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Rheological properties of asphalt binder modified with recycled asphalt materials and light-activated self-healing polymers

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HIGHLIGHTS

- Increased stiffness due to the addition of recycled materials and polymer.
- Improved HT performance due to the addition of recycled materials and polymer.
- Enhanced LT performance for samples with 5% polymer and 48h UV exposure.
- Improved elastic behavior of the unmodified binder due to the addition of polymer.
- Improved fatigue performance of the unmodified binder due to polymer application.

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ABSTRACT

Ultraviolet (UV), light-activated, self-healing polymers are an emerging technology that was proposed to enhance the elastic behavior of asphalt binder, while improving its self-healing properties. The objective of this study was to evaluate the effects of self-healing polymer on the rheological properties of binder blends prepared with or without recycled asphalt materials. Binder blends were prepared with two different binders (PG 67-22 and PG 70-22M), with or without recycled asphalt materials, and 5% self-healing polymer (Oxetane-substituted Chitosan-Polyurethane). High-Pressure Gel Permeation Chromatography (HP-GPC) results showed an increase in High Molecular Weight (HMW) components in the binder with an increase in stiffness through the addition of recycled materials. A further increase was observed with the addition of self-healing polymer. Fourier Transform Infrared Spectroscopy (FTIR) confirmed High-Pressure Gel Permeation Chromatography (HP-GPC) results with an increase in the carbonyl index. Furthermore, the addition of recycled materials led to an increase in the high-temperature grade and the low-temperature grade of the binder blends, while the self-healing polymer did not have a significant effect on the PG-grade. Overall, the addition of self-healing polymer led to an increase in stiffness and an improvement in the rutting performance, while it did not have a positive effect on low-temperature cracking performance. For unmodified binder (PG 67-22), self-healing polymer incorporation improved the elastic and fatigue cracking properties of the binder. However, when it was added to a polymer-modified binder (PG 70-22M) and/or binder blends containing recycled asphalt materials, the potential of this material was low to negative on the low temperature and fatigue cracking performances.

1. Introduction

Asphalt binder is a viscoelastic material with self-healing abilities, which can restore its original properties by healing the micro-cracks and providing an asphalt mixture with higher durability. Yet, the rate of asphalt mixture's crack healing process is slow for conventional asphalt binders at ambient temperature and under continuous loading [1]. On the other hand, the application of recycled asphalt materials such as Reclaimed Asphalt Pavement (RAP) and Recycled Asphalt Shingle (RAS) has received considerable attention due to its economic and environmental

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advantages. Various studies have been conducted in recent years with the aim to produce asphalt mixtures with high percentages or even 100% of recycled materials [2–5]. Even with these advantages, the use of high content of recycled asphalt materials is challenging as the recycled binder is subjected to oxidation and aging during its service life. A severely aged binder is hardened and brittle, and as a result, it may increase the cracking susceptibility of the newly constructed mixture. In addition, the increase in the binder's viscosity and the loss of relaxation can negatively affect the self-healing properties of the binder, possibly causing premature failure of the pavement.

During the last decade, researchers have introduced different innovative self-healing approaches with the aim to enhance self-healing properties of asphalt mixtures. Using these emerging approaches, the rate of crack-healing increases resulting in an asphalt binder with superior performance [1]. A smart self-healing technique detects the damage and autonomously starts the repair. Based on this repair mechanism, self-healing techniques can be categorized into two groups of intrinsic and extrinsic mechanisms. In the intrinsic approach, a self-healing agent is embedded in a container such as microcapsules or hollow fibers [6,7], and is released through the appearance of the crack and breakage of the containers shell. For the extrinsic group, the self-healing agent is present in the material in a reactive form. In this case, self-healing mechanism is activated with external stimuli such as UV light, heat, or chemicals [8]. Self-healing UV-light activated polymer is a novel technique that combines two approaches of self-healing and polymer modification to enhance the self-healing and rheological properties of the asphalt binder while providing benefits of a polymer modification.

2. Objectives and scope

The objective of this study was to investigate the rheological properties of asphalt binder blends containing different percentages of extracted binder from recycled asphalt materials (5% RAS, 20% RAP, and 5% RAS + 20% RAP) and self-healing polymer. Chemical tests (High-Pressure Gel Permeation Chromatography (HP-GPC), and Fourier Transform Infrared Spectroscopy (FTIR)) were conducted to achieve a better understanding of recycled materials and self-healing polymers effects on the aging process of the binder blends. In addition, rheological properties of the prepared binder blends were examined using rheological tests (Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR), and the Multiple Stress Creep Recovery (MSCR)), and by comparing the Superpave Performance Grade (PG) of the blends. Finally, fatigue behavior of binder blends was evaluated using the Linear Amplitude Sweep (LAS) test.

3. Background

Asphalt binder is a viscoelastic material that is used in asphalt mixture to provide the required adhesion between the aggregate. Therefore, asphalt binder has a vital role in providing the necessary stability of the asphalt mixture under traffic loads. A viscous binder with high stiffness provides a good rutting resistance at high temperature, while the elastic properties at ambient temperature may lead to an enhanced cracking performance. Incorporation of recycled asphalt materials such as RAS and/or RAP in the construction of new pavements can significantly affect the properties of asphalt binder and the mixture. Although RAS and RAP can improve the rutting resistance through the increase in stiffness, cracking performance may be affected negatively. Concerns related to the premature failure of the pavement is more serious when air blown binder from RAS is incorporated into an asphalt mixture [9].

Self-healing properties of asphalt binder can be used to address concerns related to cracking performance. Self-healing of asphalt mixtures occurs when micro-cracks are closed because of inter-diffusion between the materials on the faces of the cracks. However, the rate of crack closing is highly dependent on the temperature and rest period [1]. This behavior is also affected by the thixotropy of the binder, which causes the asphalt binder to transform from the solid to the gel state at high temperature. As a result, cracks close during the warm weather and re-open when there is a decrease in the temperature or when they are subjected to high traffic loads [10].

Due to the temperature dependency of self-healing properties of the binder, heating of the pavement using electromagnetic induction was suggested as a solution. However, in order to make the pavement a conductive material, metallic additives such as steel wool should be added to the mixture [11]. In another approach, healing agents or rejuvenators were used to reverse the aging process of the oxidized binder, and to reduce its stiffness, providing a better flow to fill the cracks [12]. Furthermore, rejuvenator can be preserved in a microcapsule during the early years of the pavement service life. When micro-cracks appear, the load on the microcapsule shell leads to its breakage. As a result, rejuvenator is released in the vicinity of the micro-cracks, improving binders property in that area, and enhancing its self-healing properties [6,13]. Nanomaterials were also used to enhance the rheological properties of the binder and to increase thermal and fatigue cracking resistance [14]. The high surface energy of the nanomaterials tends to move them toward the tip of the crack delaying crack propagation [15].

