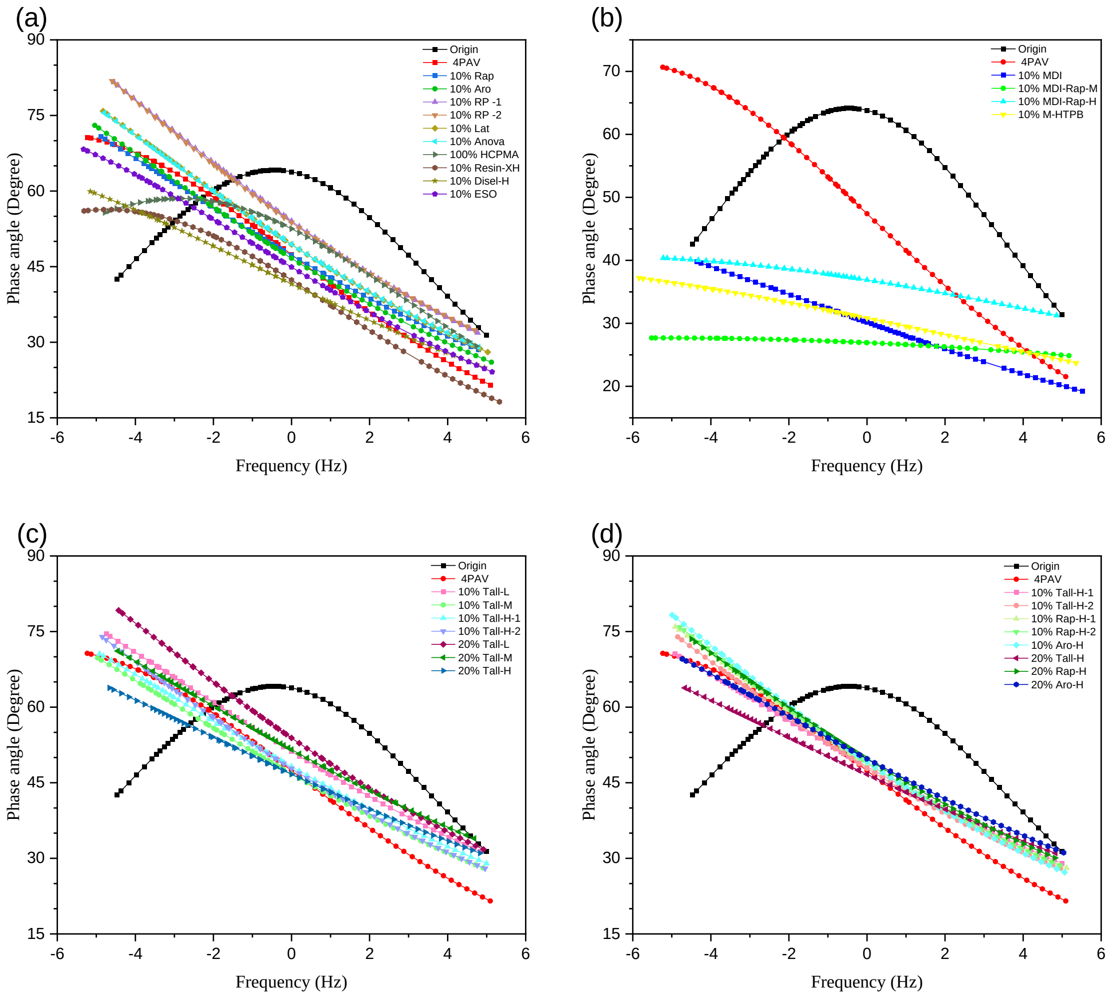



Figure 8. Phase angle master curves for rejuvenated bitumen samples at a reference temperature of 30 °C, (a) rejuvenated bitumen with reference rejuvenators; (b) rejuvenated bitumen with chemical rejuvenators; (c) rejuvenated bitumen with physical rejuvenators in different SBS content; (d) rejuvenated bitumen with physical rejuvenators in different oil type.

Similar to the results of the phase angle master curves, the area under the phase angle curve at 80 °C of aged bitumen increased significantly when compared to the origin bitumen, as presented in Figure 9, indicating that the aged bitumen is becoming more viscous due to the SBS polymer degradation. For rejuvenated bitumen with pure oil based rejuvenators, it can be seen that the area is smallest with aromatic oil, followed by rapeseed oil and RP1000. It is worth noting that the phase angle area of the rejuvenated bitumen with chemical rejuvenators is the smallest of all samples, particularly the rejuvenator with medium rapeseed oil content (10% MDI-Rap-M), which is also consistent with the phase angle master curves results. In terms of physical rejuvenators, increasing the SBS content reduces the area, implying that the bitumen is becoming more elastic. The effect of different oil types and proportions for physical rejuvenators on the phase angle area has shown the same pattern as the results of phase angle master curves. For physical rejuvenators with low or medium SBS polymer content, raising the rejuvenator proportion will increases the phase angle area, suggesting that the oil in the rejuvenators has a leading role. In the case of physical rejuvenators containing a high SBS polymer content, increasing the rejuvenator proportion decreases the phase angle area, indicating that the SBS polymer is currently dominant. That being said, increasing the rejuvenator proportion in physical rejuvenators containing rapeseed oil and a high SBS polymer content barely changes the phase angle area because the high viscosity of rapeseed oil has neutralized the effect of the high SBS polymer content.

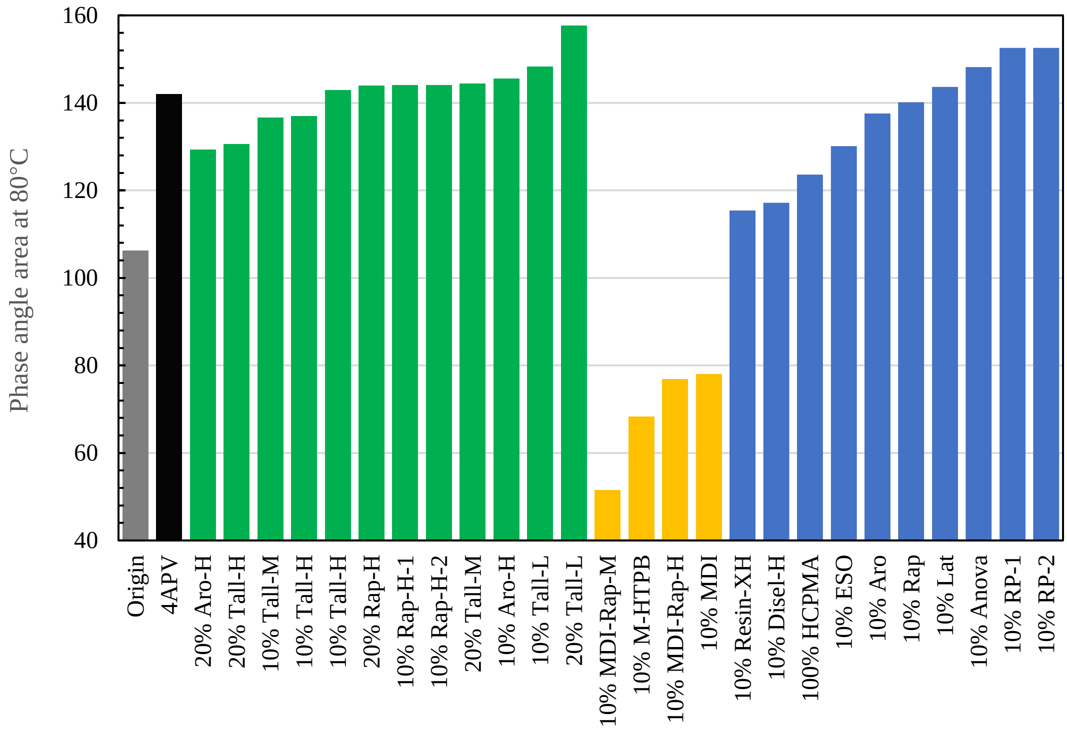



Figure 9. 80 °C phase angle curve area results of origin, aged and rejuvenated bitumen samples.

### 3.3.2. MSCR Analysis

The MSCR tests were carried out at the temperature of 70 °C and 76 °C, respectively, to assess the high temperature performance of the rejuvenated bitumen. In general, there is a certain similarity between the MSCR and phase angle area results.

At the temperature of 70 °C, as presented in both Figure 10 and Figure 11, aromatic oil has the best MSCR performance for pure oil based rejuvenators by having a higher $R_{3.2}$ value and a lower $J_{nr3.2}$ value, followed by rapeseed oil and RP1000. Furthermore, when compared to all the other samples, rejuvenated bitumen samples with chemical rejuvenators have the best performance in terms of high average percent recovery value and low nonrecoverable creep compliance value. As for the physical rejuvenators, rising the SBS content improves the MSCR performance, indicating that the bitumen has become more elastic at the high temperatures. The effect of different oil types and proportions for physical rejuvenators on the MSCR performance followed a pattern similar to the results of frequency sweep tests. Raising the rejuvenator proportion in physical rejuvenators with low or medium SBS polymer content reduces the MSCR performance, implying that the oil has taken the lead and made the bitumen softer at high temperatures. Increased rejuvenator proportion improves performance in the scenario of physical rejuvenators with a high SBS polymer content, suggesting that the SBS polymer is currently dominant and has made the bitumen more elastic. Additionally, the rejuvenation effect pattern of the rejuvenator containing rapeseed oil and a high SBS polymer content (Rap-H) differs from that described above. For this rejuvenator, the average percent recovery $R_{3.2}$ value is higher at the proportion of 20% and the nonrecoverable creep compliance $J_{nr3.2}$ value is lower at the proportion of 10%, implying that the rapeseed oil in this rejuvenator may reduce the effect of a high content SBS polymer.

According to AASHTO MP 19-10, to satisfy the extremely heavy traffic “E” grade, the maximum allowed nonrecoverable creep compliance at 3.2 kPa $J_{nr3.2}$ is 0.5 $kPa^{-1}$. As illustrated in Figure 11, except the rejuvenated bitumen samples with 20% Tall-L and 10% RP, all the other rejuvenated bitumen has met the requirement.

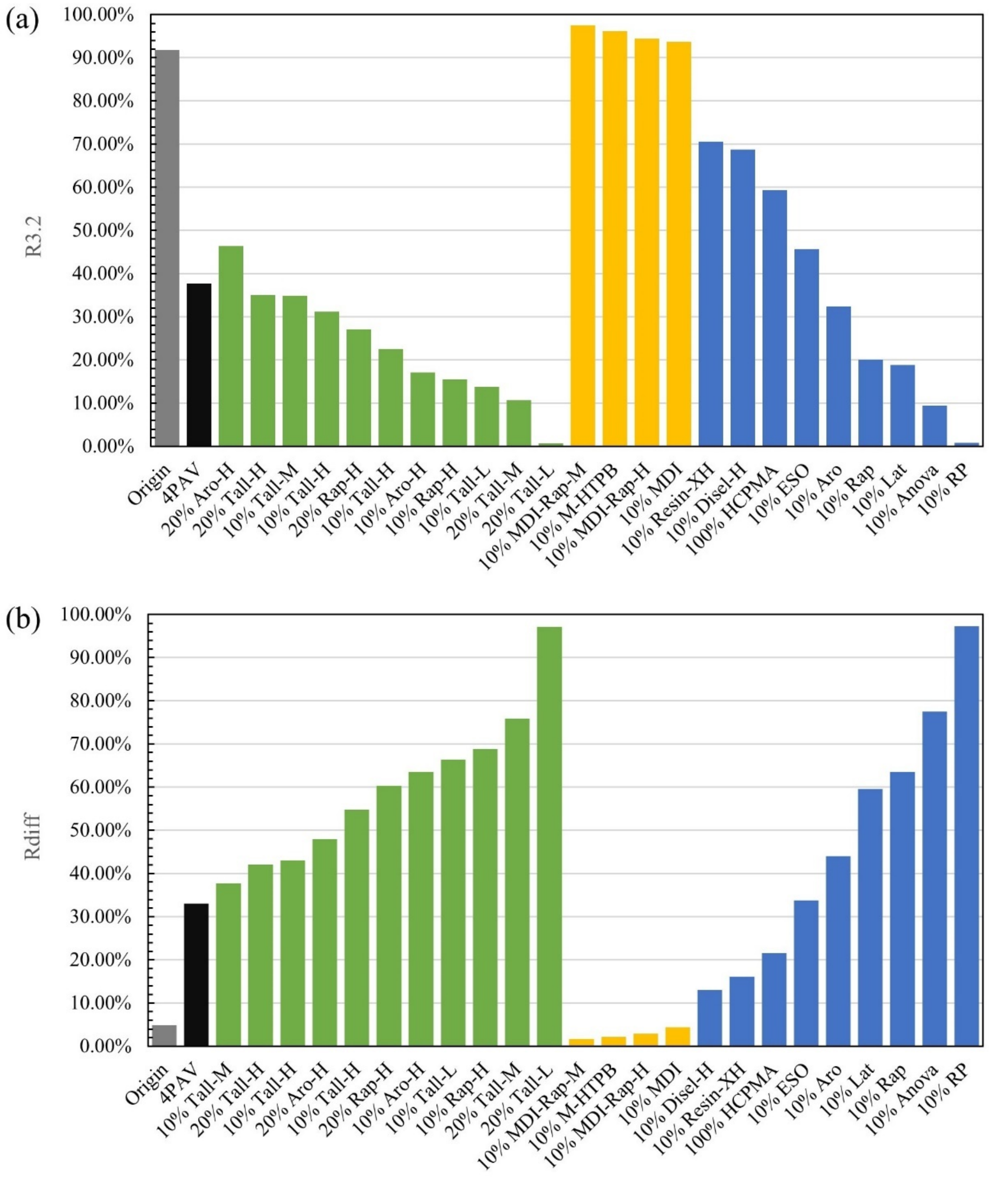



Figure 10. 70 °C MSCR results of origin, aged and rejuvenated bitumen samples, (a) average percent recovery at 3.2 kPa; (b) percent difference between average recovery at 0.1 kPa and 3.2 kPa.

