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Rheological and Component Characterization of an Innovative Bio-Binder Using Guayule Resin in Partial and Entire Asphalt Replacement

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ABSTRACT

Asphalt cement will not last for a long time as the world encounters a diminishment in the crude oil. For sustainable, flexible pavement development, new resources can provide a contribution to replace it partially or entirely. In this study, asphalt was partially and entirely replaced by guayule resin as a bioresource by-product, extracted during the guayule natural rubber production. Crumb rubber modifier (CRM) was used as an asphalt enhancer. The Superpave grading system was followed at high, intermediate, and low temperatures to evaluate such innovative binder for rutting, fatigue, and thermal cracking, respectively, in addition to viscosity. Therefore, the original, short-term aging and long-term aging were simulated using tank, rolling thin film oven, and pressure aging vessel materials. Additionally, component analysis using Fourier-transform infrared spectroscopy was provided to link the rheological properties with the chemical changes. Outcomes showed a relatively much lower viscosity of guayule in the same high-temperature asphalt grade indicating savings in plant energy consumption and reduced environmental emissions. CRM enhanced guayule, but not as much as asphalt, proven by polymeric component migration through liquid binder. This enhancement was reflected in the rheological performance besides other factors. As-received guayule seems to have high oxygen content proven by strong absorption peak intensities of oxidative bonds (e.g., Carbonyl and sulfoxide). Such pre-oxidation was negatively reflected in the intermediate- and low-temperature performance of guayule and guayule-based binders. However, the investigated guayule had potential to compensate for asphalt replacement in the presence of CRM by 23–42% by weight of blend.

Keywords: Asphalt Rheology, Asphalt Rubber, Component Analysis, Crumb Rubber Modifier, FTIR, Guayule Resin, Infrared Spectra, Superpave

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1. INTRODUCTION

Guayule resin is a bio-based by-product extracted during the guayule natural rubber production, the current main guayule shrub product (*1*). Guayule shrub is cultivated in the arid zones of the Southwestern U.S. (*2-4*). Guayule natural rubber has encountered challenges since the 1900s (*4*) concerning commercialization due to the overall production cost associated with the guayule plant cultivation through the final product (*1*). Such a challenge has made it not competitive to the dominant source of the natural rubber (Hevea) (*4*). Nevertheless, several researchers ensured that co-products such as guayule resin and bagasse could reduce the guayule production costs to a great extent. Schloman et al. (*5*) mentioned that the guayule by-product commercialization could reduce the gross production costs by 26-49%. Additionally, the guayule-rubber binder has potential to be more distinctive than Hevea rubber for relatively better factors such as being a domestic source of natural rubber (i.e., U.S. national security) (*6*), not a food crop, not labor-intensive and easily mechanized (*4*), and safe for people with Type I latex allergy as no allergenic proteins involved (*4*). Subsequently, we look forward to getting advantage of guayule resin, which almost has no commercial value by this moment, in the massive asphalt industry.

In general, natural resins are amorphous hydrocarbons insoluble in water (*7*). Concerning the asphalt industry, guayule resin is an asphalt-like material (*8*). It is flexible adhesive, very susceptible to temperature change and viscoelastic at room temperature, liquid at high temperatures, and solid at low temperatures (*8*). Hemida and Abdelrahman (*8*) reported that 25–50% asphalt replacement by guayule resin had the potential to provide better high-temperature performance than the conventional asphalt (PG64) but in case of using crumb rubber modifier (CRM) as an enhancer. Likewise, it was evident that there was no liquid phase separation between asphalt and guayule with or without dissolved CRM but poor storage stability due to the CRM particle residue precipitation (*9*). Guayule resin was not only investigated for partial asphalt replacement, but also entire replacement. In a study by Hemida and Abdelrahman (*10*), a soft graded guayule resin (PG52) was compared to a soft graded asphalt cement (PG52). The rheological performance was investigated for the entire asphalt replacement (i.e., studying the virgin guayule resin with and without CRM) under the Superpave grading criteria). Nevertheless, we still need to link such innovative binder performance to the associated chemical changes with considering the aging stages, so adjustments to improve such a binder could be followed in the future.