Polymer modifiers are another group of additives that have been incorporated into an asphalt mixture to improve its performance. When a polymer is blended with asphalt, the polymer absorbs part of the low molecular weight oil portions of the asphalt binder and become swollen. Next, the polymer modifier creates a network within the asphalt binder, providing a stronger bond with the aggregate. This mechanism results in a more durable asphalt mixture with a longer service life. However, because of the higher viscosity, polymer modifiers may demonstrate difficulties in workability. There are also issues with respect to polymer thermal degradation at high temperature [16,17]. Properties of the polymer-modified binder are highly dependent on the type and properties of the polymer, the content of the polymer, properties of the binder, and mixing process of the binder and polymer [18].

A new group of polymers is self-healing polymers, which contain inherent repeatable healing abilities. The healing process occurs at the molecular level, without the presence of healing agents or catalyst. However, different external stimuli are required for triggering the self-healing process [8]. For photochemical self-healing polymers, the healing process is triggered with UV light exposure and by re-bonding reactive groups. Ghosh et al. [19] introduced a UV light-activated, self-healing polyurethane. This polymer is developed by combining polyurethane and oxetane-substituted chitosan (OXE-CHI) into a cross-linked polymer of oxetane substituted chitosan-polyurethane (OXE-CHI-PUR). The appearance of micro-cracks in the mixture containing UV light activated self-healing polymer leads to cleavage of the polymers bond. As the result of this bond cleavage, unstable free radicals are produced. During the recombination of free radicals through UV light exposure, micro-cracks are sealed and the damaged area is repaired [19]. Therefore, the use of UV-light activated self-healing polymer in asphalt pavements may result in improved performance due to the polymer modification and an enhanced crack healing property because of the self-healing capabilities of the polymer.

4. Experimental program

4.1. Test materials

In order to gain a better understanding of the effects of self-healing polymers on the viscoelastic properties of the binder, two binders, a neat binder (PG 67-22) and a polymer modified binder (PG 70-22M), were used in this study. RAS used was a Post-Consumer Waste Shingle (PCWS), provided by a local contractor. The RAS and RAP used had a binder content of 20% and 5%, respectively. Binder extraction was performed based on AASHTO T 164. The binder was separated from aggregate using trichloroethylene as a solvent. Then, the trichloroethylene was removed based on the procedure described in AASHTO R 59. Furthermore, a High-Pressure Gel Permeation Chromatography (HP-GPC) test was conducted on the extracted binder from RAS and RAP to obtain the molecular weight distribution. Results are presented in Table 1.

The UV light activated self-healing polymer used in this study is oxetane substituted chitosan-polyurethane (OXE-CHI-PUR). The three main components of OXE-CHI-PUR were selected based on their functionality. Chitosan (CHI) is used to provide UV light sensitivity, while oxetane (OXE) is a cyclic oxide compound and was opted to deliver a four-member ring. In addition, polyurethane (PUR) provides mechanical integrity, network heterogeneity and facilitates the cleavage of the oxetane ring. Further information related to the self-healing polymer test material, production process, and characterization were presented in a previous study [20].

Binder blends were prepared with two different binders, with and without extracted binder from recycled asphalt materials (5% RAS, 20% RAP, 5% RAS + 20% RAP by the weight of the binder), and with and without 5% self-healing polymer. The percentage of RAP in the experimental program was selected based on the maximum allowable RAP percentage in Louisiana. For RAS, since it is not allowed in Louisiana, the maximum allowable percentage in Texas was used. In order to achieve a uniform distribution of self-healing polymer in the binder blends, a mechanical mixer rotating at a shear rate of 3600 rpm for 30 min was used. Furthermore, samples were exposed to UV light for three different durations of 0, 1 h, and 48 h. A UV lamp with a 302 nm wavelength was placed at a 100-mm distance from the samples to provide a UV radiation intensity of 1 mW/cm^2. The UV light set up was selected based on the typical intensity of sunlight, which is between 1 and 2 mW/cm^2 at a wavelength below 350–400 nm. Binder blends composition used in this study are presented in Table 2.

It should be noted that in a previous study [20], the authors performed Superpave PG grading and MSCR on binder blends prepared with PG 67-22, with or without 5% RAS, and using three different percentages of self-healing polymer (1%, 3%, and 5%). The most significant improvements were observed for blends containing 5% self-healing polymer. Therefore, 5% self-healing polymer was selected for further testing and evaluation in the present study.

Table 1
HP-GPC Results for RAS and RAP Used in this Study.

Components	Molecular Weight		
	Others (>50 K Daltons)	HMW (3 K-50 K Daltons)	LMW (<3K Daltons)
RAS (PCWS)	8.10%	26.69%	65.21%
RAP	13.31%	30.31%	56.38%

4.2. Chemical tests

In order to study the aging and molecular distributions of the different binder blends, HP-GPC and FTIR were conducted. High-Pressure Gel Permeation Chromatography identifies the fraction of High-Molecular Weight (HMW), Low-Molecular Weight (LMW), and polymer present in a binder sample based on their molecular weight (MW) distributions. The maltenes have an average MW less than 3000 Daltons while the MW for asphaltenes is between 3000 and 50,000 Daltons. The MW of polymers is significantly greater than the MW of asphalt binder components making it possible to be identified [21]. Using this approach, the aging and brittleness levels in the blends can be evaluated through the change in the ratio of HMW to LMW components.

Fourier transform infrared spectroscopy was used to evaluate oxidative aging of asphalt binder through the formation of carbonyl ($C{=}O$) group. Aging cause an increase in the carbonyl absorbance around the 1695 cm^{-1} peak. Carbonyl index can be defined as the ratio of the area around this peak divided by a reference area. The aliphatic group (around 1460 cm^{-1} and 1376 cm^{-1} peaks) is usually selected as a reference group since they are considered stable during the aging process. The increase in the ratio is an indication of higher levels of oxidation and therefore, a stiffer binder [22,23].

4.3. Rheological testing

In order to evaluate the effect of self-healing polymers on the binder rheological properties, binder blends were characterized with and without recycled asphalt materials using laboratory rheological tests (the Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR), and the Multiple Stress Creep Recovery (MSCR)), and by comparing the Superpave Performance Grade (PG) of the modified binder blends to the unmodified binder. Furthermore,

Table 2
Binder Blends Compositions.