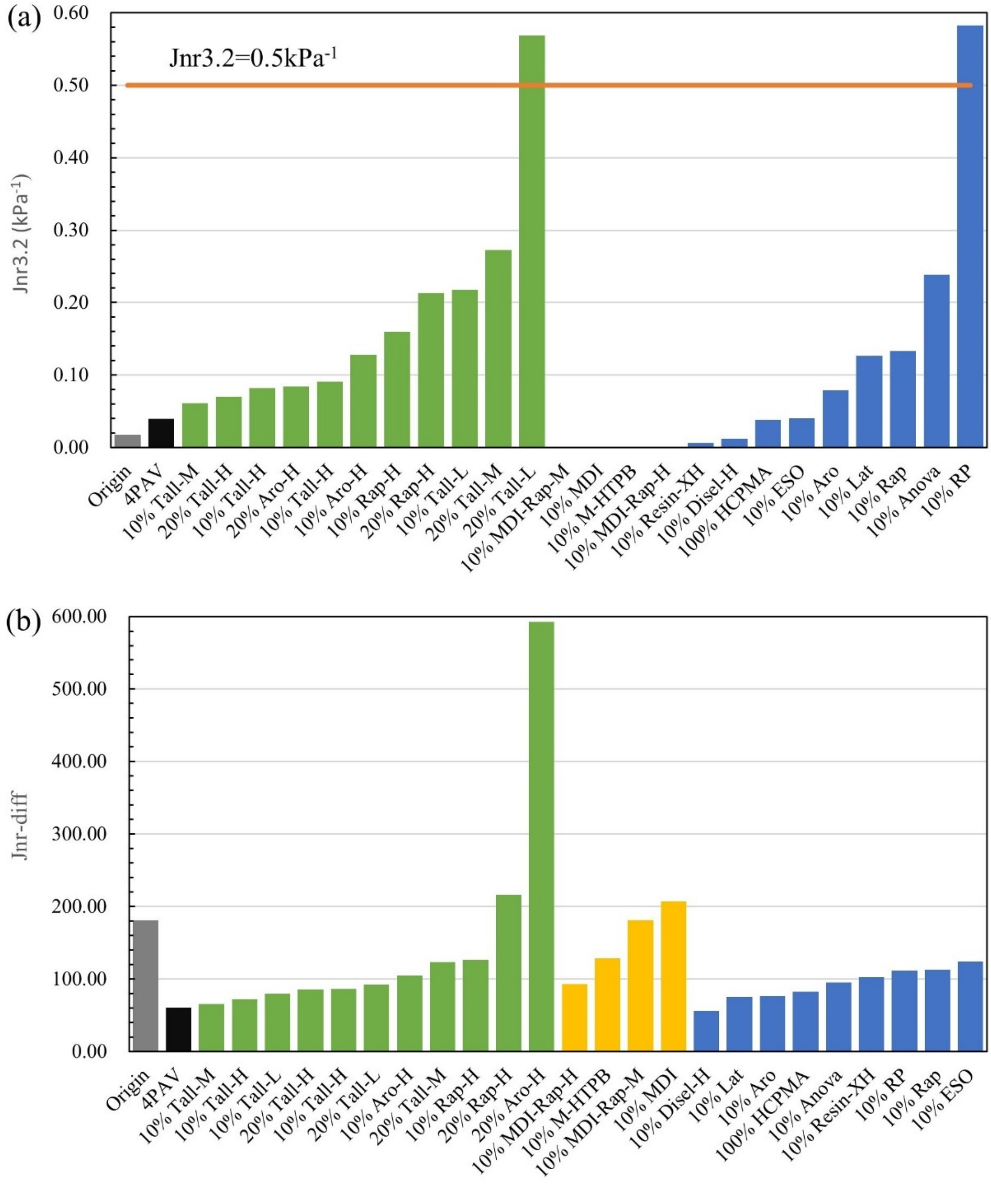



Figure 11. 70 °C MSCR results of origin, aged and rejuvenated bitumen samples, (a) nonrecoverable creep compliance at 3.2 kPa; (b) percent difference between nonrecoverable creep compliance at 0.1 kPa and 3.2 kPa.

The results of MSCR tests performed at 76 °C generally have the same pattern as at 70 °C, as demonstrated in Figure 12 and Figure 13. Overall, the MSCR performance of rejuvenated bitumen with physical or reference rejuvenators degrades as temperature rises, indicating that the bitumen softens and rutting resistance reduces. However, as for the chemical rejuvenators rejuvenated bitumen samples, the MSCR results showed good consistency as the temperature increased, implying that the high temperature performance of rejuvenated bitumen with chemical rejuvenators is very stable. Moreover, at the temperature of 76 °C, there are more samples that do not meet the AASHTO MP 19-10 extremely heavy traffic “E” grade $J_{nr3.2} \leq 0.5$ kPa$^{-1}$ requirement, as presented in Figure 13.

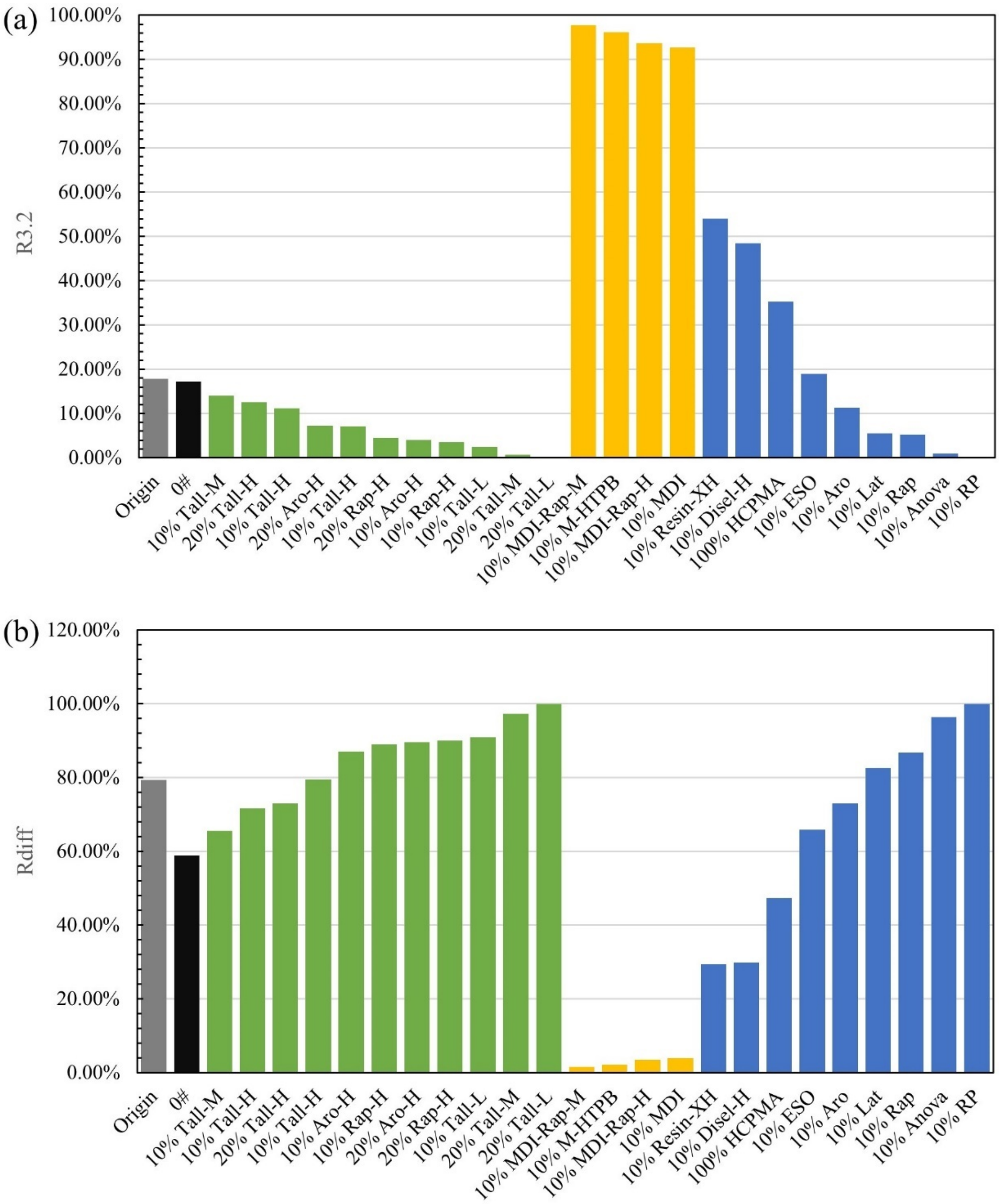



Figure 12. 76 °C MSCR results of origin, aged and rejuvenated bitumen samples, (a) average percent recovery at 3.2 kPa; (b) percent difference between average recovery at 0.1 kPa and 3.2 kPa.