Guayule resin (with or without modifications) has the potential to be an asphalt cement replacer since it is a renewable material (bioresource) (*9*), fast cultivation process (2–3 years) (*6*), less environmental influence (*4*), potential to be cheaper (*8; 9*). On the other hand, the global price of crude oil sharply increases (*11*), and it is expected no fossil fuel is remaining after the year 2042 other than coal (*12*). Such inevitable depletion in crude oil has to be substituted by innovative approaches (*13; 14*). We believe that guayule resin could be utilized in the flexible pavement industry for sustainable development since it had signs to provide an asphalt binder replacement (*8-10; 15*).

According to the Superpave grading system, asphalt cement could be classified as regular asphalt (e.g., PG52-16, PG52-28, PG64-22, and PG70-16), high-quality asphalt (e.g., PG52-34, PG70-22, and PG76-16, and modified asphalt (could reach up to PG76-40) (*16*). Guayule resin could be classified as a small range of the Superpave grade based on its temperature tolerance, unlike asphalt cement that has various grades discovered for an extended time by research (*10*). The virgin guayule resin (used after heat-treatment in this study) could reach up to a 57.4℃ high-temperature grade (*8*), a 24.8℃ intermediate-temperature grade, and a -16.4℃ low-temperature grade (as discussed in this study). Literature reported that in general, there is a difficulty in using bio-binders at low temperatures since they present a low performance (*17; 18*). Nevertheless, there is a belief that guayule modifications could raise the temperature range. A blend of 62.5% asphalt, 12.5% rubber, and 25% guayule resin resulted in a 72.2℃ high-temperature grade (*8*). More details are provided in this study regarding low- and intermediate-temperature performance and attempts to link the mechanical behavior of guayule-based binders to the associated chemical changes.

This study aimed to investigate the utilization of guayule resin for partial and entire asphalt binder replacement. The designated binders in this research involved a wide range of material parameters that might relieve the primary role of guayule resin for sustainable, flexible pavement industry. These binders represented virgin asphalt cement (control), virgin guayule resin, asphalt-guayule, guayule-rubber, asphalt-rubber, and asphalt-guayule-rubber binders. The study established the Superpave requirements to evaluate all designated binders. Such designated binders were exposed to tests that address construction process (mixing and compaction requirements), rutting, fatigue, and thermal cracking resistance through viscosity, high-, intermediate-, and low-temperature measurements, respectively. Additionally, they were exposed to the Fourier-transform infrared spectroscopy (FTIR) with an attempt to chemically understand the clue behind the presented rheological performance in various conditioning: as-received materials, after blending (interaction), after rolling thin film oven (RTFO), and pressure aging vessel (PAV) conditioning.

2. MATERIALS AND METHODS

2.1 Raw Materials

Sampling in this research was based on asphalt cement (control), guayule resin (the so-called "guayule" hereafter), and CRM, as shown in **Figure 1a**. Asphalt cement was received from Conoco Phillips terminal in Granite City, Illinois, had a grade of PG52-28 according to the Superpave grading system. Guayule was received from Bridgestone Crop. CRM was received in multiple gradations from Liberty Tire Recycling. However, the only used grade was 30–40 (i.e., passed mesh #30 and retained on mesh #40) according to the US standard system (*19*).