Binder Blend	Binder Type	RAS/RAP (by weight of binder)	Self-Healing Polymer (by weight of binder)	UV exposure
67CO	PG 67-22	0	0%	0
67-5P	PG 67-22	0	5%	0, 1 h, 48 h
67-5RAS	PG 67-22	5% RAS	0%	0
67-5RAS-5P	PG 67-22	5% RAS	5%	0, 1 h, 48 h
67-20RAP	PG 67-22	20% RAP	0%	0
67-20RAP −5P	PG 67-22	20% RAP	5%	0, 1 h, 48 h
67-5RAS-20RAP	PG 67-22	5% RAS + 20% RAP	0%	0
67-5RAS-20RAP −5P	PG 67-22	5% RAS + 20% RAP	5%	0, 1 h, 48 h
70CO	PG 70-22M	0	0%	0
70-5P	PG 70-22M	0	5%	0, 1 h, 48 h
70-5RAS	PG 70-22M	5% RAS	0%	0
70-5RAS-5P	PG 70-22M	5% RAS	5%	0, 1 h, 48 h
70-20RAP	PG 70-22M	20% RAP	0%	0
70-20RAP −5P	PG 70-22M	20% RAP	5%	0, 1 h, 48 h
70-5RAS-20RAP	PG 70-22M	5% RAS + 20% RAP	0%	0
70-5RAS-20RAP −5P	PG 70-22M	5% RAS + 20% RAP	5%	0, 1 h, 48 h

prepared samples (DSR and BBR samples) were exposed to two different duration of UV light (1 h and 48 h) to examine the effect of various UV exposure on the properties of the binder blends containing self-healing polymers. Using BBR results, Delta Tc was calculated as the difference between the critical stiffness temperature and the m-value critical temperature. The Useful Temperature Interval (UTI) of the binder blends was also calculated as the range between the minimum and maximum temperatures where the binder is expected to have adequate performance. The Linear Amplitude Sweep (LAS) test was performed based on AASHTO TP101, to measure the fatigue cracking resistance of the different binder blends, and to provide a quantitative assessment of the blends' fatigue resistance. The LAS test uses the following fatigue law to characterize the fatigue performance of asphalt binder:

$$\text{Number of Cycles to Failure} = A \times (\text{Applied Load})\ B \qquad (1)$$

where *A* and *B* are Viscoelastic Continuum Damage (VECD) model coefficients that depend on the material characteristics, and N_f is the number of cycles to failure. The *A* parameter relates to the materials ability to preserve its integrity during loading cycles and is directly related to the storage modulus. The *B* parameter represents the sensitivity of the asphalt binder to change in strain level.

5. Results and analysis

5.1. High-Pressure Gel Permeation Chromatography results

Based on the HP-GPC results presented in Fig. 1, the addition of 5% self-healing polymer was found to cause an increase in the HMW/LMW ratio of 67CO and 70CO from 0.21 and 0.26 to 0.35 and 0.36, respectively. Furthermore, the addition of recycled materials led to an increase in HMW components and a decrease in LMW components, resulting in a higher HMW/LMW ratio compared to the control binders (67CO and 70CO). The HMW/LMW ratio increased further through the addition of self-healing polymer to the blends. This may due to the absorption of the oil fraction in the binder through the self-healing polymer, resulting in higher proportion of asphaltenes.

5.2. Fourier transform Infrared Spectroscopy results

Carbonyl group of different binder blends was obtained and were compared to examine the effect of recycled asphalt materials and self-healing polymer addition on the aging process in asphalt binder. The carbonyl index was calculated based on Equations (2):

$$I_{CO} = \frac{\sum \text{Area of the carbonyl centered around } 1700\ \text{cm}^{-1}}{\sum \text{Area of the spectral bands between } 1350 \text{ and } 1525\ \text{cm}^{-1}} \qquad (2)$$

The results from the measured carbonyl index are presented in Fig. 2. When 5% self-healing polymer was added to the virgin binder, carbonyl index did not change significantly for 67-5P, while a decrease was observed for 70-5P carbonyl index. As expected, the addition of recycled materials and the incorporation of aged binder resulted in an increase in the carbonyl index. The addition of self-healing polymer resulted in a further increase in the carbonyl

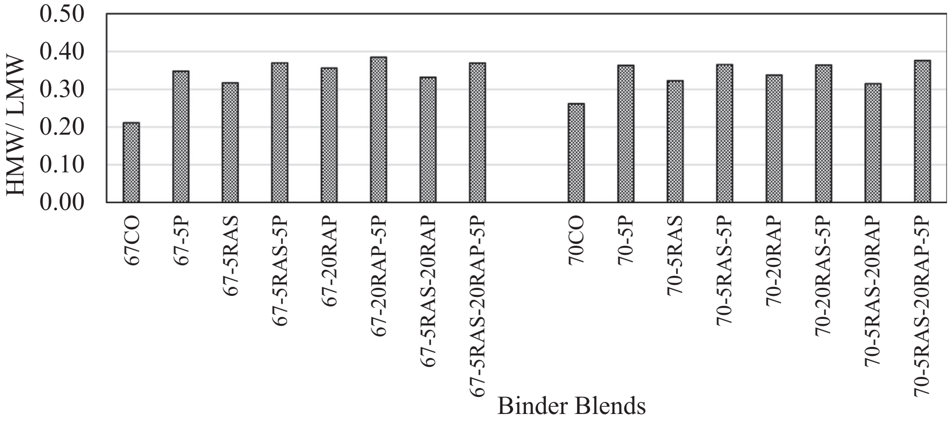

Fig. 1. HP-GPC Results for HMW/LMW Ratio.

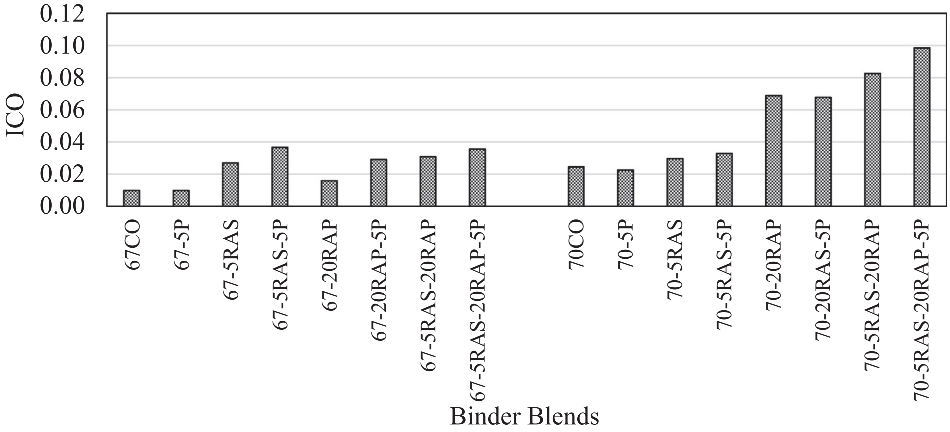

Fig. 2. FTIR Test Results.

index, which can be due to the carbonyl group present in the self-healing polymer and the absorption of the oil fraction in the binder, resulting in greater proportion of asphaltenes.