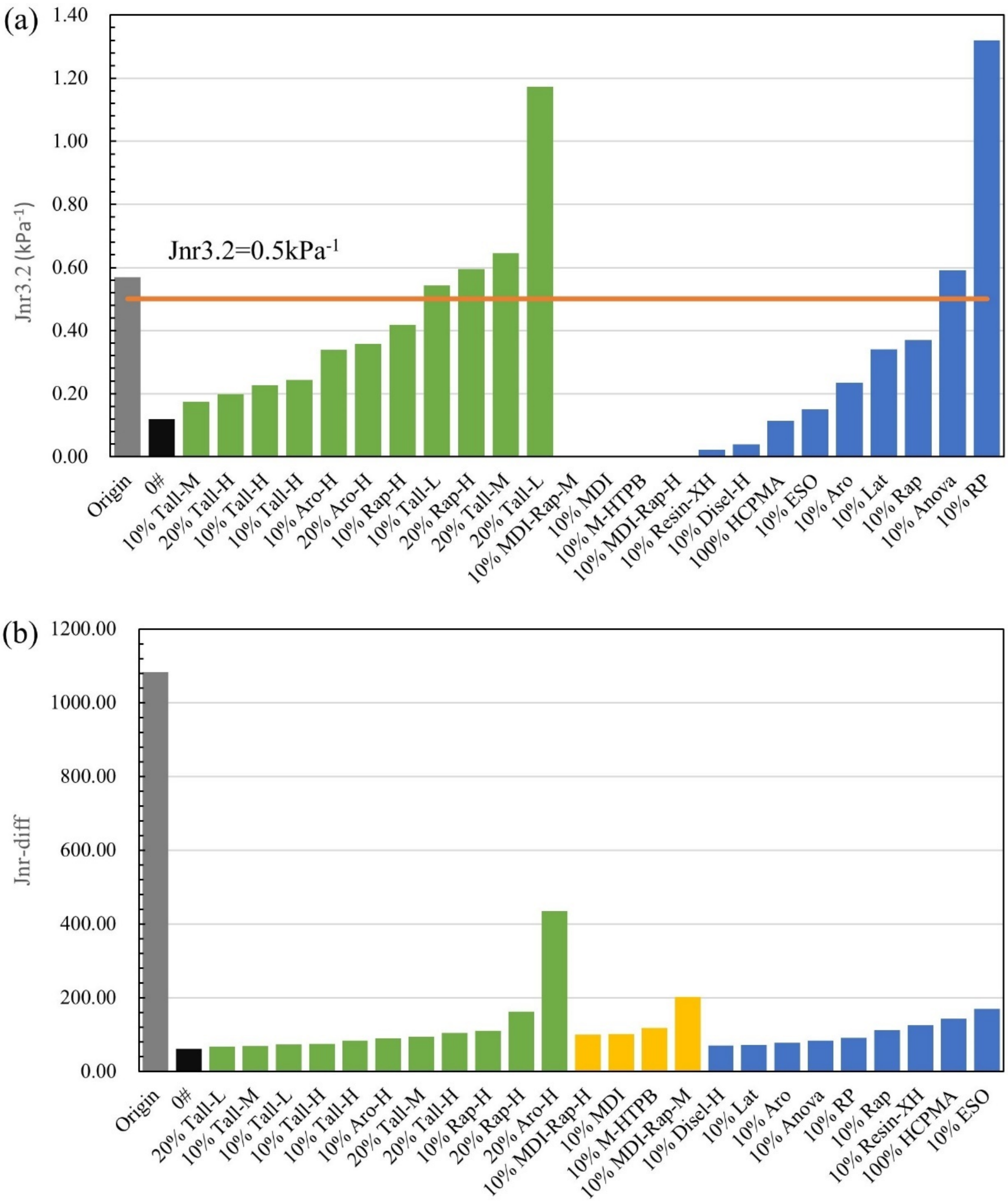



Figure 13. 76 °C MSCR results of origin, aged and rejuvenated bitumen samples, (a) nonrecoverable creep compliance at 3.2 kPa; (b) percent difference between nonrecoverable creep compliance at 0.1 kPa and 3.2 kPa.

### 3.3.3. Creep-Relaxation Analysis

Combine the results of maximum shear stress, time for stress reduced by 50% and 90% from the maximum respectively, as presented in Figure 14, Figure 15 and Figure 16, for pure oil based rejuvenators, the creep-relaxation performance of rejuvenated bitumen with RP1000 is better than rapeseed oil, followed by aromatic oil. In general, chemical rejuvenators performed less well in terms of maximum shear stress and stress reduction time, implying that rejuvenated bitumen treated with chemical rejuvenators would accumulate more stress at low temperatures, making it more prone to cracking. In the case of physical rejuvenators, increasing the SBS content will result in higher maximum shear stress and longer stress reduction time for the rejuvenated bitumen. In terms of oil types, physical rejuvenators containing aromatic oil perform worse in the creep-relaxation tests than tall oil and rapeseed oil. When it comes to proportion of physical rejuvenators, increasing it will reduce the maximum shear stress and stress reduction time, which should be attributed to the increased amount of oil added to the aged bitumen.

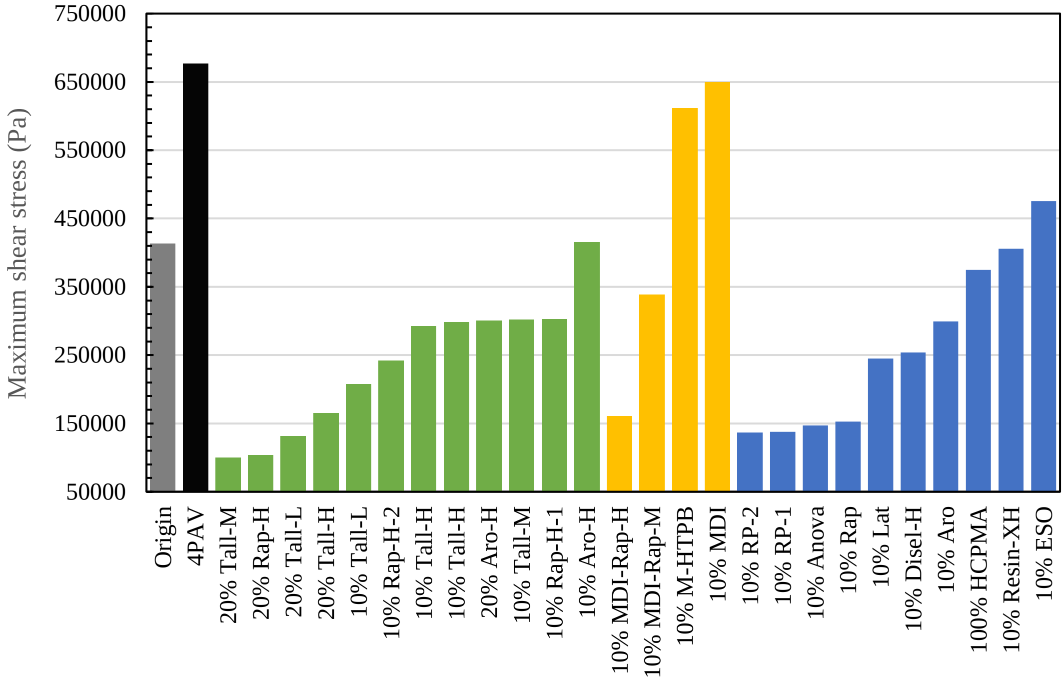



Figure 14. Maximum shear stress results of origin, aged and rejuvenated bitumen samples in creep-relaxation tests.

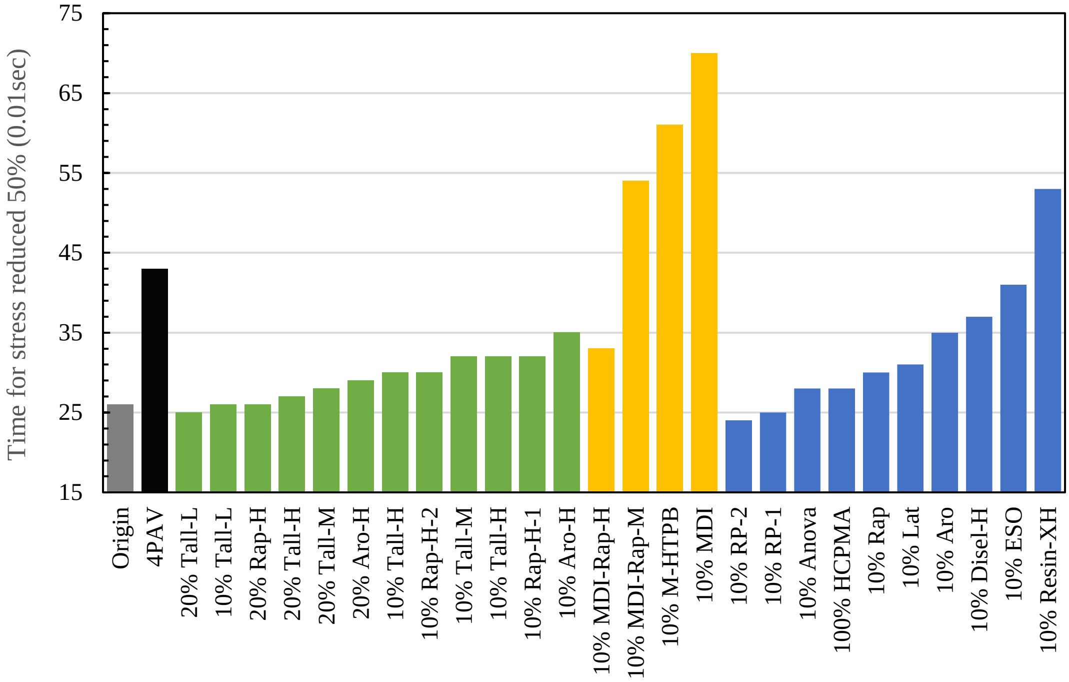



Figure 15. Time for stress reduced 50% from the maximum of origin, aged and rejuvenated bitumen samples in creep-relaxation tests.

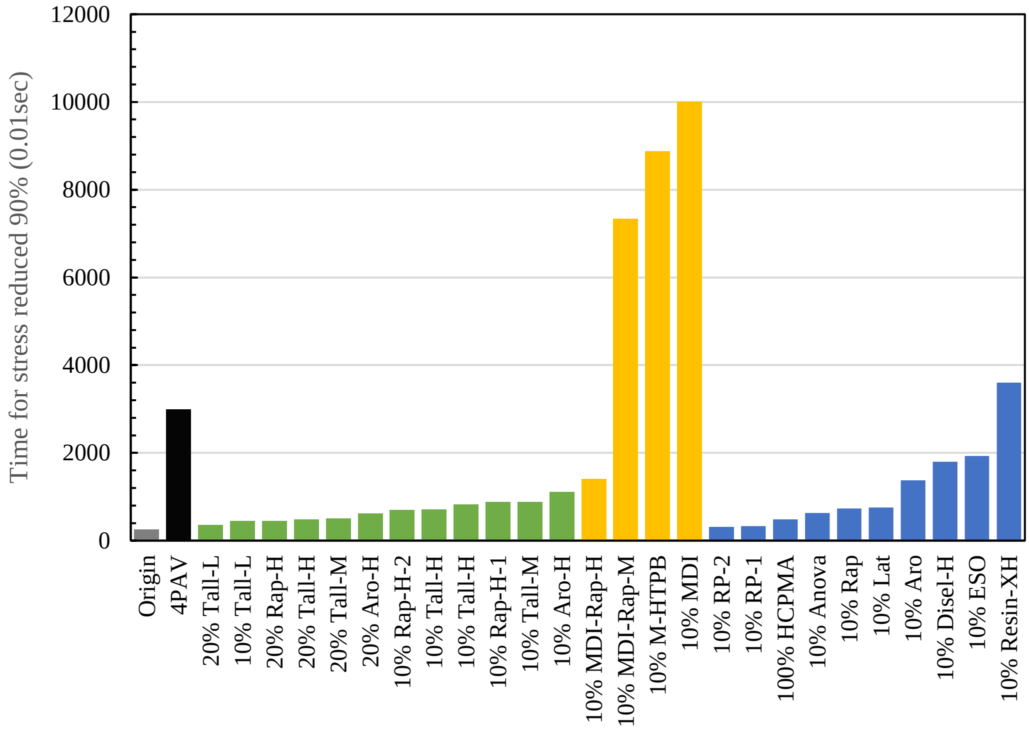



Figure 16. Time for stress reduced 90% from the maximum of origin, aged and rejuvenated bitumen samples in creep-relaxation tests.

### 3.3.4. Glover-Rowe Parameter Analysis

Overall, the G-R parameter analysis results followed the same pattern as the creep-relaxation results. As illustrated in Figure 17, pure oil based rejuvenators containing RP1000 have the smallest G-R parameter value, followed by rapeseed oil and aromatic oil. Furthermore, with the exception of the chemical rejuvenator including a high rapeseed oil content, the other three chemical rejuvenators rejuvenated bitumen samples have the highest G-R parameter value, indicating that they are more easily cracked. When it comes to physical rejuvenators, increasing the SBS content raises the G-R parameter value of the rejuvenated bitumen. In terms of oil types, rejuvenated bitumen with physical rejuvenators containing aromatic oil has a higher G-R parameter value than containing tall oil and rapeseed oil. Similar to the creep-relaxation analysis, a higher proportion of physical rejuvenators reduces the G-R parameter value, which should be attributed to the greater amount of oil added to the aged bitumen.

Moreover, according to Rowe, King and Anderson (2014), there are two criteria for the G-R parameters as follows:

$$\text{Damage onset: } G - R = 180\ kPa \tag{5}$$

$$\text{Significant cracking: } G - R = 450\ kPa \tag{6}$$

As demonstrated in Figure 17, most of the rejuvenated bitumen samples have fulfilled the above two criteria, except the samples rejuvenated with 10% M-HTPB, 10% MDI-Rap-M, 10% MDI and 10% Resin-XH. For these four samples, the G-R parameter for the first three chemical rejuvenator rejuvenated samples is beyond 450 kPa, and the G-R parameter for the last reference rejuvenator rejuvenated bitumen sample is slightly greater than 180 kPa.