2.2 Sampling

To evaluate guayule as an innovative asphalt replacer, multiple samples were prepared based on asphalt (A), guayule (G), asphalt-guayule (AG), guayule-rubber (GR), asphalt-rubber (AR), and asphalt-guayule-rubber (AGR) binders, as listed in **Figure 1b**. For the binder interaction process, a high shear mixer (HSM), heating mantle, and temperature controller were used. For heat treatment, guayule was heat-treated with stirring at 160℃ using the HSM until no foaming (bubbling) noticed indicating no further moisture involved (*10; 20*). All interactions were conducted at a 190℃ interaction temperature and a 3000-rpm interaction speed throughout different durations. The designated amounts were based on quart cans. Asphalt-guayule blend was mixed for 2 h (labeled AG-2h). The GR, AR, and AGR had two scenarios of blending: one with 20% CRM and the other with 10% CRM (by wt. of the liquid portion: asphalt, guayule, or asphalt-guayule blend). The 20% CRM-involved binders were blended for 4 h [GR(10:2)-4h, AR(10:2)-4h, AGR(5:5:2)-4h]. The 10% CRM-involved binders were blended for 6 h [GR(10:1)-6h, AR(10:1)-6h, and AGR(5:5:1)-6h]. To assess the effect of the CRM parameter on asphalt-guayule-rubber, a 10% CRM-involved binder was created at 4 h (labeled AGR(5:5:1)-4h). To compare the effect of asphalt vs. guayule, two other blends were created, which were AGR(7.5:2.5:1)-6h and AGR(2.5:7.5:1)-6h to be compared to AGR(5:5:1)-6h. All designated binder proportions are presented in **Table 1**.

2.3 Methods

In this study, the Superpave grading system was followed to evaluate the designated binders in addition to component analysis by FTIR. All used techniques are shown in **Figure 1c** and demonstrated in the following Method sections.

