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Exploring the Self-Healing Capability and Fatigue Performance of Modified Bitumen Incorporating Waste Cooking Oil and Polyphosphoric Acid

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Abstract: Bitumen's self-healing capability is critical to the bitumen industry's sustainable development. This work attempts to examine the self-healing property and fatigue behavior of bitumen using waste cooking oil (WCO) and polyphosphoric acid (PPA) in bitumen modification. Different components of WCO were mixed with PPA and bitumen for the initial modification. The linear amplitude sweep (LAS) test was used to evaluate the fatigue behavior of the modified bitumen. To assess the extent of bitumen healing after a fatigue-healing test, evaluation indicators, including fatigue life recovery (FLR), modulus recovery (MR), and dissipated energy recovery (DER), were selected. Meanwhile, a radar chart was used to analyze the integrated performance of WCO/PPA (WP)-modified bitumen. Lastly, the SARA fractions were separated from the bitumen to evaluate the modification mechanism. It was observed that the inclusion of PPA and WCO enhanced fatigue behavior. For 2% PPA and an intermediate component (IC) of WCO, the fatigue life of the LAS prediction model showed extreme values, with an increase of 669% over virgin bitumen. Regardless of the PPA concentration, a considerable increase in FLR, MR, and DER was seen in the bitumen processed with IC compared to virgin bitumen. Additionally, as the healing time was extended, the increment in the virgin bitumen's healing indicators was higher than that of the modified bitumen. SARA results indicated that adding PPA changes the bitumen from a soluble state to a gel state. An innovative approach has been proposed to promote sustainable development within the bitumen industry.

Keywords: modified bitumen; waste cooking oil; self-healing property; polyphosphoric acid

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1. Introduction

Bitumen has been used extensively in the construction of pavement. Environmental conditions, oxidation, and polymerization affect the material's behavior [1]. Inevitably, bitumen will deteriorate over time, eventually requiring rehabilitation, significantly increasing costs, and potentially affecting the environment [2,3]. The effects associated with this issue must be dealt with practically and efficiently. In general, bitumen is a self-healing material because of its viscoelastic properties [4,5]. This characteristic helps it restore its mechanical and fatigue properties [6]. Self-healing techniques benefit the environment and are more economically favorable than passive fracture repair techniques, and this finding is aligned with the UN's Sustainable Development Goals (SDGs) [7,8]. Therefore, the self-healing property of bitumen is crucial for the long-term development of pavement.

Generally, the bitumen's flow behavior is essential in achieving bitumen pavement healing [9]. Relying on the virgin bitumen's flow characteristics can improve the pavement's self-healing performance to a certain extent [10]. In terms of material composition, adding a light component to bitumen is a practical way to improve the flow of virgin bitumen. Waste cooking oil (WCO) is seen as an excellent modification to help bitumen self-healing due to its low cost and ability to replenish the light component [11]. The use of WCO as a modified material reduces dependence on fossil fuels and promotes sustainable resource management. WCO has considerable potential to enhance the performance of aged bitumen because it has many advantageous characteristics, including its chemical composition and molecular structure [12]. For example, Li et al. investigated the capability of WCO and waste engine oil (WEO) to regenerate aged bitumen by retrieving its basic physical properties. The result shows that bitumen's performance after regeneration can reach the before-aging index [13,14]. According to Asli et al., using WCO helps enhance the rheological qualities of aged bitumen [15]. However, WCO has a negative impact on high-temperature performance since it adds a light component. In addition to conventional performance, more interest has been devoted to the self-healing ability of WCO [16]. Using a three-point bending beam test, Yamaç et al. examined the self-healing capabilities of bitumen containing WCO and WEO. The results suggested that adding WEO and WCO improves bitumen binding's capacity for self-healing. Notably, adding WCO to bitumen enhances anti-cracking and improves the performance of aging bitumen. However, this negatively affects the high-temperature performance of the binder to a certain extent and limits its application [17]. Research has shown that the use of biomaterials in asphalt mixtures can improve the stability and durability of the mixtures as well as reduce the environmental impact of their production and use. However, there are also concerns about the potential for the biodegradation of these materials over time, which could lead to reduced performance and increased maintenance costs [12,15].

Polyphosphoric acid (PPA)-modified bitumen has garnered increased interest due to its more notable alteration effect and reduced cost. It shows a lot of promise for improving bitumen's rheological and fatigue characteristics. A model was created by Jiang et al. to characterize flow behavior at high temperatures [18]. Hao et al. employed a cutting-edge methodology to examine how PPA affected the performance of bitumen and discovered that it had a favorable impact on the bitumen binder's long-term deformation [19]. By using a fatigue factor based on a DSR test, Liu et al. analyzed the fatigue performance of several types of bitumen [20]. It has been discovered that PPA's increment effect is superior to SBS and rubber in terms of fatigue performance. Based on the linear amplitude sweep (LAS) test, it can be concluded that the inclusion of PPA enhanced bitumen's fatigue performance [21].

In summary there is a lack of literature on the synergistic mechanisms between the different components of PPA and WCO that affect bitumen properties. This study aims to determine whether utilizing different components of WCO and PPA (WP) to improve the self-healing and fatigue behavior of bitumen is feasible. First, the fatigue behavior of bitumen was assessed using the LAS test. Then, the assessment indices FLR, MR, and DER were chosen to evaluate the level of bitumen healing. The FLR of bitumen refers to the ability of asphalt pavement to regain its resistance to fatigue cracking after being subjected to certain treatments or conditions. The MR of bitumen refers to the ability of an asphalt mixture to regain its stiffness and strength after being subjected to certain conditions or treatments that may cause deformation or damage. The MR of bitumen refers to its resistance to deformation or ability to withstand stress under loading. The DER of bitumen refers to the ability of an asphalt mixture to regain its ability to dissipate energy under repeated loading and unloading cycles, after being subjected to certain conditions or treatments that may affect its performance. The comprehensive performance of bitumen was then assessed using the radar chart approach with various combinations of PPA and WCO. Finally, the saturates, aromatics, resins, and asphaltenes (SARA) component test was used to explore the self-healing mechanism of the modified bitumen. The present study elucidates the practicality of employing WCO and PPA to augment the self-healing potential of asphalt binder, thereby bolstering its fatigue performance and ushering in an era of sustainable growth for the asphalt pavement industry.