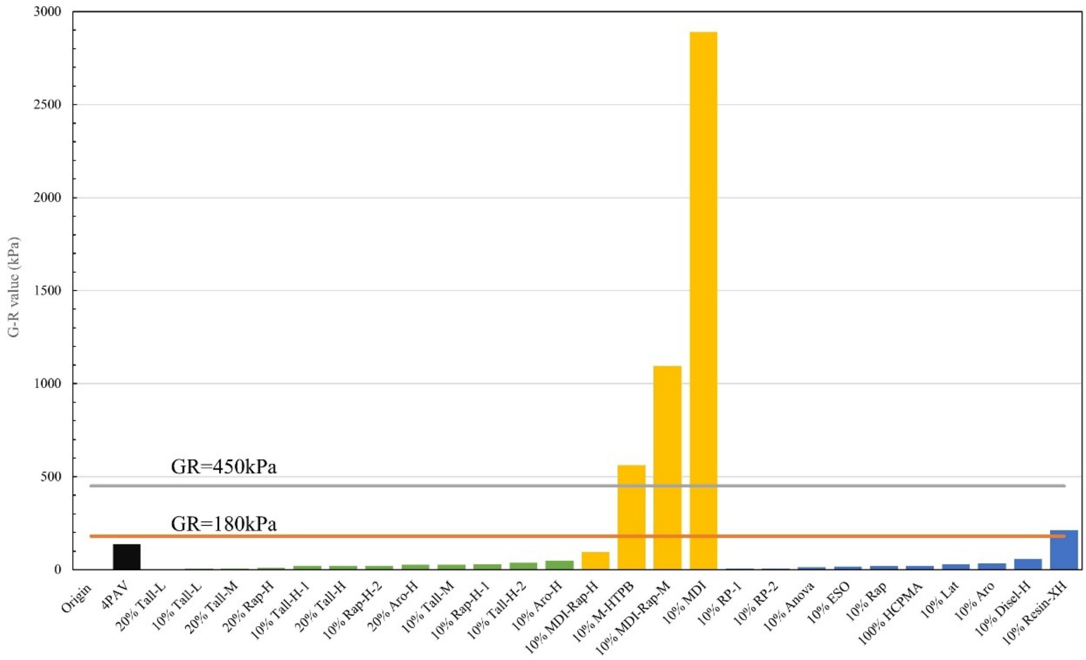



Figure 17. Glover-Rowe parameter calculation results of origin, aged and rejuvenated bitumen samples.

### 3.3.5. Linear Amplitude Sweep (LAS) Analysis

As illustrated in Figure 18 (a), rejuvenated bitumen by pure oil based rejuvenators with RP1000 have a longer fatigue life than rapeseed oil, followed by aromatic oil. The fatigue life performance of aged bitumen rejuvenated with chemical rejuvenators is not ideal, particularly at high strains, owing to the chemical rejuvenators making the bitumen too hard (Figure 18 (b)). For physical rejuvenators, the higher the SBS content, the shorter the fatigue life of rejuvenated bitumen (Figure 18 (c)). The fatigue life of rejuvenated bitumen is also affected by the different oils in the physical rejuvenators. As demonstrated in Figure 18 (d), the fatigue life of rejuvenated bitumen using a rejuvenator with added aromatic oil was the worst, followed by tall oil and rapeseed oil. In terms of rejuvenator proportion, the fatigue life will increase as the proportion of physical rejuvenators increases, owing to the bitumen becoming softer as more oil is added in (Figure 18 (c) & (d)).

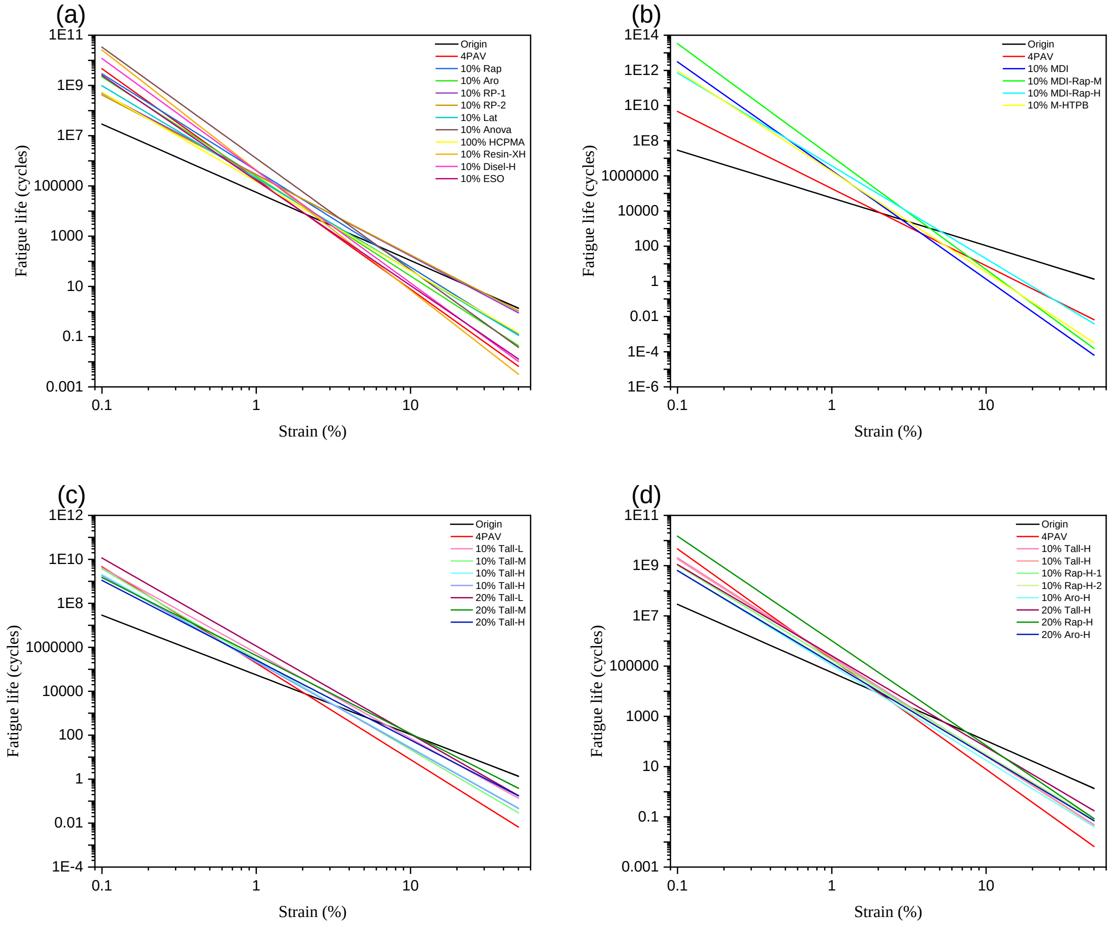



Figure 18. Fatigue life results of origin, aged and rejuvenated bitumen samples, (a) rejuvenated bitumen with reference rejuvenators; (b) rejuvenated bitumen with chemical rejuvenators; (c) rejuvenated bitumen with physical rejuvenators in different SBS content; (d) rejuvenated bitumen with physical rejuvenators in different oil type.

Moreover, for origin, aged and different rejuvenated bitumen samples, the A and B parameters from the bitumen fatigue performance model as indicated in AASHTO TP 101-14 were also compared in Figure 19 and Figure 20 below.

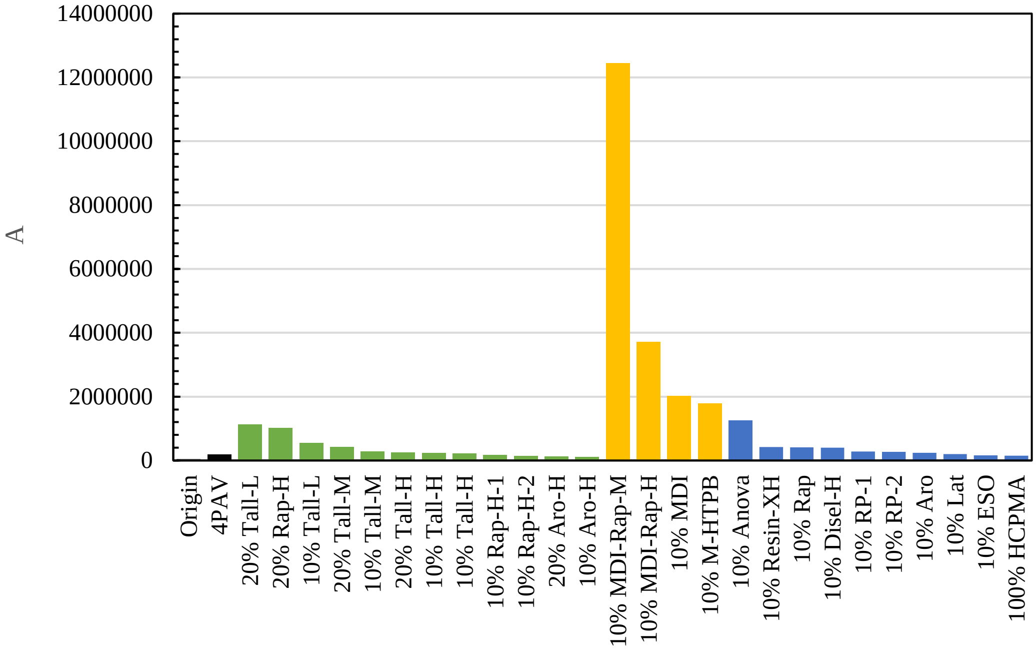



Figure 19. Parameter "A" value from the bitumen fatigue performance model of origin, aged and rejuvenated bitumen samples.

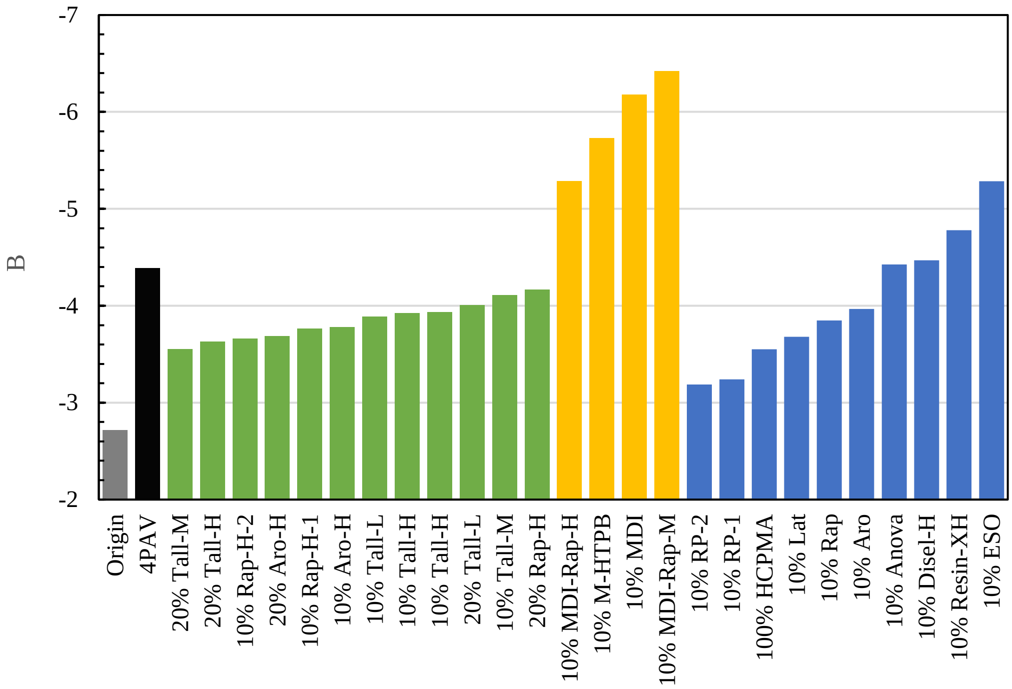



Figure 20. Parameter "B" value from the bitumen fatigue performance model of origin, aged and rejuvenated bitumen samples.