5.3. Superpave performance grade results

Results of PG-grading, continuous grading, and UTI (Useful Temperature Interval) of the tested binder blends are presented in Table 3. The stiffness of the binder blends and their high-temperature grading increased due to the addition of recycled materials. For example, the high-temperature grading of 67CO increased from 67 °C to 76 °C due to the addition of 20% RAP, and 5% RAS + 20% RAP. Based on the continuous grading, the addition of a self-healing polymer to the virgin binder resulted in an increase in the high temperature; however, it was not significant enough to change its grading. The highest temperature was observed for the blend containing 20% RAP and 5% self-healing polymer, exposed to UV light for 48 h (67-20RAP-5P-48 h), with a temperature of 81.9 °C. The same behavior was observed in the PG 70-22M binder blends. Self-healing polymer application caused an increase in the high temperature grade of the virgin binder. The addition of 5% RAS (70-5RAS), 20% RAP (70-20RAP), and 5% RAS + 20% RAP (70-5RAS-20RAP) to the virgin binder resulted in the high-temperature grade of 76 °C, 82 °C, and 82 °C, respectively.

At low temperature, the addition of self-healing polymer caused an improvement in the low-temperature behavior of the blends; however, it was not significant to change the low-temperature grade. The addition of recycled materials caused an increase in stiffness and a decrease in relaxation due to the incorporation of the aged and brittle binder. Based on these results, the addition

Table 3
PG-grading results for (a) 67-22 binder blends, (b) 70-22M binder blends.

Binder Blend	PG-Grading	Continuous-Grading	UTI (°C)
67CO	67-22	68.0-23.6	91.6
67-5P	67-22	68.6-23.5	92.1
67-5P-1 h	67-22	69.0-24.4	93.4
67-5P-48 h	67-22	69.4-24.8	94.2
67-5RAS	67-22	71.2-22.3	93.5
67-5RAS-5P	67-22	70.8-24.9	95.7
67-20RAP	76-16	81.8-18.3	100.1
67-20RAP −5P	76-16	80.8-18.9	99.7
67-20RAP −5P-1 h	76-16	81.1-20.1	101.2
67-20RAP −5P-48 h	76-16	81.9-19.5	101.4
67-5RAS-20RAP	76-16	81.8-18.0	99.8
67-5RAS-20RAP −5P	76-16	81.2-18.9	100.1
67-5RAS-20RAP −5P-1 h	76-16	81.3-19.3	100.6
67-5RAS-20RAP −5P-48 h	76-16	81.5-19.2	100.7
Binder Blend	PG-Grading	Continuous-Grading	UTI (°C)
70CO	70-22	73.8-26.7	100.5
70-5P	70-22	74.3-25.8	100.1
70-5P-1h	70-22	74.2-25.7	99.9
70-5P-48h	70-22	74.9-25.6	100.5
70-5RAS	76-22	78.2-25.3	103.5
70-5RAS-5P	76-22	77.1-25.0	102.1
70-5RAS-5P-1h	76-22	78.1-24.6	102.7
70-5RAS-5P-48h	76-22	78.5-24.4	102.9
70-20RAP	82-16	84.1-18.4	102.8
70-20RAP-5P	82-16	84.2-19.8	104.0
70-20RAP-5P-1h	82-16	84.7-20.7	105.4
70-20RAP-5P-48h	82-16	85.4-19.1	104.5
70-5RAS-20RAP	88-16	88.8-18.2	107.0
70-5RAS-20RAP-5P	82-16	85.8-18.0	103.8
70-5RAS-20RAP-5P-1h	82-16	85.8-19.4	105.2
70-5RAS-20RAP-5P-48h	86-16	86.2-19.0	105.2

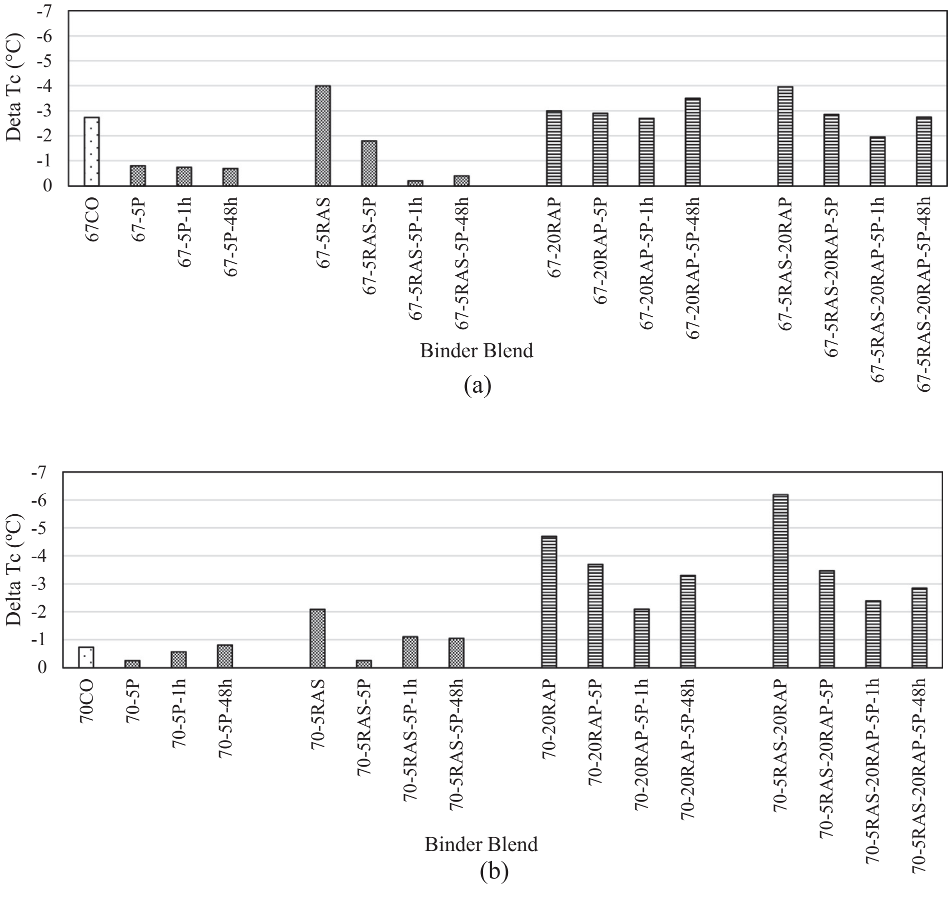

Fig. 3. Delta Tc Results for (a) PG 67-22 Binder Blends, (b) PG 70-22M Binder Blends.