2. Materials and Preparation

2.1. Raw Materials

The virgin bitumen used was SK-90#; Table 1 lists its physical characteristics, and the basic characteristics of PPA are listed in Table 2.

Table 1. The performance parameters of virgin bitumen.

Technical Indexes	Measured Results	Test Method
Ductility (15 °C, cm)	93.1	T0604
Penetration (25 °C, 0.1 mm)	>150	T0605
Softening Point (°C)	46.2	T0604

Table 2. The fundamental properties of PPA.

Index	Unit	Test Results
Density (25 °C)	g/cm^3	2.15
Viscosity (85 °C)	mPa.s	562
Surface tension	$N{\cdot}cm^{-1}$	7.5×10^{-4}

The quality of the finished product varies greatly between different sources and types of WCO, and this has a significant impact on the properties of bitumen. First, it is crucial to ensure the source of WCO is consistent before practical engineering applications. An oil refinery supplied the WCO used in this study. Before use, the WCO was first vacuum distilled to separate the different components according to their boiling point differences [22,23]; the distillation process to obtain the light component (LC), intermediate component (IC), and heavy component (HC) is depicted in Figure 1. In this study, LC, IC, and HC as modifiers of bitumen are all blended at 4% of the bitumen mass. The compositions of the three different types of WCO are shown in Table 3.

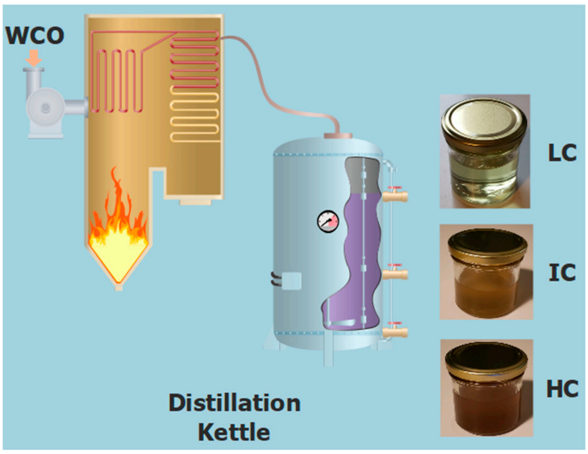


Figure 1. WCO refining schematic.

2.2. Preparation of Samples

The best methods for preparing WP-modified bitumen were identified in agreement with earlier investigations and are summarized as follows [23]. Virgin bitumen binder was heated to a liquid state at 135 °C prior to the addition of the modifiers. After that, heated virgin bitumen was slowly mixed with LC using a batch high shearing apparatus at a low speed of 1500 rpm; referred to previous studies, 4% of LC was selected [23,24]. After the virgin bitumen had been well mixed with the LC, the mixture was sheared at 150 °C for 30 min at a speed of 4000 rpm to produce the LC-modified bitumen. Following the addition of 0.5%, 1%, 1.5%, and 2% PPA to the bitumen, the mixture was stirred mechanically for

20 min at a speed of 1000 rpm to produce the modified bitumens WP-LC0.5, WP-LC1, WP-LC1.5, and WP-LC2. The WP-IC and WP-HC samples' preparation techniques were the same as those used for the WP-LC sample.

Table 3. Basic parameters of WCO.

Index	Test Results		
	LC	IC	HC
Viscosity (50 °C, cP)	66	85	219
Flash point (°C)	197	219	242
Fire point (°C)	216	233	264
Density (g/cm^3)	0.89	0.92	0.97
Mechanical impurity (%)	0.425	0.002	0

3. Experimental Methods

3.1. LAS

According to the AASHTO TP 101 standard procedure, LAS tests on all the adhesives examined in this study were conducted at 25 °C [25]. This method used a setup with a 2 mm gap and an 8 mm parallel plate geometry [26]. Samples were evaluated at a constant frequency (10 Hz) utilizing a series of oscillatory load cycles with linearly increasing amplitude (from 0.1% to 30%) to accelerate fatigue damage [27]. At least three parallel samples were tested for each kind of bitumen binder. Following the test, parameters A and B pertaining to the bitumen's fatigue behavior could be acquired [28]. Equation (1) was used to calculate fatigue life.

$$N_f = A(\gamma_{max})^{-B} \tag{1}$$

$$A = \frac{f\left(D_f\right)^k}{k(\pi D C_1 C_2)^{\alpha}} \tag{2}$$

$$D_f = \left(\frac{C_0 - C_{atPeakStress}}{C_1}\right)^{\frac{1}{C_2}} \tag{3}$$

$$k = 1 + (1 - C_2)\alpha \tag{4}$$

where N_f is the fatigue parameters, C_0 = 1, C_1 and $C2$ represent fitting coefficients, γ_{max} is the maximum strain of bitumen (%), $B = 2\alpha$, α is associated with curve storage modulus, and D_f represents the damage accumulation.

3.2. Fatigue-Healing Test

A fatigue-healing test based on a dynamic shear rheometer (DSR) was used to evaluate the healing performance of bitumen binder-modified WCO and PPA. Using a fatigue-healing test carried out under controlled stress at 25 °C, the healing capacity of WP-modified bitumen was evaluated. The loading frequency was 10 Hz. A parallel plate with a diameter of 8 mm was used to place the sample. The test run times were set at 30 min and 60 min to investigate the effects of healing time. Each type of bitumen had to be tested in three samples. As stated in Equations (5)–(7), indicators were utilized to evaluate the degree of self-healing [24,29].

$$TD_1 = \frac{\Delta G_{after}}{\Delta G_{before}} \tag{5}$$

where G_{after} represents the initial complex modulus of WP-modified bitumen after fatigue healing; G_{before} represents the initial complex modulus of WP-modified bitumen before fatigue healing.

$$TD_2 = \frac{T_{after}}{T_{before}} \tag{6}$$

where T_{after} is the times of loading cycles at which G drops to 60% G_{after} after healing; T_{before} is the times of loading cycles at which G drops to 60% G_{before} before healing.

$$TD_3 = \frac{E_{after}}{E_{before}} \tag{7}$$

where E_{after} is the dissipated energy of the samples at which G drops to 60% G_{after} after healing; E_{before} is the dissipated energy of the samples at which G drops to 60% G_{before} before healing.