In addition, the fatigue performance parameters $N_f$ at 30% strain level of origin, aged and rejuvenated bitumen samples were calculated according to AASHTO TP 101-14 and the results are shown in Figure 21 below.

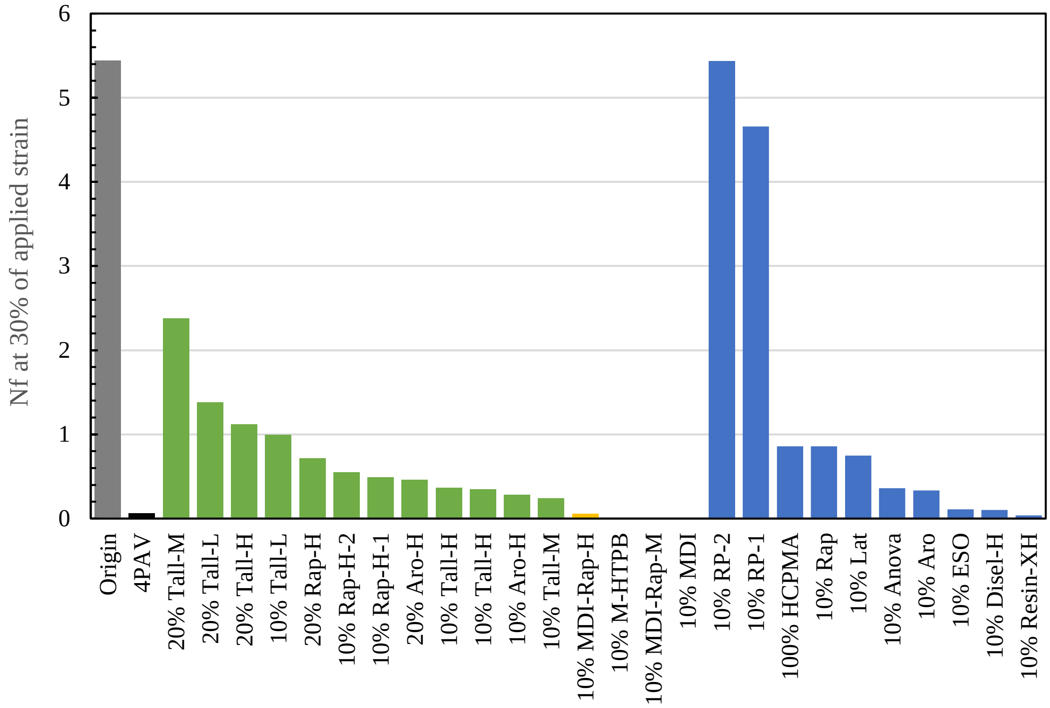



Figure 21. Fatigue performance parameter $N_f$ at 30% strain level of origin, aged and rejuvenated bitumen samples.

Parameter "A" represents the fatigue performance at low strain levels, as illustrated in Figure 19, the larger the "A" value, the better the fatigue performance. It can be seen that for rejuvenated bitumen with pure oil based rejuvenators, the fatigue performance is better with rapeseed oil, followed by RP1000 and aromatic oil. Under this evaluation index, rejuvenated bitumen using chemical rejuvenators shines brightly, and its "A" value is higher than that of other rejuvenator types. In the case of physical rejuvenators, increased SBS content reduces fatigue performance, and physical rejuvenators containing aromatic oil perform worse than tall oil and rapeseed oil. As for the proportions, raising the physical rejuvenators proportion will improve the fatigue performance of the rejuvenated bitumen.

The fatigue performance at high strain levels can be represented with parameter "B" and fatigue performance parameter $N_f$ at 30% strain level, as demonstrated in Figure 20 and Figure 21, the larger the "B" value and the $N_f$ value, the better the fatigue performance. At high strain levels, the fatigue performance of rejuvenated bitumen with pure oil based rejuvenators is best with RP1000, followed by rapeseed oil and aromatic oil. The rejuvenated bitumen with chemical rejuvenators does not achieve ideal results for both parameter "B" and fatigue performance parameter $N_f$. When it comes to physical rejuvenators, the outcomes become more complicated. For SBS polymer content in the physical rejuvenators, at 10% rejuvenator proportion, rejuvenated bitumen with low SBS content rejuvenator performed best, and at 20% rejuvenator proportion, rejuvenated bitumen with medium SBS content rejuvenator performed best.

As for the effect of different oil types, at 10% rejuvenator proportion, rejuvenated bitumen with physical rejuvenators containing rapeseed oil performed best, and at 20% rejuvenator proportion, rejuvenated bitumen with physical rejuvenators containing tall oil performed best. When the physical rejuvenators proportion increased from 10% to 20%, the parameter “B” value increased for rejuvenators containing aromatic oil and tall oil with medium and high SBS content, and decreased for rejuvenators containing rapeseed oil and tall oil with low SBS content. For the fatigue performance parameter $N_f$, as the physical rejuvenators proportion increased from 10% to 20%, all the rejuvenated bitumen improved their performance.

The damage curves of viscoelastic continuum damage (VECD) mechanics were plotted in Figure 22 below. For the VECD damage curves, rejuvenated bitumen sample is considered good performance if the decline is gradual and the C value remains high near the end point. It can be seen that for rejuvenated bitumen with pure oil based rejuvenators, the performance is better with RP1000, followed by rapeseed oil and aromatic oil (Figure 22 (a)). With this evaluation criteria, the performance of aged bitumen rejuvenated with chemical rejuvenators is not ideal (Figure 22 (b)). When it comes to physical rejuvenators, higher SBS content increases performance (Figure 22 (c)), and physical rejuvenators containing rapeseed oil outperform tall oil, followed by aromatic oil (Figure 22 (d)). In terms of proportions, increasing the proportion of physical rejuvenators will improve the performance of the rejuvenated bitumen (Figure 22 (c) & (d)).

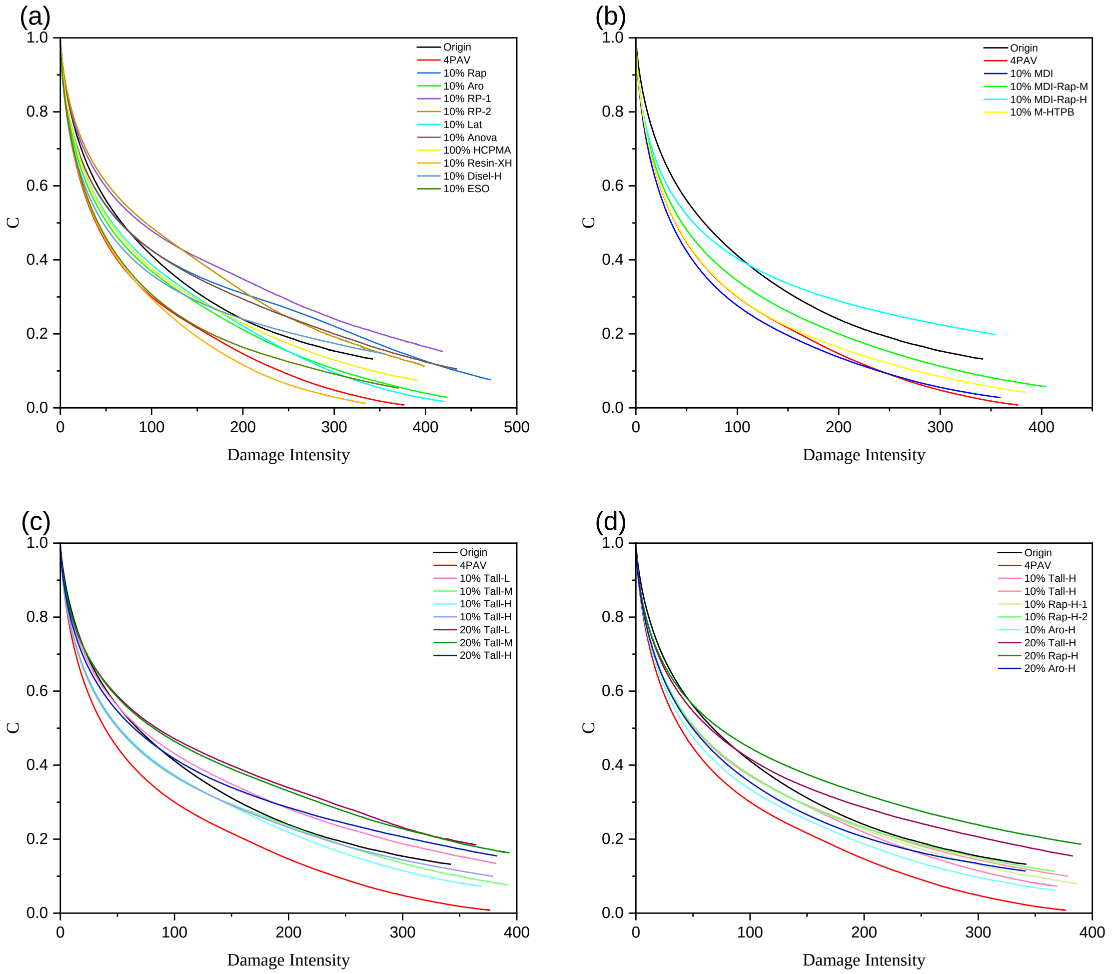



Figure 22. VECD damage curve results of origin, aged and rejuvenated bitumen samples, (a) rejuvenated bitumen with reference rejuvenators; (b) rejuvenated bitumen with chemical rejuvenators; (c) rejuvenated bitumen with physical rejuvenators in different SBS content; (d) rejuvenated bitumen with physical rejuvenators in different oil type.

The stress and strain results from the LAS amplitude sweep tests were plotted in Figure 23 below. Rejuvenated bitumen by pure oil based rejuvenators with RP1000 performs better as it has a higher stress at a larger strain level, followed by rapeseed oil and aromatic oil (Figure 23 (a)). As demonstrated in Figure 23 (b), rejuvenated bitumen with chemical rejuvenators performs well, particularly 10% MDI-Rap-H, which has a very flat curve and retains relatively high stress even at large strains. In the case of physical rejuvenators, higher SBS content improves performance (Figure 23 (c)), and physical rejuvenators containing aromatic oil outperform tall oil, followed by rapeseed oil (Figure 23 (d)). In terms of proportions, increasing the proportion of physical rejuvenators reduces the performance of the rejuvenated bitumen (Figure 23 (c) & (d)).