of 20% RAP, and 5% RAS + 20% RAP caused a decrease in low temperature of the binder blends from –23.6 °C for 67CO to −18.3 °C (67-20RAP) and −18 °C (67-5RAS-20RAP). For binder blends with 20% RAP, and 5% RAS + 20% RAP, the low-temperature grade decreased to −16 °C. It should be mentioned that the effect of the self-healing polymer on the binder blends containing recycled materials was not sufficient to change the low-temperature grade of the binder blends.

5.3.1. Useful temperature Interval (UTI)

UTI was calculated as the range of temperature that the binder is expected to have a satisfactory performance. Based on the results presented in Table 3, the addition of 5% self-healing polymer, 5% RAS, 20% RAP, and 5% RAS + 20% RAP to the PG 67–22 binder blends led to increase the UTI of the virgin binder from 91.6 °C to 92.1 °C, 93.5 °C, 100.1 °C, and 99.8 °C, respectively. For blends containing the self-healing polymer, a further increase in the UTI value was observed with exposure to UV light, however, these changes were insignificant and within the expected variability range of the test. The same behavior was observed in blends prepared with PG 70-22M. In summary, self-healing polymer application followed by UV light exposure increased UTI and therefore, the temperature susceptibility of the virgin binder was improved.

5.3.2. Delta Tc (ΔTc)

Delta Tc results for binder blends prepared with PG 67-22 and PG 70-22M binders are presented in Fig. 3. For binder blends prepared with virgin binders PG 67-22 and PG 70-22M, delta Tc values of −2.7 and −0.7 were obtained, respectively. Both binders were m-controlled; however, as expected, virgin binder PG 70-22M showed a greater binder performance at low temperature. The addition of recycled materials (5% RAS, 20% RAP, and 5%RAS + 20% RAP) to the virgin binder, led to a decrease in Delta Tc of the binder blends. The increase in Delta Tc is due to the loss of relaxation caused by the incorporation of the aged recycled binder. The addition of self-healing polymers to the virgin binders resulted in a decrease in the calculated Delta Tc; this decrease was more significant for unmodified binder (PG 67-22).

The decrease in Delta Tc caused by the self-healing polymer may be attributed to the increase in stiffness and the decrease in relaxation of the binder. The increase in self-healing polymer content resulted in a further decrease in Delta Tc. 1 h of UV exposure improved the low-temperature cracking performance, while 48 h UV increased the Delta Tc, slightly. The loss of relaxation through 48 h of UV light exposure can be due to aging caused by the UV light. In other words, aging that occurred through UV light exposure was greater than the enhancement provided by the polymer. The same behavior was observed when the self-healing polymer was added to the binder blends containing 5% RAS and 5% RAS + 20% RAP. From these results, the self-healing polymer did not substantially affect the low-temperature grade of the binder blends; therefore, self-healing polymer did not substantially improve the thermal cracking resistance of the binder based on PG testing.

5.4. Multiple Stress creep recovery results

The MSCR test was conducted at 67 °C and the results for the percent recovery and non-recoverable creep compliance (Jnr) are presented in Figs. 4 and 5. For binder blends prepared with PG 67-22 virgin binder, a percent recovery of 1.6% was measured, while the addition of 5% self-healing polymer resulted in 3%

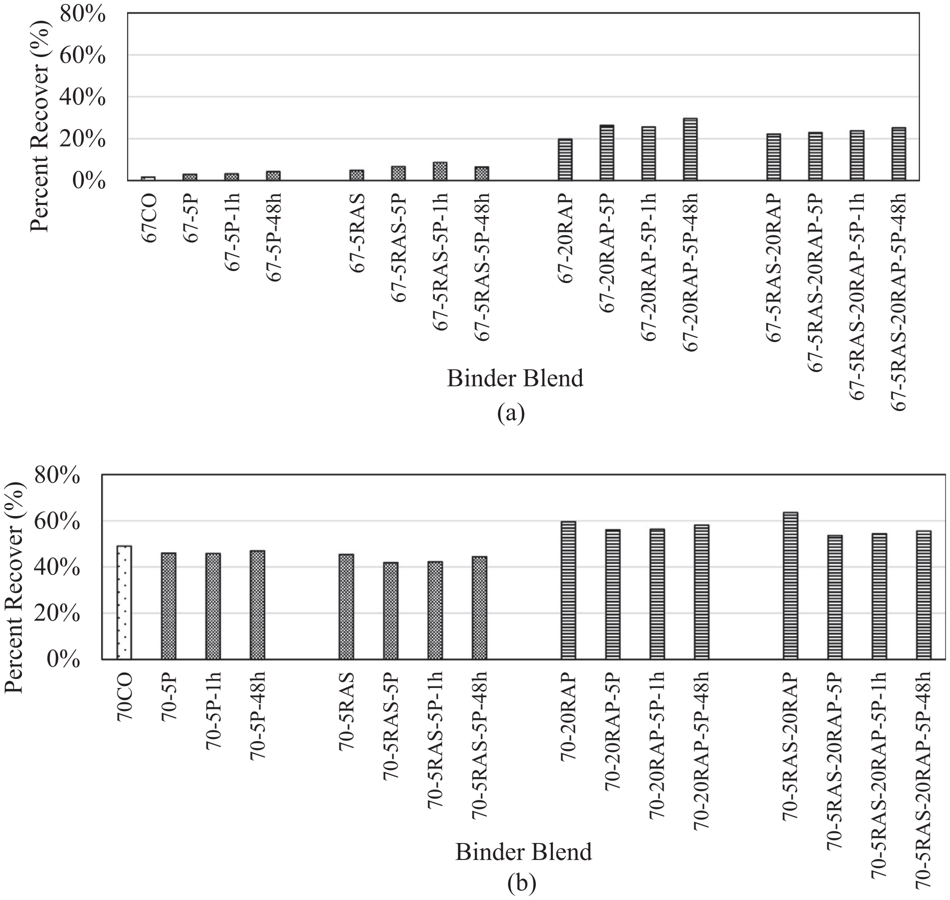

Fig. 4. Percent recovery Results for (a) PG 67-22 Binder Blends, (b) PG 70-22M Binder Blends.