3.3. Radar Chart Method

The radar chart method, a procedure for examining several factors, was used in this study to evaluate the bitumen's properties thoroughly. For comparison and analysis, parameters A and B in the LAS-predicted model, FLR, MR, and DER were used, which would first be normalized and then obtained using Equation (8) [30].

$$b_{ij} = \frac{a_{ij} - E\left(y_j\right)}{\sigma(y_i)} \tag{8}$$

where a_{ij} and b_{ij} represent the parameter values before and after normalization; Equations (9) and (10) can be used to calculate $E\left(y_j\right)$ and $\sigma(y_i)$, which are the average value of each parameter value before and after normalization, respectively; i and j are the serial number of the assessment subject and selected parameters.

$$E\left(y_j\right) = \frac{1}{k}\sum_{j=1}^{k} a_{ij} \tag{9}$$

$$\sigma\left(y_j\right) = \sqrt{\frac{\frac{1}{k}\sum_{j=1}^{k}\left(a_{ij} - E\left(y_j\right)\right)^2}{k}} \tag{10}$$

After the data are standardized, they need to be normalized to calculate the r_{ij}, as shown in Equation (11), so that the processed data can be represented in the radar chart as depicted in Figure 2.

$$r_{ij} = \frac{2}{\pi} arctan\left(b_{ij}\right) + 1 \tag{11}$$

Although each bitumen's overall performance is depicted on the radar chart, the ranking of each bitumen requires the calculation of the radar chart's graphical vectors of area and perimeter (*Ga* and *Gp*). Equation (12) represents the characteristic vector consisting of the *Ga* and *Gp*.

$$U_i = [A_i, L_i] \tag{12}$$

where U_i is the characteristic vector of the i-th object; A_i and L_i are the *Ga* and *Gp*, which can be calculated by Equation (13).

$$\begin{cases} A_i = \frac{\pi}{k}\sum_{j=1}^{k} r_{ij}^2 \\ L_i = \frac{2\pi}{k}\sum_{j=1}^{k} r_{ij} \end{cases} \tag{13}$$

where k is the number of evaluation indicators. The evaluation vector (Si) is defined as in Equation (14).

$$S_i = [s_{i1}, s_{i2}] \tag{14}$$

where s_{i1} and s_{i1} are the evaluation indicators of the relative *Ga* and *Gp*, respectively. Their calculation method is shown in Equation (15).

$$\begin{cases} s_{i1} = \frac{A_i}{maxA_i} \\ s_{i2} = \frac{L_i}{2\sqrt{\pi A_i}} \end{cases} \quad (15)$$

The comprehensive evaluation index can be calculated by Equation (16).

$$W_i = \sqrt{z_{i1} \times z_{i2}} \quad (16)$$

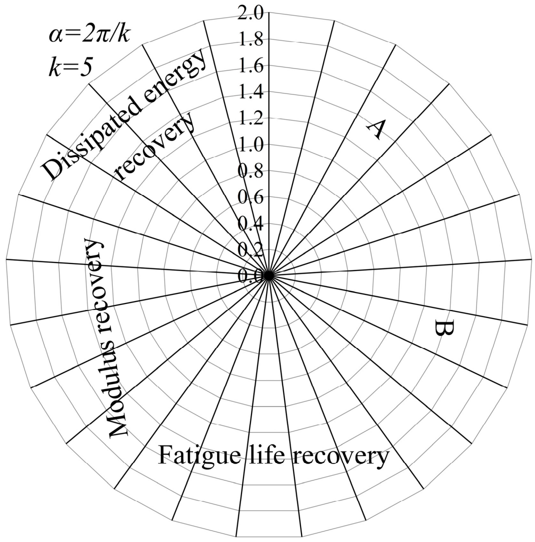


Figure 2. Schematic diagram of a radar chart.

3.4. SARA Fractionation

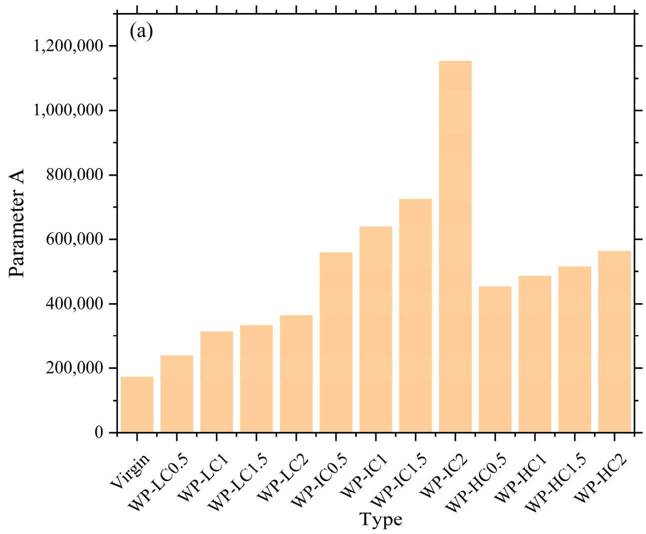
A quantitative study of SARA in bitumen using a bar thin layer chromatograph (BTLC) analyzer was performed to assess the changes in the four components before and after bitumen modification. As a diluent, analytically pure benzene was utilized. For the developing solutions of asphaltene, resin, and aromatic hydrocarbons, n-heptane, toluene, and mixed solution (toluene:ethanol = 55:45) were used, respectively. The frequency was set to 60 Hz, and the scanning speed was 100 mm per minute. Each type of bitumen had to be tested in three samples.

4. Results

4.1. Linear Amplitude Sweep Test

When bitumen is under 1% strain in the LAS test, parameter A represents the bitumen's fatigue life. The bitumen's sensitivity to strain is represented by parameter B [31]. A higher B value indicates that bitumen's fatigue life will attenuate more quickly. Typically, bitumen with a higher A and a lower B can provide better fatigue properties.