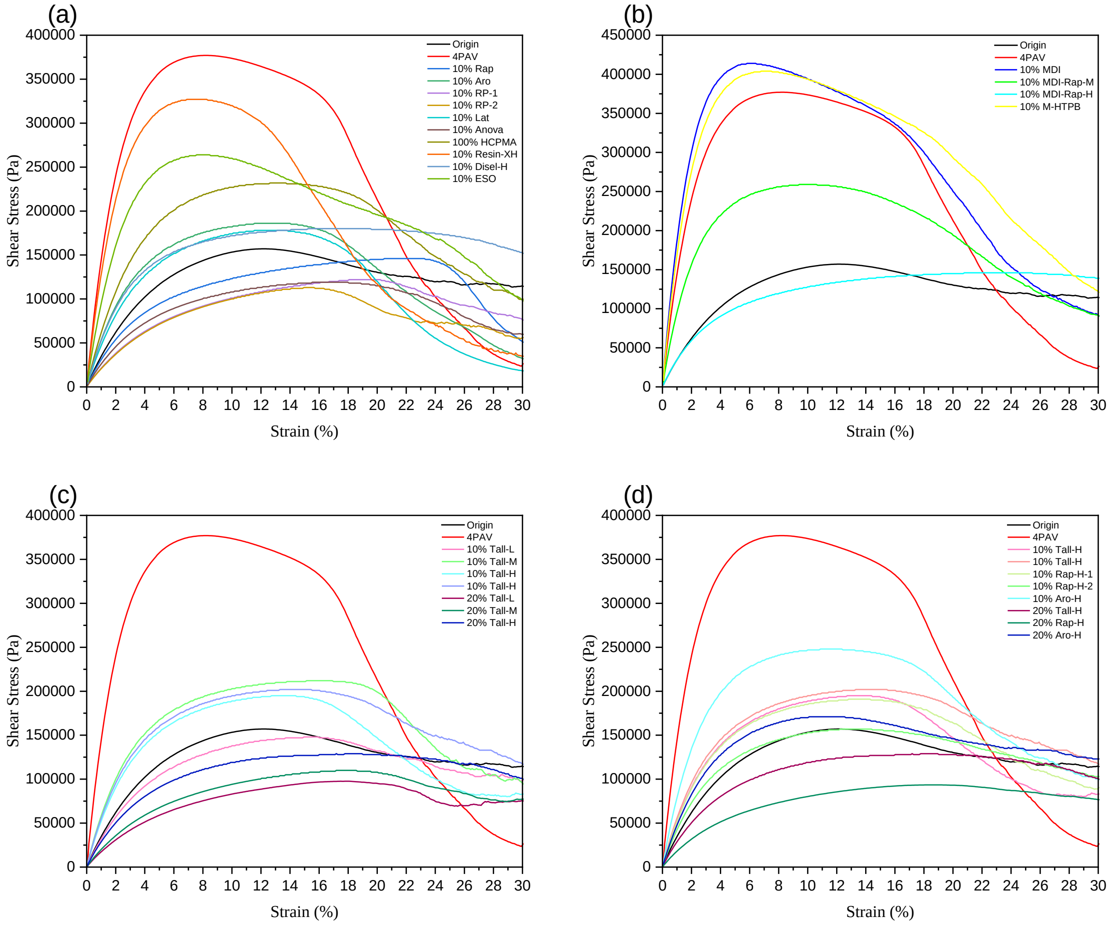



Figure 23. Stress and strain curves from LAS amplitude sweep results of origin, aged and rejuvenated bitumen samples, (a) rejuvenated bitumen with reference rejuvenators; (b) rejuvenated bitumen with chemical rejuvenators; (c) rejuvenated bitumen with physical rejuvenators in different SBS content; (d) rejuvenated bitumen with physical rejuvenators in different oil type.

### 3.3.6. Fracture Index Analysis

The crack growth rate ($da/dN$) against the crack length $a$ curves of aged and rejuvenated bitumen samples were plotted in Figure 24 below, and the results of crack length at failure $a_f$ for different samples were summarized in Figure 25. According to Hintz's (2012) theory, a longer crack length indicates better fatigue performance because it implies that the bitumen sample can withstand more load cycles before failing. Unfortunately, most rejuvenated bitumen samples perform worse than aged bitumen under such evaluation criteria. As demonstrated in Figure 25, the rejuvenated bitumen by pure oil based rejuvenators with rapeseed oil has better performance, followed by aromatic oil and RP1000. Overall, the chemical rejuvenators rejuvenated bitumen performed well, with two of them outperforming the aged bitumen. In the case of physical rejuvenators, higher SBS content improves performance, and physical rejuvenators containing aromatic oil outperform tall oil and rapeseed oil. In terms of proportions, when the physical rejuvenators proportion increased from 10% to 20%, the performance increased for rejuvenators containing aromatic oil and tall oil with high SBS content, and decreased for rejuvenators containing rapeseed oil and tall oil with medium or low SBS content. This part may indicate that a stiffer bitumen will have a better performance in the fracture index analysis.

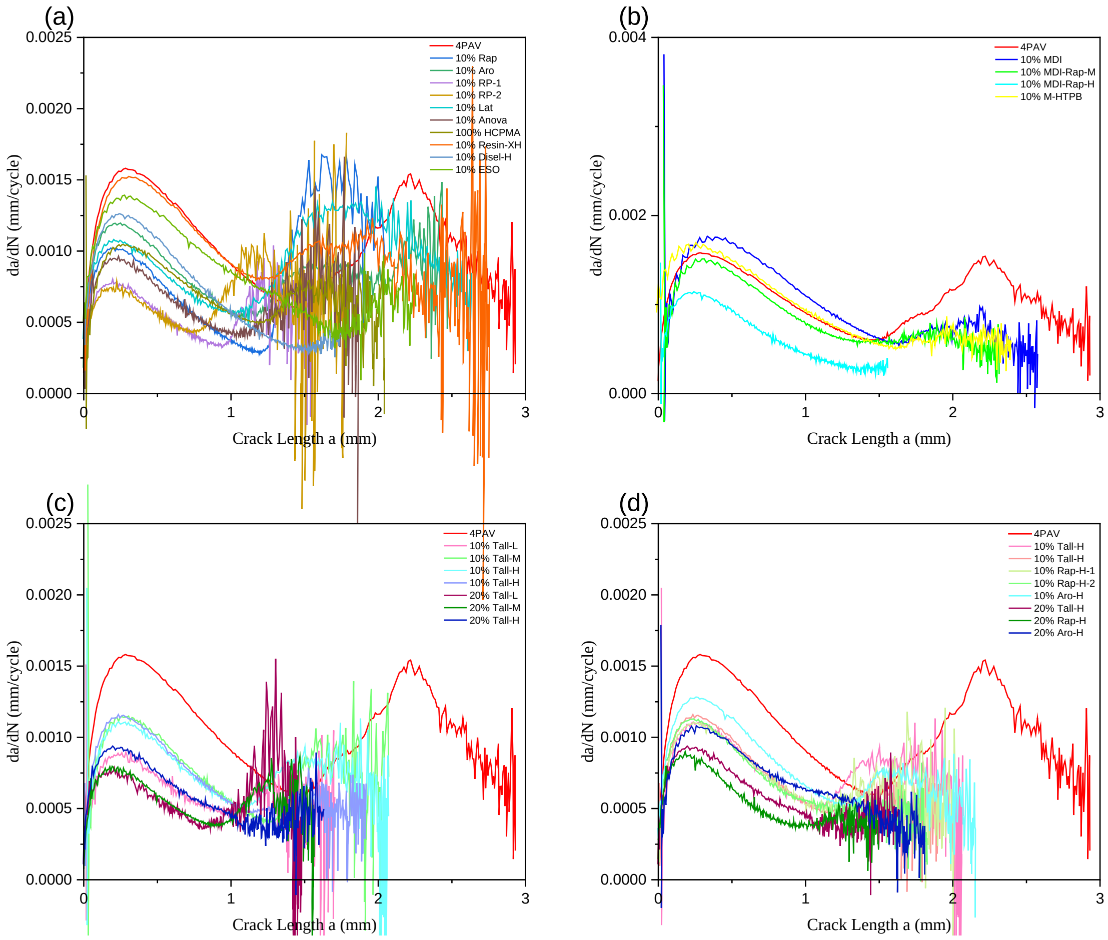



Figure 24. Crack length curves of aged and rejuvenated bitumen samples, (a) rejuvenated bitumen with reference rejuvenators; (b) rejuvenated bitumen with chemical rejuvenators; (c) rejuvenated bitumen with physical rejuvenators in different SBS content; (d) rejuvenated bitumen with physical rejuvenators in different oil type.

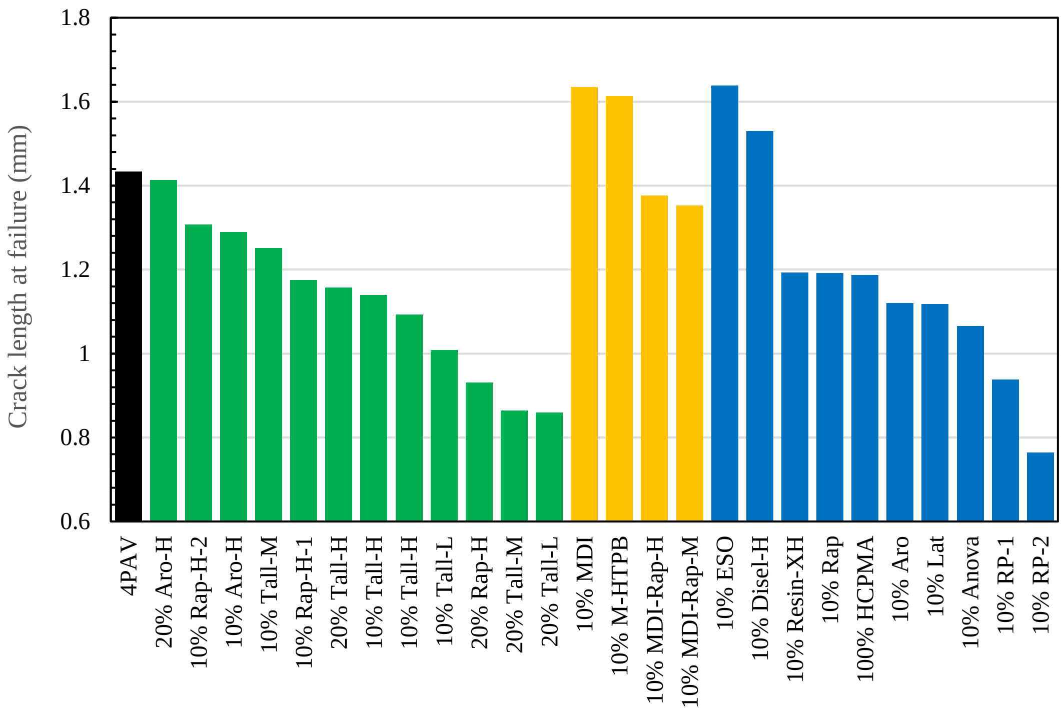



Figure 25. Crack length at failure results of aged and rejuvenated bitumen samples.

## 3.4. Conclusion

In conclusion, the effect of rejuvenators on rheological properties of aged SBS modified bitumen can be divided into two categories – high temperature performance and low temperature performance.

For high temperatures, ideally, the bitumen should have excellent hardness or elasticity to ensure its rutting resistance. According to the experimental results, when compared to the physical and reference rejuvenators used in this project, the rejuvenated bitumen using chemical rejuvenators demonstrated excellent performance at high temperatures, which is unmatchable for other rejuvenators. When it comes to the pure oil based rejuvenators, rejuvenated bitumen with aromatic oil generally outperforms rapeseed oil and RP1000, which is largely attributable to low molecular weight oil include rapeseed oil and RP1000 making the aged bitumen too soft and viscous. In the case of physical rejuvenators, raising the SBS content will make the rejuvenated bitumen more elastic, thus improving its high temperature performance. The effect of oil types and proportions of physical rejuvenators on the high temperature performance is a little complicated. For the physical rejuvenators with low or medium SBS content, increasing the rejuvenator proportion will reduce the high temperature performance, indicating that the oil is currently dominant. For the physical rejuvenators with high SBS content, raising the rejuvenator proportion will improve the high temperature performance, implying that the SBS currently has a lead role. That being said, increasing the rejuvenator proportion in physical rejuvenators containing rapeseed oil and a high SBS content barely affects the high temperature performance, possibly because the high viscosity of rapeseed oil has defused the effect of the high SBS content.

For low temperatures, the viscous properties of bitumen must be improved in order to maintain good cracking resistance and fatigue resistance. As expected, the low temperature performance of rejuvenated bitumen with chemical rejuvenators is not ideal in general, the main reason is that the chemical rejuvenators make the rejuvenated bitumen too hard. In the case of pure oil based rejuvenators, rejuvenated bitumen with RP1000 performs better than rapeseed oil, followed by aromatic oil, indicating that low molecular weight oil could improve the low temperature performance. When it comes to physical rejuvenators, higher SBS content in the physical rejuvenators may reduce the cracking resistance while partially improving the fatigue resistance of rejuvenated bitumen. As for different oil types in physical rejuvenators, rejuvenated bitumen by physical rejuvenators containing aromatic oil has the worst low temperature performance overall, followed by tall oil and rapeseed oil. Finally for the rejuvenators proportion, raising the proportion in rejuvenated bitumen improves cracking and fatigue performance across most evaluation indices.

In accordance with the above summary, the effect of rejuvenators on the rheological properties of aged bitumen varies with temperature, which also reflects the viscoelastic characteristics of bitumen. Based on the current findings, while the chemical rejuvenators perform admirably at high temperatures, they still need to be improved at low temperatures. The pattern at high and low temperatures is exactly the opposite for pure oil based rejuvenators, reflecting the different needs at various temperatures. As for the physical rejuvenators, it is necessary to continue adjusting the rejuvenators' formula until a perfect temperature-performance balance is achieved.