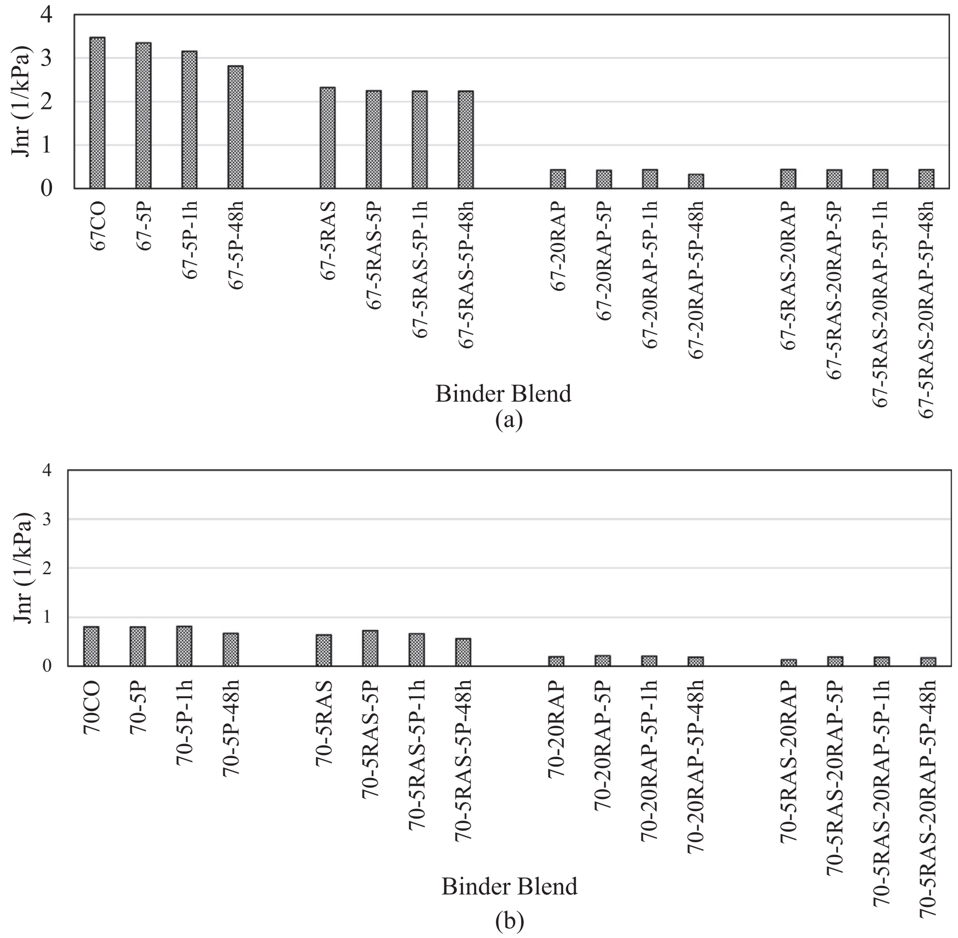

Fig. 5. Non-recoverable Creep Compliance (Jnr) Results for (a) PG 67-22 Binder Blends, (b) PG 70-22M Binder Blends.

percent recovery. This indicates the improvement in the elastic behavior of unmodified binder through the addition of self-healing polymer. Furthermore, the addition of 5% RAS, 20% RAP, and 5% RAS + 20% RAP, led to a percent recovery of 4.9%, 19.8%, and 22.2%, respectively. Moreover, the percent recovery of the binder blends increased with UV light exposure while the non-recoverable creep compliance (Jnr) decreased. The results obtained from the MSCR test for the PG 67-22 binder blends indicate an improvement in the rutting susceptibility of the binder blends. On the contrary, for PG 70-22M binder blends, the percentage recovery and the non-recoverable creep compliance (Jnr) of the binder blends respectively decreased and increased with the use of self-healing polymer. Therefore, the addition of self-healing polymer improved the performance of unmodified binder, while it failed to enhance the properties of polymer modified binder blends. The lack of enhancement in the case of the PG 70-22M binder blends may be due to the interaction of SBS polymer with polyurethane in the self-healing polymer and the RAS materials.

5.5. Linear Amplitude Sweep test results

The LAS test was performed in accordance with AASHTO TP 101 at a testing temperature of 18 °C and 21 °C for PG 67-22 and PG 70-22M binder blends, respectively. The fatigue characteristics of the binder blends obtained from LAS test are presented in Fig. 6. Based on the equation of the fatigue law, a higher “A” parameter indicates an increase in fatigue life, while a higher “B” parameter indicates a decrease in fatigue life at a constant A. The results for the number of cycles to failure (N_f) at two strain levels (2.5% and 5%) are presented in Fig. 6. For the PG 67-22 binder blends, the addition of 5% polymer increased the fatigue life (N_f) while the addition of 5% RAS, 20% RAP, and 5% RAS + 20% RAP resulted in a decrease in fatigue life (N_f). Furthermore, the addition of self-healing polymer to the binder blends containing recycled materials caused a further decrease in the fatigue life (N_f). Exposure to UV light also led to a decrease in the fatigue life of the binder. When 5% RAS was added to PG 70-22M binder blends, the fatigue life was not affected significantly. However, the addition of 5% self-healing polymer and UV exposure negatively affected the fatigue life. It should be mentioned that UV light can negatively affect the fatigue properties of the blend through aging of the samples.