Figure 3 displays the result of LAS. According to the test, WP-modified bitumen has greater A and B values than virgin bitumen. Meanwhile, it is also feasible to note that the growth in A is more pronounced than in B. We can infer that WCO and PPA significantly impact fatigue sensitivity. Regarding parameter A, which exhibits a higher increase in fatigue life, the following values are given: 138%, 181%, 192%, 211%, 324%, 371%, 421%, 669%, 263%, 282%, 299%, and 326%; WP-IC2 modified bitumen has the largest parameter value of over 1 million. This trend indicates that the introduction of WCO and PPA is beneficial to the fatigue resistance of bitumen. When keeping the WCO composition (LC, IC and HC) constant, the fatigue life of WP-modified bitumen increases by 7.1%, 6.2%, 9.2%, 14.3%, 13.9%, 58.9%, 31.1%, 6.1%, and 9.3% with an increasing amount of PPA. Nevertheless, when keeping the PPA amount constant, there is no significant linear relationship between the fatigue performance and the molecular weights of the different components of WCO. Moreover, IC and HC are found to greatly increase the modified bitumen's fatigue resistance through their softening characteristic. This phenomenon may be explained by the fact that the use of WCO can reduce bitumen stiffness and increase fluidity, improving the bitumen's fatigue property [32]. Surprisingly, the fatigue coefficient of LC-modified bitumen is not satisfactory. As a rule, LC with the least molecular weight often exhibited superior softening and permeability properties. In contrast, the LC-modified bitumen's improvement of the fatigue coefficient did not produce the desired effects. The reason for this phenomenon is that the primary ingredient in LC is methyl palmitate, which has a freezing point of about 30 °C [33]. At this test temperature, the fatigue performance of the bitumen could not be effectively enhanced and improved. It is speculated that the self-healing properties of LC-modified bitumen may gradually decrease as the temperature decreases.



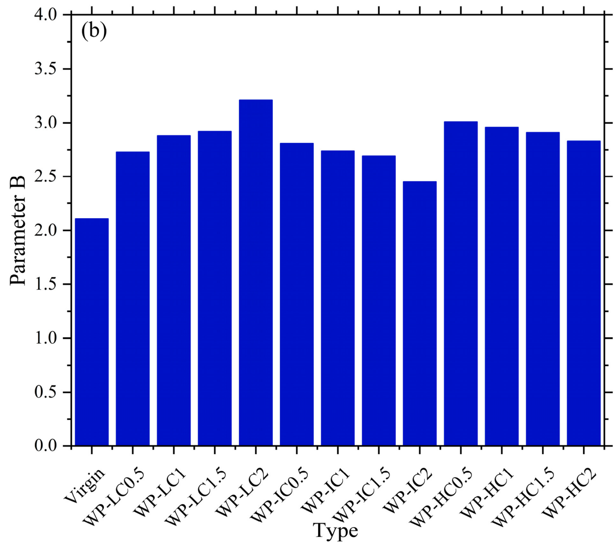


Figure 3. LAS results of bitumen (**a**) parameter A and (**b**) parameter B.

4.2. Self-Healing Property

4.2.1. Fatigue Life Recovery

The fatigue life recovery (FLR) was measured by a fatigue-healing test used as a self-healing index. The results for the sample after 30 min of loading and recovery test are shown in Figure 4a. When WCO and PPA were added, the FLR rose, reaching various values of 133%, 78%, 44%, 23%, 711%, 656%, 623%, 578%, 412%, 389%, 356%, and 312% in comparison to virgin bitumen. With an increase in the WCO component when the doping PPA content (0.5%) was at the same level, the FLR was observed to rise by 247% and 119%. In the meantime, when the WCO composition was fixed, the value decreased as the PPA content increased. The impact of PPA's hardening action surpassed that of WCO's softening action when the WCO composition consisted primarily of light components (LC), which reduced the bitumen's ability to recover from fatigue life. However, once the WCO refining was composed mainly of IC and HC, its softening effect on the bitumen became more pronounced than the hardening effect caused by PPA, thus increasing the fatigue recovery of the bitumen.

The results of the fatigue life ratio after executing the 60 min test are shown in Figure 4b. The FLR of all samples increased by 119%, 175%, 231%, 272%, 11%, 16%, 20%, 26%, 41%, 43%, 48%, and 62% in comparison to the 30 min value in Figure 4a. This trend indicates that extending the test time facilitates the fatigue recovery of the bitumen. In addition, the analysis also revealed that the different components in WCO had different degrees of influence on the fatigue recovery performance of PPA-modified bitumen. Consider modified bitumen with 0.5% PPA as an example: with the increasing molecular weight of the doped WCO component, the FLR increased significantly by 76% and 41%, respectively.

Additionally, it was discovered that the LC-modified bitumen's FLR was unsatisfactory. The best LC for softening and penetrating has the smallest molecular weight, yet its primary ingredient, methyl palmitate, has a freezing point of roughly 30 °C [34]. At this test temperature, in addition to providing a light component to the bitumen, more of the LC component is in solid form in the bitumen and acts as a reinforcing agent for the filler, which is not conducive to the fatigue recovery of the bitumen under repeated external loading [35].

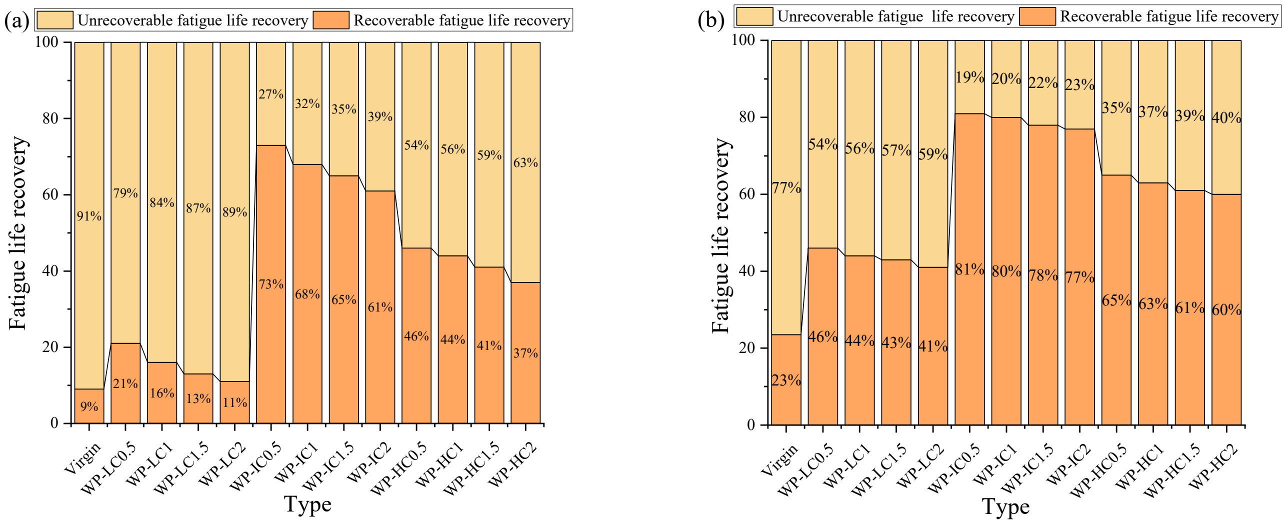


Figure 4. Fatigue life recovery of WP-modified bitumen at different healing times (**a**) 30 min and (**b**) 60 min.