# 4. Effects of Rejuvenators on Chemical Properties of Aged SBS Modified Bitumen

## 4.1. Introduction

The performance of rejuvenated bitumen is closely related to the proportions, contents, and types of rejuvenators, based on the results of rheological tests. Furthermore, the SBS segment and polymer network structure in SBS modified bitumen is critical to the performance (Cai *et al.*, 2019). The waste bitumen will not be fully utilized if the rejuvenator is unable to restore the SBS content and reconstruct the polymer network structure (Han *et al.*, 2021). To observe a variety of chemical properties of rejuvenated bitumen, including SBS polymer chemical structure, using FTIR (Fourier transform infrared) is the most convenient solution.

## 4.2. Experimental Method

The FTIR tests were conducted on a Thermo Fisher FTIR equipment with attenuated total reflection (ATR) mode. The scan range is from 4000 to 400 $cm^{-1}$, with a 4 $cm^{-1}$ resolution and 32 scan numbers. The FTIR test results were analysed with OMNIC software.

## 4.3. Results and Discussion

Figure 26 presents the FTIR spectrum of aged and rejuvenated bitumen samples with reference rejuvenators. 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 (Castro and Vazquez, 2009). The 1600 $cm^{-1}$ peak next to them corresponds to the aromatic C=C stretching vibration (Gaweł, Eftekhardadkhah and Øye, 2014). As illustrated in Figure 26, for bio-oil based rejuvenators including rapeseed 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 functional group and stretching vibration of the C-O ester groups, respectively (Vlachos *et al.*, 2006). 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 (Luo *et al.*, 2020).

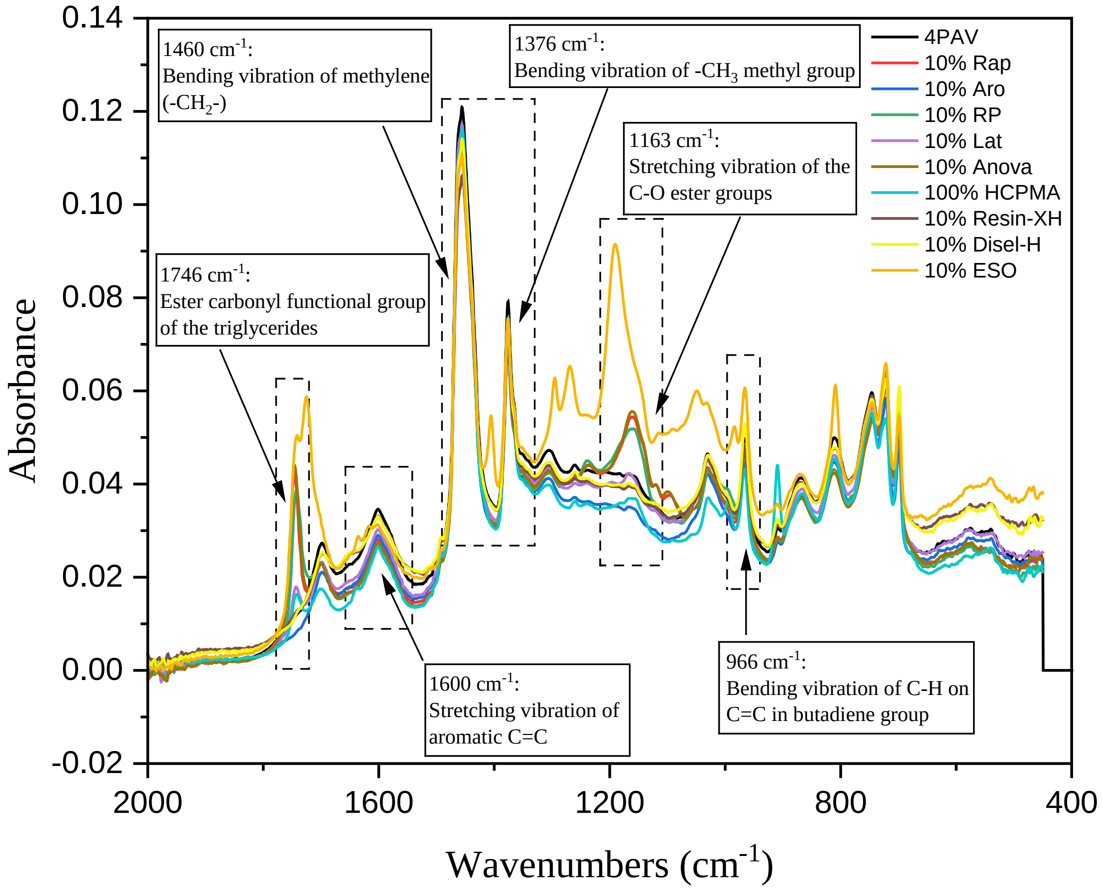



Figure 26. FTIR spectrum of aged and rejuvenated bitumen samples with reference rejuvenators.

All of the absorption peaks mentioned above, including peaks at 1746, 1600, 1460, 1376, 1163, and 966 $cm^{-1}$, were seen again in the rejuvenated bitumen samples with physical rejuvenators, as illustrated in Figure 27 (a). Moreover, as demonstrated in Figure 27 (b), after adding physical rejuvenators containing SBS polymer, the polybutadiene group peak of rejuvenated bitumen has a significant height increase. Furthermore, 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 (Vlachos *et al.*, 2006). 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 illustrated in the following equation.

$$I_{PB} = \frac{A_{966}}{A_{1460} + A_{1376}} \tag{7}$$

The results of $I_{PB}$ of aged and rejuvenated bitumen samples with various rejuvenators were presented in Figure 29.

As illustrated in Figure 29, the polybutadiene group index $I_{PB}$ rose dramatically after adding the physical rejuvenators containing SBS, and it continued to increase as the proportion of the rejuvenator or the content of SBS in the rejuvenator was increased.

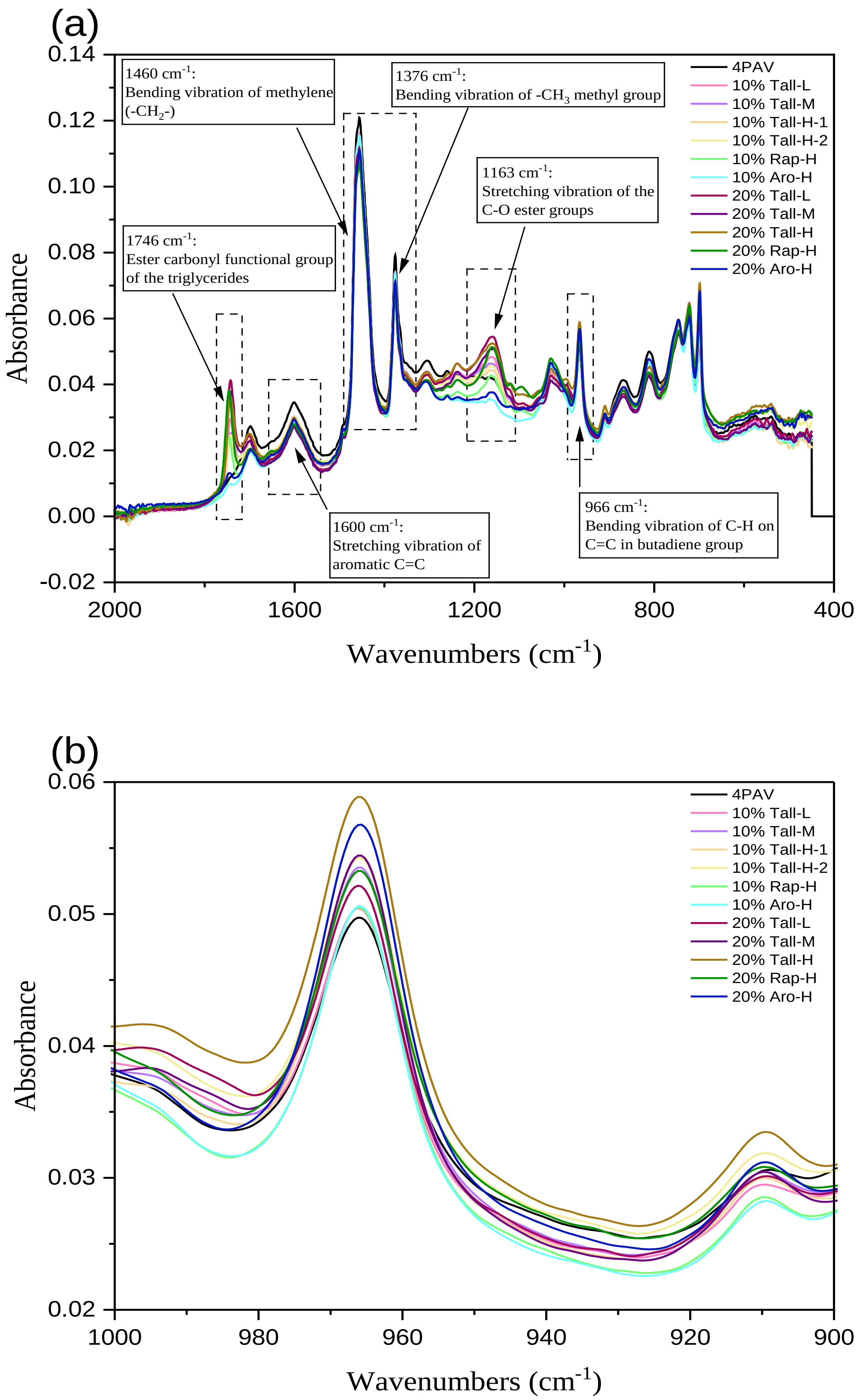
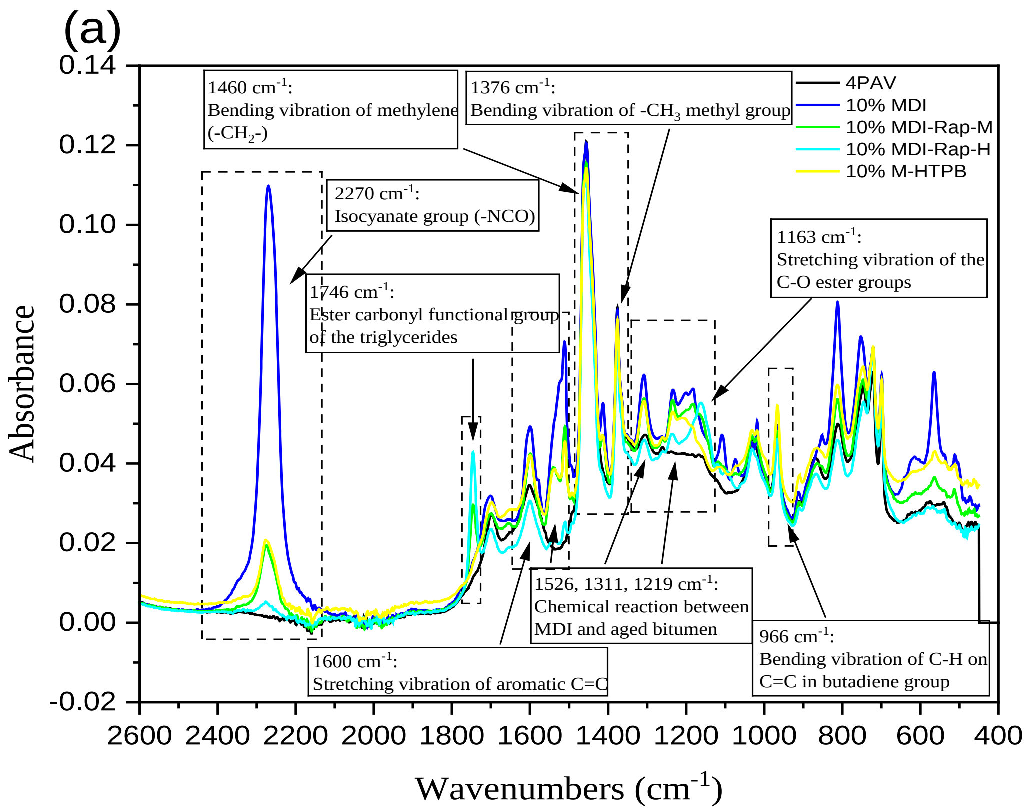



Figure 27. (a) FTIR spectrum of aged and rejuvenated bitumen samples with physical rejuvenators; (b) FTIR spectrum of butadiene group in aged and rejuvenated bitumen samples with physical rejuvenators.