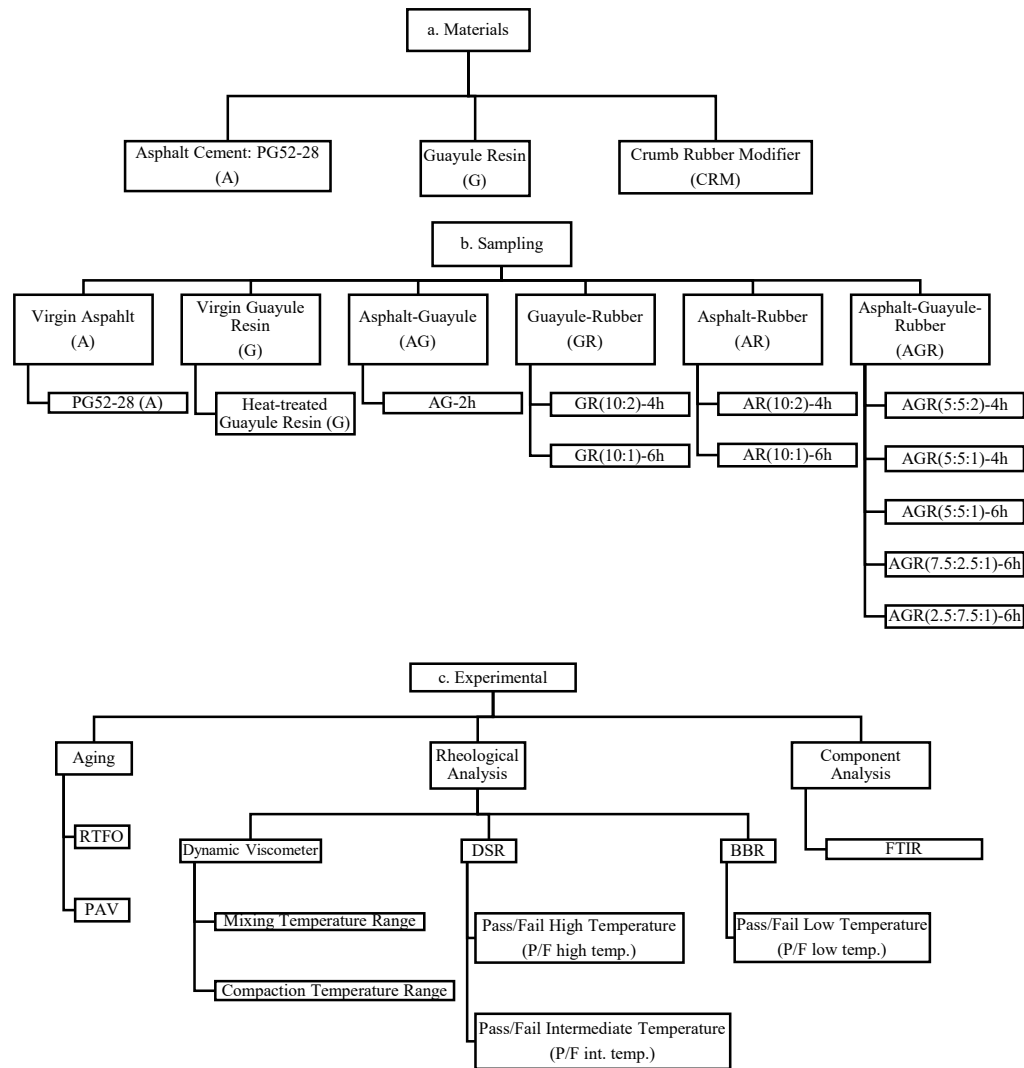Ahmed Hemida and Magdy Abdelrahman

Figure 1 Materials, sampling, and experimental flow charts: (a) materials, (b) sampling, and (c) experimental

Table 1. Binder Codes and Proportions

Binder code	A%	G%	CRM%
	by wt. blend		
A	100%		
G		100%	
AG-2h	50%	50%	
GR(10:2)-4h		83.3%	16.7%
GR(10:1)-6h		90.9%	9.1%
AR(10:2)-4h	83.3%		16.7%
AR(10:1)-6h	90.9%		9.1%
AGR(5:5:2)-4h	41.65%	41.65%	16.7%
AGR(5:5:1)-4h	45.45%	45.45%	9.1%
AGR(5:5:1)-6h	45.45%	45.45%	9.1%
AGR(7.5:2.5:1)-6h	68.18%	22.73%	9.1%
AGR(2.5:7.5:1)-6h	22.73%	68.18%	9.1%

A: asphalt cement (PG52-28); G: heat-treated guayule resin; AG: asphalt-guayule blend; GR: guayule-rubber blend; AR: asphalt-rubber blend; AGR: asphalt-guayule-rubber blend.

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2.3.1   Rheological Methods

Dynamic Viscometer

The dynamic viscometer was used according to AASHTO T 316 (*21*) to obtain the viscosity at 135℃ and 165℃ with applying a 20-rpm revolution speed. Thus, a diagram of dynamic viscosity against temperature was created for asphalt, guayule, and asphalt-guayule binders. Such a diagram illustrates the mixing and compaction temperature ranges based on viscosity values of 0.170±0.020 Pa.s and 0.280±0.030 Pa.s for mixing and compaction, respectively (*22*). Thus, the influence of guayule in different material parameters could be preliminary expected.

Dynamic Shear Rheometer

The dynamic shear rheometer (DSR) was used to investigate the rheological behavior of the designated binders at high and intermediate temperatures. Hence, the rutting and fatigue resistances could be evaluated. The rutting resistance was assessed by determining the pass/fail high temperature (P/F high temp.) based on original, and RTFO-aged materials. The fatigue resistance was evaluated by determining the pass/fail intermediate temperature (P/F int. temp.) based on the PAV-aged materials. The AASHTO T 315 (*23*) was followed for these kinds of tests except for the parallel plate geometry for all binders involving CRM particles. The gap between the upper and lower plates was applied to be 2 mm to ensure no particle effect on the oscillation process (*24-26*).