4.2.2. Modulus Recovery

The degree of modulus recovery (MR) of different WP-modified bitumens is depicted in Figure 5. It can be clearly seen that WP-IC2 has the highest recoverable value, followed closely by WP-IC1.5, WP-IC1, WP-HC2, WP-HC1.5, WP-IC0.5, WP-HC1, WP-HC0.5, WP-LC2, WP-LC1.5, WP-LC1, and WP-LC0.5. The corresponding increment was 116%, 208%, 200%, 225%, 342%, 400%, 434%, 450%, 334%, 358%, 375%, and 417% compared with that of virgin bitumen. Except for WP-LC-modified bitumen, the other samples had similar recoverable modulus. This is because LC contains methyl palmitate, which tends to solidify at this test temperature and provides limited improvement in the flexibility recovery properties of the bitumen.

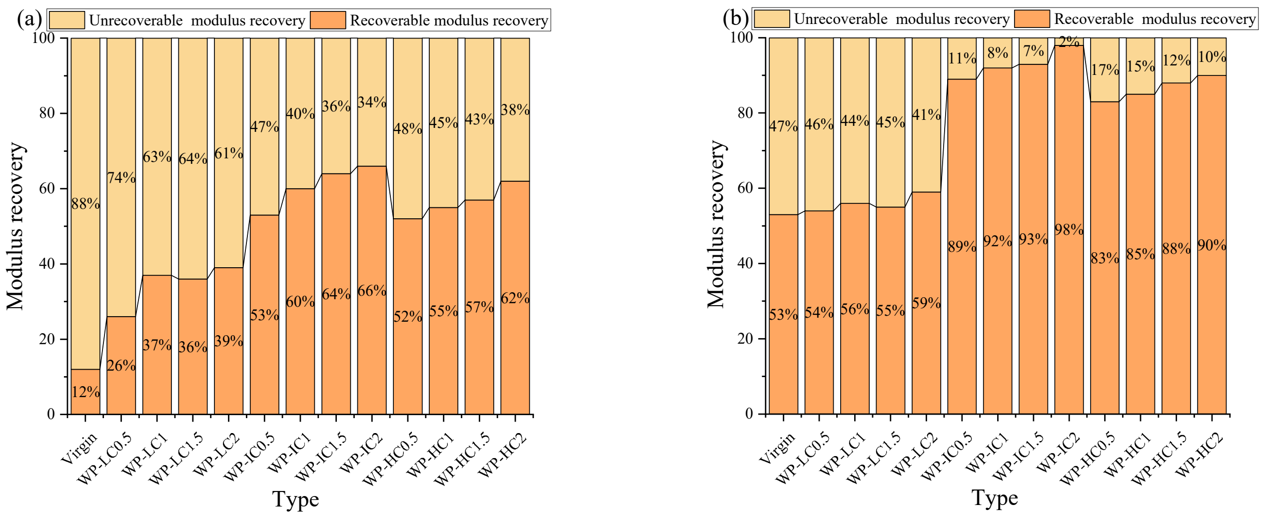


Figure 5. Modulus recovery of WP-modified bitumen at different healing times (**a**) 30 min and (**b**) 60 min.

Figure 5a,b shows the recovery values at 60 min compared to the modulus of the specimens healed for 30 min. It is clear that the WP-modified bitumen had a higher modulus value than the virgin bitumen. Specifically, the modified bitumen increased by 2%, 6%, 4%, 11%, 7%, 8%, 9%, 5%, 6%, 6%, 7%, and 7%. In addition, it can be found when it comes to healing times of 60 min that the modulus recovery rates were 342%, 108%, 51%, 53%, 51%, 68%, 53%, 45%, 48%, 60%, 55%, 54%, and 45% higher than those for 30 min. Moreover, it can be seen that the virgin bitumen had a higher effective dependence on healing time than the modified bitumen, with a maximum modulus recovery of 342% at 60 min, verifying this conclusion. Furthermore, the recoverable modulus of WP-IC2-modified bitumen at a healing time of 60 min was 98%, indicating that the bitumen's modulus was fully recovered. Therefore, extending the healing time can effectively enhance the healing efficiency of bitumen; both virgin and modified bitumen had the same effect [28].

4.2.3. Dissipated Energy Recovery

As shown in Figure 6, the DER of WP-LC, WP-IC, and WP-HC, in comparison to virgin bitumen, rose by 182%, 136%, 91%, 73%, 527%, 500%, 355%, 273%, 391%, 364%, 282%, and 182%, respectively. This result reveals that the WCO and PPA are beneficial in increasing dissipated energy recovery. Taking the modified bitumen with 0.5% PPA as an example, the dissipated energy recovery reached 113% and 74% when the molecular weight of the WCO component increased. However, the increase in PPA concentration had a negative effect on dissipative energy recovery (DER) under the same molecular weight of the WCO component. This indicates that WCO and PPA have opposite effects on the fatigue recovery performance of bitumen, with the former favoring performance recovery and the latter having a negative effect. The reason for this phenomenon is that the components of WCO have the effect of softening the bitumen, regardless of the molecular weight of the WCO components, which can increase the mobility of bitumen, while PPA makes the bitumen hard and restricts its free flow to some extent [18].