6. Conclusions

The objective of this study was to evaluate the effects of a UV light activated self-healing polymer (OXE-CHI-PUR) on the chemical and rheological properties of asphalt binder. Different binder blends were prepared using two different binders (an unmodified binder and a polymer modified binder), with or without extracted binder from recycled asphalt materials (RAS and/or RAP), and with or without 5% self-healing polymer. Chemical tests such as HP-GPC and FTIR evaluated the aging and molecular distributions of the prepared blends, while DSR, BBR, and LAS were used in rheological testing. Based on the results of the experimental program, the following conclusions may be drawn:

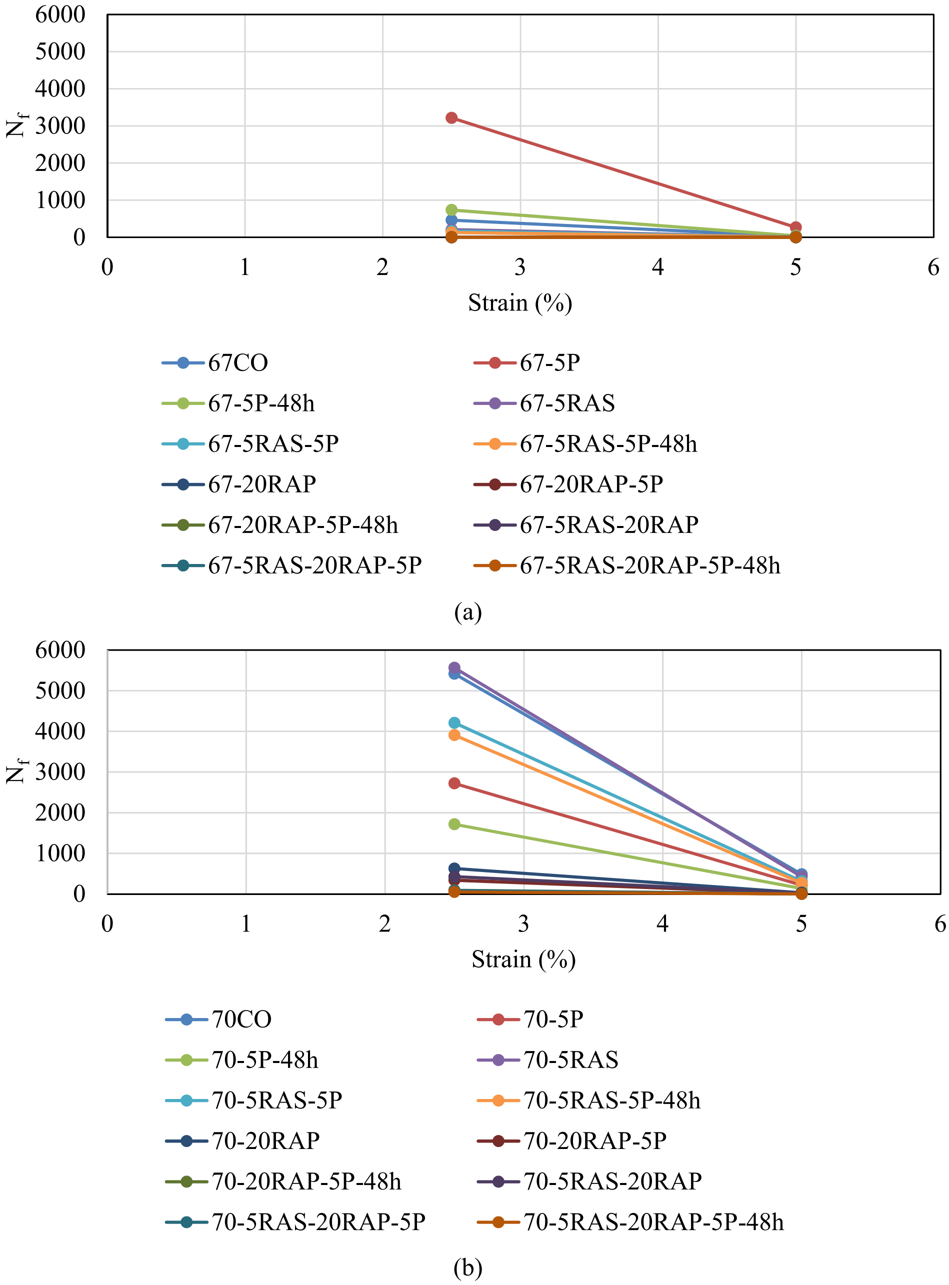

Fig. 6. LAS Results for (a) PG 67-22 Binder Blends, (b) PG 70-22M Binder Blends.

6.1. Molecular distributions and aging

- HP-GPC test results showed that the HMW/LMW ratios of the binder blends increased through the addition of recycled materials. Furthermore, self-healing polymer incorporation led to a further increase in the ratios, resulting in a higher stiffness. The expected increase caused by the addition of recycled materials relates to the incorporation of the oxidized binder, while the increase in HMW/LMW ratio for blends containing self-healing polymer, may be due to the absorption of the light fractions in the binder by the polymer.
- FTIR test results showed that the addition of recycled materials led to an increase in carbonyl index resulting in an increase in stiffness. The measured index further increased with to the addition of 5% polymer due to the absorption of the oily fractions by the self-healing polymer.

6.2. Rheological testing

- Performance grade results showed that 5% RAS caused a one-grade increase in the high-temperature grade of the binder blends, while 20% RAP and 5% RAS + 20% RAP had more significant effects with two grades increase. The addition of self-healing polymer led to an increase in the continuous high temperature; however, it was not significant enough to change the high-temperature grade.
- The difference between the critical stiffness temperature and the m-value critical temperature (Delta Tc) showed an improvement at low service temperature for samples with 5% self-healing polymer when exposed to UV light.
- Based on the results of the MSCR test, the elastic behavior of the unmodified binder improved with the use of self-healing polymer. However, for modified binders, the percent

recovery decreased by increasing the contents of self-healing polymer.

- LAS results showed that self-healing polymer improved the fatigue performance of the unmodified binder. However, when it was added to the binder blend containing recycled materials, negative effects were observed. Self-healing polymer addition to modified binder (PG 70-22M) also resulted in a decrease in the fatigue life.

Overall, the addition of self-healing polymer led to an increase in stiffness and an improvement in the rutting performance, while it did not have a positive effect on the low-temperature cracking performance. For unmodified binder (PG 67-22), self-healing polymer modification improved the elastic and fatigue cracking properties of the binder. However, when it was added to a polymer-modified binder (PG 70-22M) and/or binder blends containing recycled asphalt materials, the potential of this material was low to negative on the low temperature and fatigue cracking performances.

7. Future work

Results obtained from this study showed that self-healing polymer could have a positive effect on the performance of the binder blends prepared with unmodified asphalt binder (PG 67-22); while it negatively affected the PG 70-22M blends. It should be mentioned that in most cases, changes caused by the addition of self-healing polymer were insignificant, which can be an indication of poor storage stability and non-compatibility of self-healing polymer with asphalt binder. In future work, it is suggested to evaluate the effect of the polymer on the performance properties of asphalt mixture such as cracking resistance (at intermediate and low temperature), rutting resistance, and self-healing ability. In addition, for a better understanding of the effect of self-healing polymer on the rheological properties of asphalt binder, chemical and rheological tests should also be conducted on the binder extracted from asphalt mixture samples incorporating self-healing polymer.

Declaration of Competing Interest

None.