Bending Beam Rheometer

To assess the low-temperature performance of the designated binders, a bending beam rheometer (BBR) was employed according to AASHTO T 313 (*27*). The creep stiffness (S) and m-value (rate of change of stiffness with loading time) were determined after a 60-sec loading time at the low test temperature, which simulated the performance criteria after 2 h at 10℃ lower field temperature. According to the Superpave grading system, the stiffness is required to be no more than 300 MPa, and m-value is required to be no less than 0.3 (*28; 29*). Both stiffness and m-value are desired to ensure that the thermal cracking will not take place at the pass/fail low-test temperature (P/F low temp.). The P/F low temp. was determined to correspond to what passed in both stiffness and m-value (the higher P/F low temp.). Most binders were exposed to -6℃, -12℃, and -18℃ test temperatures corresponding to -16℃, -22℃, and -28℃ field temperatures, respectively (*28; 29*). Two diagrams were created to show the relationship between both creep stiffness and m-value with the test temperature. According to the least square method, the P/F low temp. was determined for each designated binder.

2.3.2   Aging Methods

To simulate the short-term aging (construction process) and long-term aging (end of in-service pavement life), the RTFO according to AASHTO T 240 (*30*) and the PAV according to AASHTO R 28 (*31*), respectively, were used. The RTFO was run at 163℃ and 4000 ml/min for 85 min. The PAV was run for 20 h at 2.1 MPa and 100℃. Besides, the RTFO was used to demonstrate the mass loss of the created binders since it mimics the loss of volatiles and oxidation through the construction process (*32*). The literature showed that the mass change of virgin asphalt through such a process reaches up to ±1% (i.e., the lower the grade, the higher the mass loss). On the other hand, the literature reported that the mass loss attributed to the bio-binders was much higher due to moisture, lightweight volatiles, or both (*32*).

2.3.3   Component Analysis

The chemical changes might help understand why rheological performance has occurred. Thus, the binder can be enhanced in the future based on conceptual research. Based on the wavenumbers, it was easy to distinguish among the material constituents and the potential of chemical changes that might take place. The FTIR was used in an attempt to depict what components might be dissolved or migrated from CRM to

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the liquid binder (asphalt, guayule, and asphalt-guayule blend) and vice versa. Additionally, the effect of oxidative aging was considered, and comparisons were made based on the original, RTFO-aged, and PAV-aged materials.

The diamond attenuated total reflection (ATR) technique was used since it provided less effort, faster testing, and did not require a solvent dilution (*9*), unlike the KBr disk technique (*33; 34*). Therefore, it presented more representative results due to its pure material dependency. A tiny sample was pulled on the diamond surface for a sufficient thickness as the absorption spectrum required a few-micrometer penetration depth (*35*). The infrared spectra were collected based on an accumulation of 32 scans with a resolution of 4 cm^{-1} in arrange of 4000–400 cm^{-1}. However, the display range presented in this study relied on the exciting range of analysis.