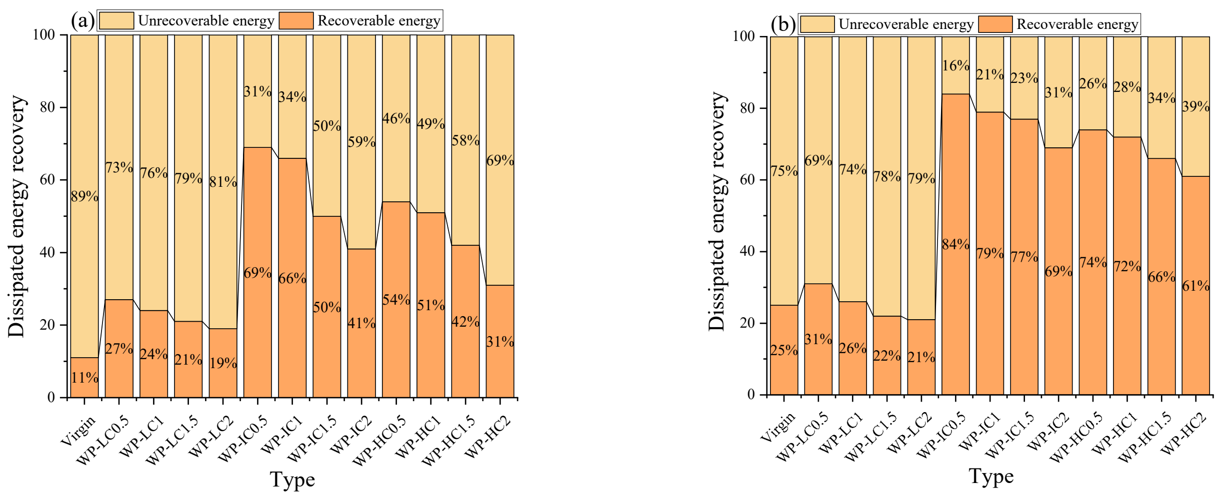


Figure 6. Dissipated energy recovery of WP-modified bitumen at different healing times (**a**) 30 min and (**b**) 60 min.

Figure 6b shows the results of DER at a healing time of 60 min. It is clear that the DER of the modified bitumen first increased and then decreased as the molecular weight of the WCO component increased, and the recovery value reached the maximum when the WCO component was IC. The difference in dissipation energy between the WP-LC-modified bitumen and the virgin bitumen was insignificant. The possible reason for this is that the high molecular weight of HC has a very low number of lightweight components and a limited softening effect, while the LC with the smallest molecular weight has the best softening and penetration ability. Still, at the test temperature, the LC appears solid in the bitumen, which is detrimental to the fatigue resistance of the bitumen binder. Meanwhile, IC with a medium molecular weight can improve mobility and promote the self-healing abilities of bitumen by lowering resistance to the movement of bitumen molecules.

Comparison of the DER at the two healing times reveals that extending the healing time increased the recovery rates of WP-LC, WP-IC, and WP-HC by 127%, 15%, 8%, 5%, 11%, 22%, 19%, 54%, 68%, 37%, 41%, 57%, and 97%, respectively. Further analysis of the enhancement rates revealed that the virgin bitumen had the highest recovery ratio. This indicates that the most effective way to enhance the healing performance of virgin bitumen is to extend the healing time accordingly; this finding is consistent with the modulus recovery rate results.

4.3. Optimum Proportion of WCO/PPA

The optimum modifier content can be obtained by analyzing the healing performance index of the bitumen, and the radar chart describing the comprehensive healing performance of the bitumen can be obtained according to the rij of Table 4, as shown in Figure 7. The area and perimeter show that the virgin bitumen has the worst healing performance, while WP-IC2 has the best healing performance. To further quantify the effect of different molecular weights of WCO and PPA on the healing performance of bitumen, Si and Wi were calculated, and the results are listed in Table 5:

Table 4. The results of rij.

Types	A	B	Fatigue Life Recovery	Modulus Recovery	Dissipated Energy Recovery
Virgin bitumen	0.5315	1.0185	1.1128	1.1637	1.0866
WP-LC0.5	0.6214	1.032	1.1956	1.2031	1.3066
WP-LC1	0.6347	1.1263	1.1196	1.2138	1.1945
WP-LC1.5	0.5388	1.0506	1.1542	1.1599	1.1043
WP-LC2	1.028	0.9025	1.4133	1.1285	1.8021
WP-IC0.5	0.5832	1.1344	1.1966	1.2201	1.1023
WP-IC1	0.7936	0.9458	1.3724	1.2166	1.563
WP-IC1.5	0.8125	1.1369	1.2524	1.3488	1.2595
WP-IC2	0.9853	1.021	1.5634	1.0224	1.637
WP-HC0.5	0.4695	1.3025	1.1589	1.2733	1.4692
WP-HC1	0.8516	1.3024	1.4428	1.3016	1.5201
WP-HC1.5	1.0238	1.002	1.4369	1.2456	1.5348
WP-HC2	0.9213	1.1148	1.4698	1.4261	1.5674

Table 5. The results of Si and Wi.

Si		Wi
s_{11}, s_{12}	0.4322, 0.6971	0.5488
s_{21}, s_{22}	0.5193, 0.7408	0.6202
s_{31}, s_{32}	0.6251, 0.7852	0.7006
s_{41}, s_{42}	0.6785, 0.7932	0.7336
s_{51}, s_{52}	0.7341, 0.8793	0.8034
s_{61}, s_{62}	0.6371, 0.8489	0.7354
s_{71}, s_{72}	0.6856, 0.9037	0.7871
s_{81}, s_{82}	0.7595, 0.9579	0.8526
s_{91}, s_{92}	0.9227, 0.9566	0.9394

Table 5. *Cont.*

Si		Wi
s_{101}, s_{102}	0.6476, 0.8038	0.7215
s_{111}, s_{112}	0.7155, 0.8643	0.7864
s_{121}, s_{122}	0.7596, 0.8961	0.8251
s_{131}, s_{132}	0.7668, 0.9543	0.8554