In the case of rejuvenated bitumen with chemical rejuvenators, as illustrated in Figure 28 (a), beyond the absorption peaks mentioned earlier, some new peaks have shown up. The first one is at 2270 $cm^{-1}$, it is related to the isocyanate group (-NCO) in the MDI, which can be used as a characteristic peak for this chemical compound (Han *et al.*, 2022). The peak at 1526 $cm^{-1}$ is associated with the bending vibration of the N-H bond from the amide bond (Xu, Yu, Zhang, Cao, Gu, *et al.*, 2017). 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 (Xu, Yu, Zhang, Cao, Gu, *et al.*, 2017). More importantly, as demonstrated in Figure 28 (b), the appearance of these three absorption peaks confirmed the chemical reactions between MDI and degraded SBS (Xu, Yu, Zhang, Cao, Gu, *et al.*, 2017). Furthermore, as presented in Figure 29, the polybutadiene group index $I_{PB}$ of rejuvenated bitumen with chemical rejuvenators increases significantly, indicating that the chemical compounds in the chemical rejuvenators have successfully connected the fracture SBS polymer segment.



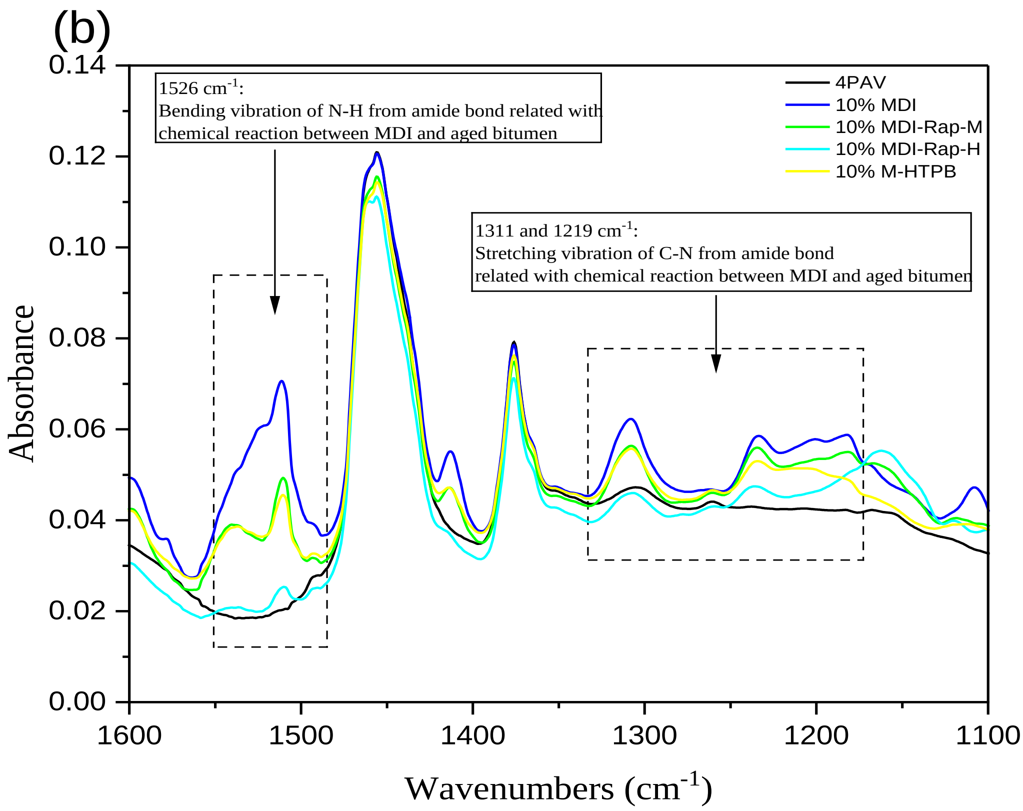




Figure 28. (a) FTIR spectrum of aged and rejuvenated bitumen samples with chemical rejuvenators; (b) FTIR spectrum of peaks caused by chemical reactions between MDI and aged bitumen in aged and rejuvenated bitumen samples.

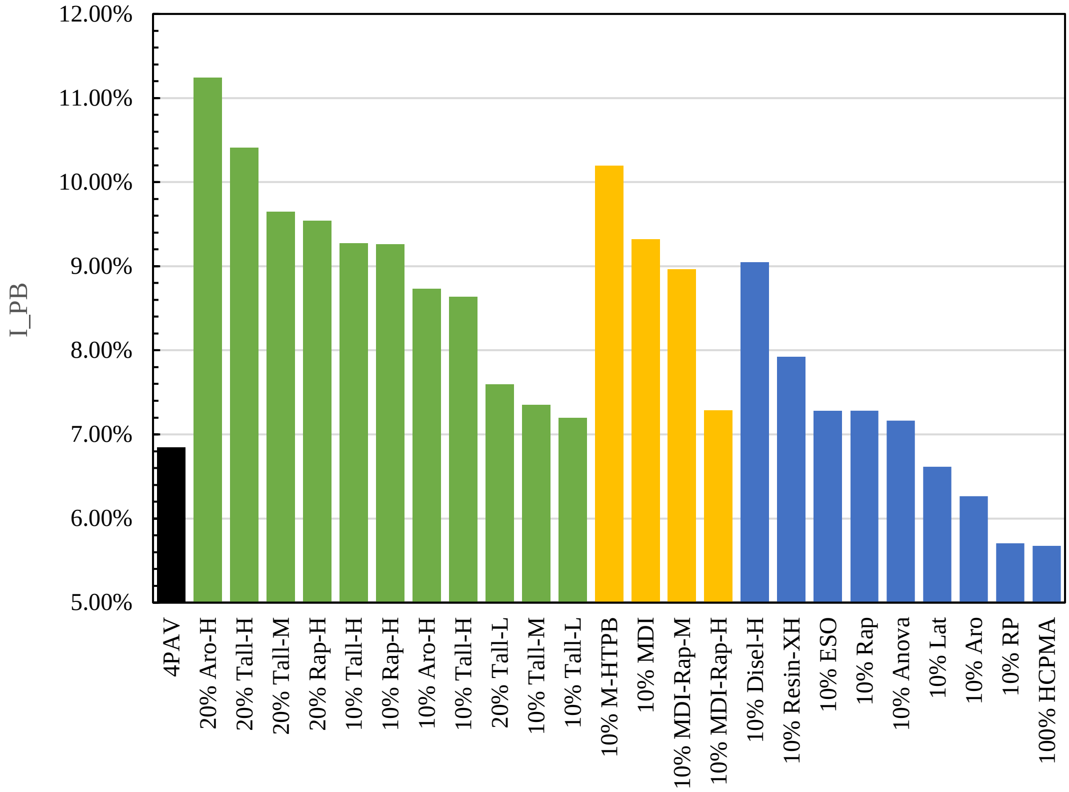



Figure 29. Polybutadiene group index $I_{PB}$ of aged and rejuvenated bitumen samples.

## 4.4. Conclusion

In this chapter, some characteristic absorption peaks in FTIR spectrum of aged and rejuvenated bitumen samples were identified and the polybutadiene group index $I_{PB}$ was calculated for different samples.

Based on the spectrum results, absorption peaks at 1746 and 1163 $cm^{-1}$ can be used as characteristic peaks to identify bio-oil content in rejuvenators. The summarized area of high absorption peaks at 1460 and 1376 $cm^{-1}$ was used as a standard reference value to calculate the polybutadiene group index $I_{PB}$ with the area of the polybutadiene group peak at 966 $cm^{-1}$. In the case of rejuvenated bitumen with physical rejuvenators, when compared to the aged bitumen sample, $I_{PB}$ of rejuvenated bitumen increases significantly, and the index continues to rise as the proportion of the rejuvenator or the content of SBS in the rejuvenators increases. When it comes to rejuvenated bitumen with chemical rejuvenators, some new characteristic absorption peaks have shown up, including the peak at 2270 $cm^{-1}$ associated with the isocyanate group (-NCO) in the MDI (Han *et al.*, 2022). Moreover, the new group of peaks at 1526, 1311 and 1219 $cm^{-1}$ are related to the chemical reactions between MDI and degraded SBS polymer, beyond that, the increased $I_{PB}$ of rejuvenated bitumen with chemical rejuvenators proved that MDI has successfully connected the fracture SBS polymer segment (Xu, Yu, Zhang, Cao, Gu, *et al.*, 2017).

# 5. Conclusion and Suggestion

In this research project, TFOT and PAV were used on the SBS modified bitumen for short-term aging and long-term aging, respectively. Various types and proportions of reference rejuvenators, physical rejuvenators, and chemical rejuvenators were used to rejuvenate the aged bitumen. By conducting DSR tests and FTIR tests on the aged and rejuvenated bitumen samples to study the rheological and chemical properties, the effect of different types and proportions of rejuvenators can be compared, and the following conclusions were reached:

- The rejuvenation effects of pure oil based rejuvenators are closely related to environmental temperature and oil molecular weight. In high temperatures, rejuvenated bitumen with large molecular weight oil such as aromatic oil has better rutting resistance. In low temperatures, rejuvenated bitumen with small molecular weight oil such as rapeseed oil and RP1000 has better cracking and fatigue resistance.

- In the case of chemical rejuvenators, compared with reference and physical rejuvenators used in this project, the rejuvenated bitumen using chemical rejuvenators demonstrated unrivalled performance at high temperatures. Unfortunately, the low temperature performance of rejuvenated bitumen with chemical rejuvenators is not preferable in general, with poor cracking and fatigue resistance at most evaluation indexes, given that the chemical rejuvenators harden the rejuvenated bitumen too much.

- When it comes to the SBS content in physical rejuvenators, at high temperatures, increasing the SBS content makes the rejuvenated bitumen more elastic, which improves rutting resistance. At low temperatures, higher SBS content reduces the cracking resistance but partially improves the fatigue resistance of the rejuvenated bitumen under some evaluation indexes.

- In terms of various oil types and proportions for physical rejuvenators, the effects at high temperatures are a little complicated. Raising the rejuvenator proportion in physical rejuvenators with low or medium SBS content brings down the high temperature performance, implying that the oil is currently dominant. Increasing the rejuvenator proportion in physical rejuvenators with high SBS content improves the high temperature performance, suggesting that SBS currently plays a leading role. Rising the rejuvenator proportion in physical rejuvenators containing rapeseed oil and a high SBS content, on the other hand, has little effect on high temperature performance, presumably due to the high viscosity of rapeseed oil has damped the effect of the high SBS content. As for the low temperature performance, rejuvenated bitumen with physical rejuvenators containing aromatic oil has the worst performance than tall oil and rapeseed oil, which is in line with the effect pattern of pure oil based rejuvenators. And for rejuvenator proportions, increasing the proportion of physical rejuvenators improves the cracking and fatigue resistance of rejuvenated bitumen under most evaluation indexes.

- For FTIR analysis, the polybutadiene group index $I_{PB}$ of rejuvenated bitumen with physical rejuvenators increases dramatically compared to the aged bitumen, and the index keeps going up as the proportion of the rejuvenator or the content of SBS in the rejuvenators increases. Furthermore, the $I_{PB}$ index also increases for rejuvenated bitumen with chemical rejuvenators, and a group of new absorption peaks in the spectrum demonstrated that MDI has chemical reactions with degraded SBS polymer and has successfully connected the fracture SBS polymer segment.

From the above summarized conclusion, it can be seen that the chemical rejuvenators perform admirably at high temperatures, but there is much room for improvement at low temperatures. Meanwhile, the physical rejuvenators have a normal high temperatures performance but a better low temperature performance. In the future, these two types of rejuvenators will be combined to produce a new rejuvenator to see whether it can have improved low temperature performance while retaining the excellent high temperature performance of chemical rejuvenators.

Moreover, it is well known that the excellent performance of SBS modified bitumen is largely attributable not only to the SBS content in the bitumen but also to the polymer network structure formed by the SBS. With that said, the current test technique employed in this research is incapable of directly observing and verifying such polymer network structures, making it impossible to demonstrate that the rejuvenators have restored the properties of aged bitumen to like a fresh one. In light of this, tests with equipment like a fluorescence microscope or environmental scanning electron microscope (ESEM) will be conducted on the rejuvenated bitumen samples to examine this kind of polymer network structure in future work.

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