3. RESULTS AND DISCUSSIONS

3.1 Mixing and Compaction Requirements

Figure 2 illustrates the mixing and compaction temperature ranges of asphalt cement (PG52-28), guayule, and asphalt-guayule binders. It seems that the trendline of the asphalt-guayule blend (AG-2h), which included 50% asphalt and 50% guayule, was located closer to the guayule trendline. Such a trendline might illustrate the slight domination of guayule on the blend viscosity. As could be seen in the figure, despite the same grade of asphalt and guayule(PG52), guayule presents a relatively much lower viscosity, which reflects reduced production temperatures, hence savings in plant energy consumption and reduced environmental emissions (*36*). For instance, it was 0.149 Pa.s for guayule, but 0.244 Pa.s for asphalt at 135℃. Asphalt and guayule had mixing temperature ranges of 140–146℃ and 129–136℃, respectively. Likewise, they had compaction temperature ranges of 129–134℃ and 114–120℃, respectively. The mixing and compaction temperatures of the asphalt-guayule blend (AG-2h) were found to be in the range of 132–139℃ and 119–125℃, respectively.
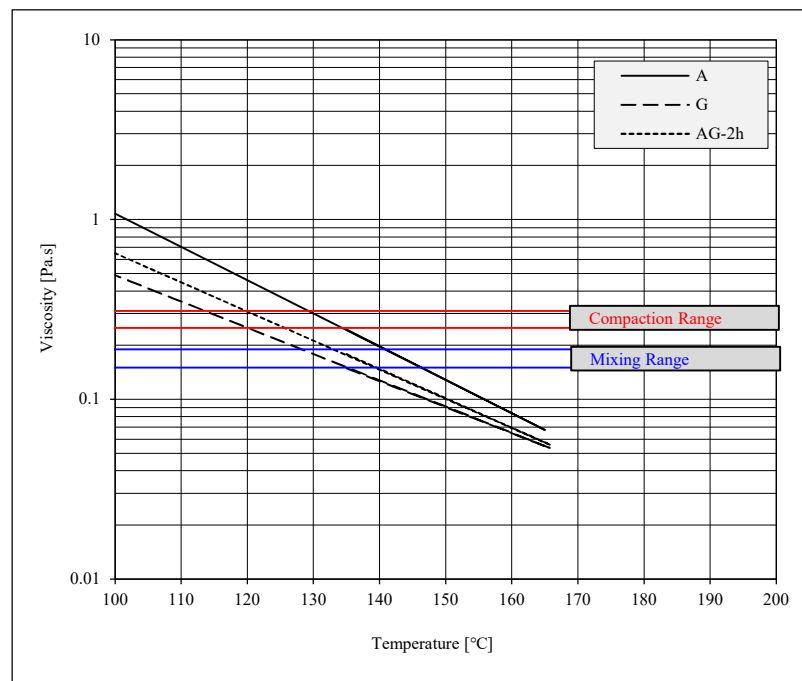
Figure 2 Mixing and compaction temperature ranges: asphalt (A), guayule (G), and asphalt-guayule blend (AG-2h)