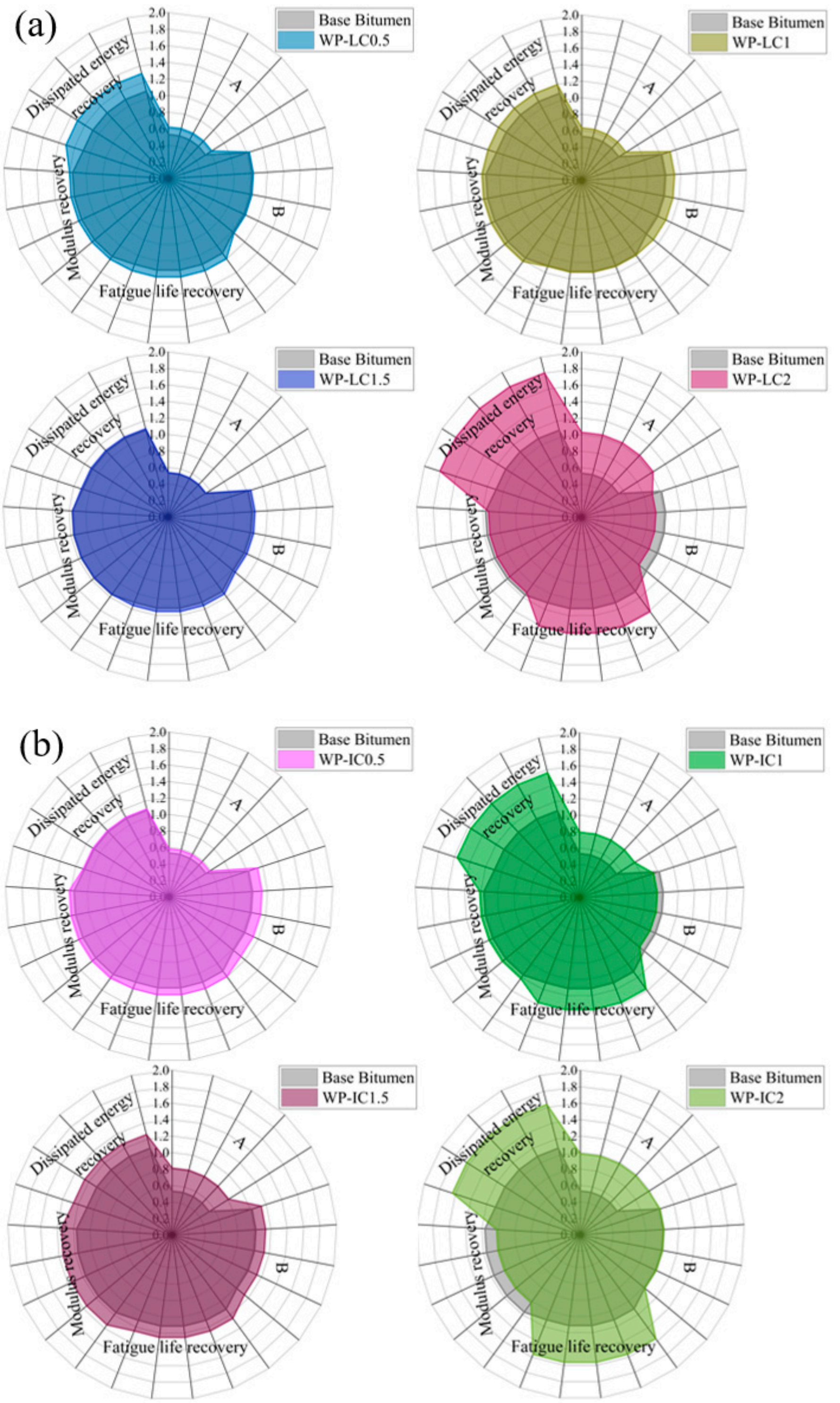


Figure 7. *Cont.*

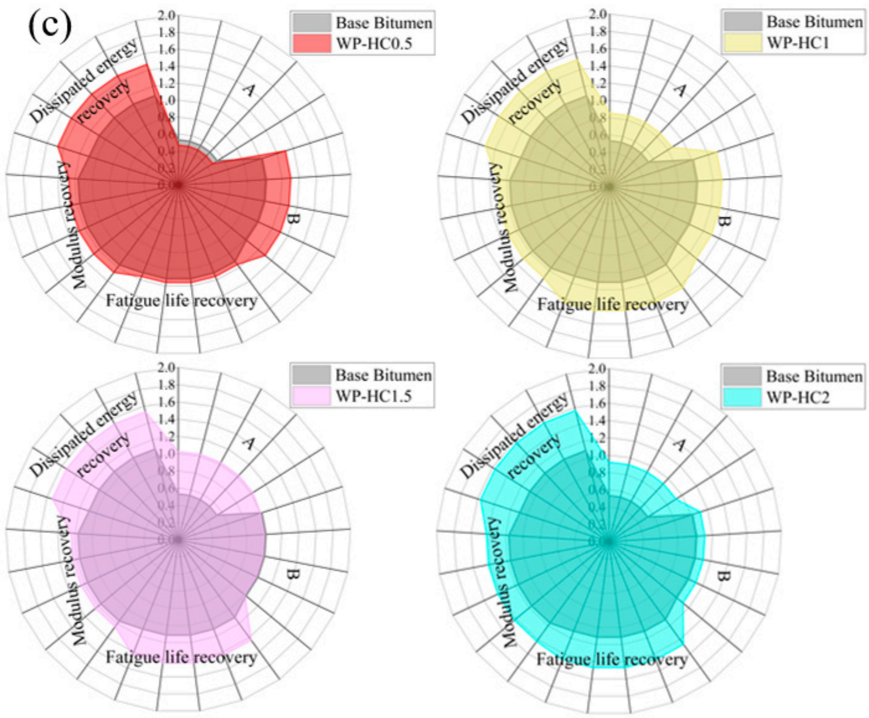


Figure 7. Evaluation of comprehensive healing properties of bitumen (**a**) WP-LC (**b**) WP-IC (**c**) WP-HC.

The order of the overall assessment index from good to bad is as follows: W9 > W13 > W8 > W12 > W5 > W11 > W7 > W6 > W4 > W10 > W3 > W2 > W1. This ranking also lists the order of the healing properties of the bitumen. It can be found that the healing properties and fatigue resistance of the virgin bitumen were improved to some extent after modification by WCO and PPA. Overall, WP-IC2 has the best healing properties, and therefore 2% PPA and 4% IC are recommended for use in bitumen.

4.4. SARA

The SARA fraction content is a crucial factor affecting the stability of the bitumen colloid system and the bitumen properties [36,37]. The results of the SARA content of WP-modified bitumen are shown in Figure 8. It is clear that the lighter components (aromatics and saturates) of all bitumen increase with the addition of WCO, regardless of the high or low molecular weight in WCO, which indicates that they have the function of lubricating and dissolving the bitumen, thus promoting the softening of the bitumen.