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References

[1] A. Tabakovic, E. Schlangen, Self-healing technology for asphalt pavements, Adv. Polym. Sci. 54 (2015) 349–359, https://doi.org/10.1007/12_2015_335.

[2] D. Xuan, M. Saleh, N.H.T. Nguyen, Effect of rejuvenator and mixing methods on behaviour of warm mix asphalt containing high RAP content, Constr. Build. Mater. 197 (2019) 792–802, https://doi.org/10.1016/j.conbuildmat.2018.11.205.

[3] B. Gómez-meijide, H. Ajam, P. Lastra-gonzález, A. Garcia, Effect of ageing and RAP content on the induction healing properties of asphalt mixtures, 179, 2018, 468–476. doi:10.1016/j.conbuildmat.2018.05.121.

[4] M. Dinis-almeida, J. Castro-gomes, C. Sangiorgi, S.E. Zoorob, M. Lopes, Performance of Warm Mix Recycled Asphalt containing up to 100% RAP, Constr. Build. Mater. 112 (2016) 1–6, https://doi.org/10.1016/j.conbuildmat.2016.02.108.

[5] M.D. Nazzal, W. Mogawer, A. Austerman, L. Abu, S. Kaya, Multi-scale evaluation of the effect of rejuvenators on the performance of high RAP content mixtures, Constr. Build. Mater. 101 (2015) 50–56, https://doi.org/10.1016/j.conbuildmat.2015.10.029.

[6] S. Shirzad, M.M. Hassan, M.A. Aguirre, L.N. Mohammad, W.H. Daly, Evaluation of sunflower oil as a rejuvenator and its microencapsulation as a healing agent, J. Mater. Civ. Eng. 28 (2016) 04016116, https://doi.org/10.1061/(ASCE)MT.1943-5533.0001625.

[7] S. Shirzad, M.M. Hassan, M.A. Aguirre, L.N. Mohammad, S. Cooper, I.I. Negulescu, Microencapsulated sunflower oil for rejuvenation and healing of asphalt mixtures, J. Mater. Civ. Eng. 29 (2017) 04017147, https://doi.org/10.1061/(ASCE)MT.1943-5533.0001988.

[8] I.L. Hia, V. Vahedi, P. Pasbakhsh, Self-healing polymer composites: prospects, challenges, and applications, Polym. Rev. 56 (2016) 225–261, https://doi.org/10.1080/15583724.2015.1106555.

[9] A.R. Abbas, U.A. Mannan, S. Dessouky, Effect of recycled asphalt shingles on physical and chemical properties of virgin asphalt binders, Constr. Build. Mater. 45 (2013) 162–172, https://doi.org/10.1016/j.conbuildmat.2013.03.073.

[10] R.B. Mallick, B.L. Chen, J.S. Daniel, P.S. Kandhal, Heating and its effect on hot in-place recycling of asphalt pavements with rejuvenator, Int. J. Pavement Res. Technol. 5 (2012) 347–359.

[11] A. Garcia, E. Schlangen, M. van de Ven, Two ways of closing cracks on asphalt concrete pavements: microcapsules and induction heating, Key Eng. Mater. 417–418 (2009) 573–576, https://doi.org/10.4028/www.scientific.net/KEM.417-418.573.

[12] M.A. Aguirre, M.M. Hassan, S. Shirzad, L.N. Mohammad, S.B. Cooper, Performance of asphalt rejuvenators in hot-mix asphalt containing recycled asphalt shingles, Transp. Res. Rec. J. Transp. Res. Board. (2017) 108–116.

[13] Á. García, E. Schlangen, M. Van De Ven, Properties of capsules containing rejuvenators for their use in asphalt concrete, Fuel 90 (2011) 583–591, https://doi.org/10.1016/j.fuel.2010.09.033.

[14] A. Kavussi, P. Barghabany, Investigating fatigue behavior of nanoclay and nano hydrated lime modified bitumen using LAS test, J. Mater. Civ. Eng. 28 (2015) 1–7, https://doi.org/10.1061/(ASCE)MT.1943-5533.0001376.

[15] J. Qiu, M.F.C. van de Ven, A.A.A. Molenaar, J. Qiu, S. Wu, J. Yu, Investigating the self healing capability of bituminous binders, Road Mater. Pavement Des. 10 (2009) 81–94, https://doi.org/10.1080/14680629.2009.9690237.

[16] M. Mazumder, H. Kim, S.J. Lee, Performance properties of polymer modified asphalt binders containing wax additives, Int. J. Pavement Res. Technol. 9 (2016) 128–139, https://doi.org/10.1016/j.ijprt.2016.03.004.

[17] G. Polacco, S. Filippi, F. Merusi, G. Stastna, A review of the fundamentals of polymer-modified asphalts: asphalt/polymer interactions and principles of compatibility, Adv. Colloid Interface Sci. 224 (2015) 72–112, https://doi.org/10.1016/j.cis.2015.07.010.

[18] W. Woo, J. Hilbrich, C. Glover, Loss of polymer-modified binder durability with oxidative aging: base binder stiffening versus polymer degradation, Transp. Res. Rec. J. Transp. Res. Board. 2007 (1998) 38–46, https://doi.org/10.3141/1998-05.

[19] B. Ghosh, K.V. Chellappan, M.W. Urban, Self-healing inside a scratch of oxetane-substituted chitosan-polyurethane (OXE-CHI-PUR) networks, J. Mater. Chem. 21 (2011) 14473–14486, https://doi.org/10.1039/c1jm12321a.

[20] S. Shirzad, M.M. Hassan, M.A. Aguirre, S. Cooper, I.I. Negulescu, Effects of light-activated self-healing polymers on the rheological behaviors of asphalt binder containing recycled asphalt shingles, Transp. Res. Rec. (2018), https://doi.org/10.1177/0361198118772726.

[21] W.H. Daly, I. Negulescu, S.S. Balamurugan, Implementation of GPC Characterization of Asphalt Binders at Louisiana Materials Laboratory, 2013.

[22] B. Hofko, L. Porot, A. Falchetto Cannone, L. Poulikakos, L. Huber, X. Lu, K. Mollenhauer, H. Grothe, FTIR spectral analysis of bituminous binders: reproducibility and impact of ageing temperature, Mater. Struct. Constr. 51 (2018), https://doi.org/10.1617/s11527-018-1170-7.

[23] B. Hofko, M. Zia, A. Hinrich, G. David, Repeatability and sensitivity of FTIR ATR spectral analysis methods for bituminous binders, Mater. Struct. 50 (2017) 1–15, https://doi.org/10.1617/s11527-017-1059-x.