In addition, each component's relative content affects the colloid structure of bitumen; the colloid index (IC) can be derived using Equation (17) to assess the colloidal structure changes of recycled bitumen. Colloid structures resemble gel structures more closely the lower the colloid index number is. The colloid structure resembles the sol structure more closely the higher the colloid index.

$$I = \frac{R_e + A_r}{A_{sp} + S_a} \quad (17)$$

where *Re*, *Ar*, *Asp*, and *Sa* are the content of resins, aromatics, asphaltenes, and saturates in bitumen, respectively.

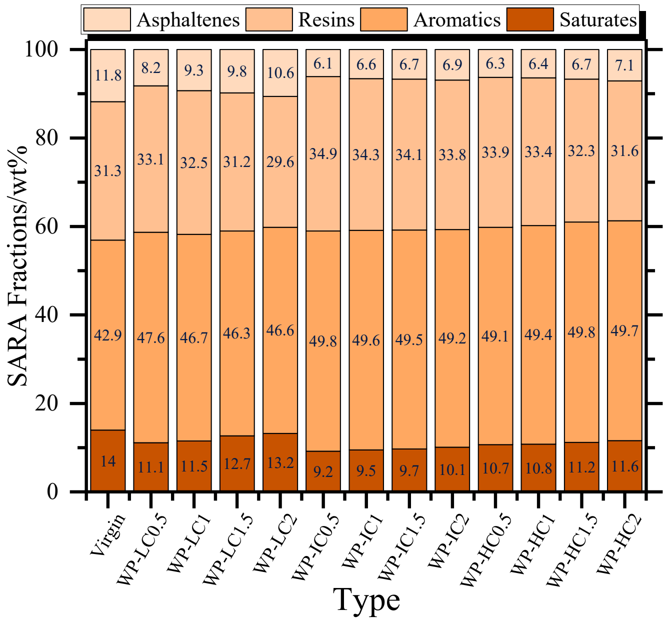


Figure 8. SARA fraction contents of WCO/PPA modified bitumen.

Table 6 shows the colloid index of the bitumen. It can be found that the I-value increased from 2.88 for the virgin bitumen to 5.54 for WP-HC2, which indicates that the colloidal structure of the virgin bitumen had been reconstructed. The significant improvement in the I-value of the virgin bitumen after incorporating the three molecular-weight WCO components can be attributed to the fact that each of the different molecular-weight WCOs contains a certain number of lighter components that complement the resins, aromatics, and saturates of the virgin bitumen. Moreover, the solubilization of asphaltenes by the light fraction also promotes the recovery of the colloidal structure [37,38]. In contrast, the I-value gradually decreases with the increase in PPA content. The reason for this phenomenon may be due to the different roles of WCO and PPA. WCO is responsible for the softening effect of the lighter components contained in the composition, which positively affects the flow properties of the bitumen, thus improving the self-healing properties. At the same time, the addition of PPA increases, to some extent, the average molecular mass and the dispersion coefficient, thus limiting the thermal movement of the bitumen molecules. The I-value results indicate that WP-IC has the highest solvation structure. This is because the HC is primarily made up of high-molecular-weight substances that are challenging to evaporate [39,40]. As a result, it has a substantially higher viscosity than LC and IC. Additionally, parts of the benzene series that thrive in a frying environment are also found in HC, making them the two classes of hydrocarbons with the most similarities to those found in bitumen's aromatic hydrocarbons [41,42]. As a result, HC's ability to soften bitumen may not be as effective as LC and IC, whereas LC is in solid form in the bitumen and acts as a filler reinforcement, which is detrimental to the fatigue resistance of the bitumen.

Table 6. The I value of different modified bitumen.

Value	Virgin	WP-LC0.5	WP-LC1	WP-LC1.5	WP-LC2	WP-IC0.5	WP-IC1	WP-IC1.5	WP-IC2	WP-HC0.5	WP-HC1	WP-HC1.5	WP-HC2
I	2.88	4.18	3.81	3.44	3.2	5.54	5.21	5.09	4.88	4.87	4.81	4.59	5.35

5. Conclusions

The paper investigated whether WCO and PPA can improve bitumen's self-healing capacity and fatigue behavior. LAS tests were used to assess the bitumen's fatigue response.

Based on the fatigue-healing test, the assessing indicators FLR, MR, and DER were chosen to estimate the bitumen's degree of healing. Radar charts were used to thoroughly evaluate the modification effect of various additives on bitumen. In the end, a quantitative examination of the four components of bitumen using the SARA test was used to investigate the self-healing mechanism. The findings can be distilled into the following:

(1) The introduction of WCO and PPA is beneficial to the fatigue resistance of bitumen. When keeping the WCO composition (LC, IC and HC) constant, the fatigue life of WP-modified bitumen increases with an increasing PPA amount.

(2) Increased fatigue life is associated with bitumen incorporating WCO and PPA. WCO can lessen the unfavorable effects of PPA on fatigue life. The fatigue life of additives containing 2% PPA and IC is quite valuable, rising by 669%.

(3) With the addition of WP and the lengthening of the healing period, the FLR, MR, and DER of the virgin bitumen increased. The modified bitumen of WP-IC2 showed the best increase in FLR, MR, and DER. Additionally, when the healing time was lengthened, the increase in the healing index of virgin bitumen was more remarkable than that of modified bitumen. Therefore, a significant part of the damage to the bitumen may have been recovered more rapidly.

(4) WP-IC2 exhibited the best healing properties; therefore, 2% PPA and 4% IC are recommended for use in bitumen.

The components of WCO with different molecular weights contain a certain number of light components, and the addition of PPA makes the bitumen change from a soluble state to a gel state. This paper presents a preliminary investigation of the feasibility of using WCO- and PPA-modified asphalt to promote the sustainable self-healing of asphalt binder and reduce the consumption of non-renewable crude resources. Although the results are promising, further research is necessary to address several outstanding issues. Firstly, the biodegradability of WP-modified bitumen needs to be studied as it relates to environmental sustainability. Secondly, the road and long-term performance of WP-modified bitumen mixtures must also be studied, which will determine whether WP-modified bitumen materials can be used on a large scale in engineering.

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