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3.2 Rutting Resistance

The P/F high temp. of each designated binder (Original and RTFO) is illustrated in **Figure 3**. The P/F high temp. of the RTFO-aged binders did not significantly differ compared to their original condition. In which, the P/F high temp. of original binders was determined at 1 kPa but 2.2 kPa for RTFO aging (*23*). It was slightly raised with RTFO aging for all bio-based binders (*17*). Such an increase of high-temperature performance with RTFO aging could be analyzed by the loss of lightweight components (as discussed in Section 3.5), ending up with a rise in average molecular weight and stiffness (*32*). The following demonstrations in this section were based on the RTFO-aged binders. The virgin asphalt (control) and virgin guayule had 57.3℃ and 54.2℃ P/F high temperatures, respectively. The asphalt-guayule blend (AG-2h) yielded a 53.9℃ P/F high temp., which indicted the same high-temperature grade (PG52). It was noticed that the 20% CRM addition differed when comparing its effect on asphalt against guayule. Rubber significantly enhanced the rheological properties of virgin asphalt by resisting rutting distress (*37*). The AR(10:2)-4h resulted in a 77.2 P/F high temperature. However, the GR(10:2)-4h resulted in a 60.4 P/F high temperature. In other words, the CRM relatively enhanced the rutting resistance of asphalt than that of guayule, as illustrated by infrared spectra later. The 20% CRM improved asphalt and guayule by four grades (about 34.7%, compared to the virgin binder) and one grade (about 11.4%), respectively. The corresponding asphalt-guayule-rubber blend (AGR(5:5:2)-4h) yielded a 60.5 P/F high temp., indicating the domination of guayule on the overall blend regarding high temperatures, which was identical to the GR(10:2)-4h. Similar behavior was observed for the 10% CRM-involved binders. The CRM enhanced the virgin guayule in GR(10:1)-6h by 4.6% and the virgin asphalt in AR(10:1)-6h by 15.9%. The AGR(5:5:1)-6h was enhanced by 10% compared to the asphalt-guayule blend (AG-2h).The AGR(7.5:2.5:1)-6h and AGR(2.5:7.5:1)-6h resulted in 59.7℃ and 56℃ P/F high temperatures, respectively. The P/F high temperature of AGR(5:5:1)-6h was located between both AGR(7.5:2.5:1)-6h and AGR(2.5:7.5:1)-6h, indicating a regular influence of asphalt and guayule concentrations on the product performance. Ultimately, the authors in this research believe that such guayule had the domination of the whole binder behavior at the end.
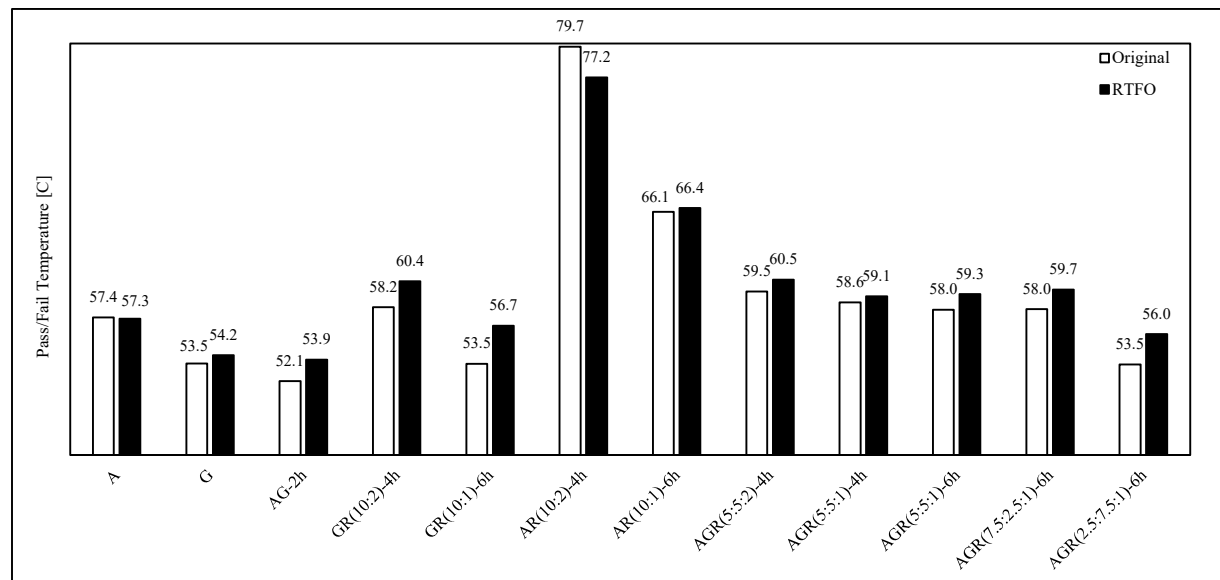

Figure 3 Pass/fail high temperatures of all designated binders (Original and RTFO)

3.3 Fatigue Resistance

Figure 4 illustrates the P/F int. temp. of all designated binders. The virgin asphalt had a 16℃ P/F int. temp., whereas the virgin guayule had a 24.8℃ P/F int. temp. With looking at the high-temperature grade and low-temperature grade (discussed later) of guayule, it was found that its intermediate-

temperature grade almost located at the average of high and low-temperature grades plus 4℃ defined by the Superpave grading system(*28*), which reflected the compatibility of the Superpave grading system with such a new binder to a great extent. As expected, the asphalt-guayule blend (AG-2h) resulted in a 20.1℃ P/F int. temp., which denoted almost the average of asphalt and guayule P/F int. temperatures. The addition of 10% or 20% CRM to guayule did not affect the intermediate-temperature grade of the guayule-rubber blend. Upon which, the GR(10:2)-4h and GR(10:1)-6h yielded 25.1℃ and 24.5℃ P/F int. temp., respectively, very close to the virgin guayule (24.8℃). On the other hand, CRM significantly enhanced the intermediate-temperature grade of the virgin asphalt as resulted by AR(10:2)-4h and AR(10:1)-6h (7.9℃ and 11℃, respectively). Thus, the higher the CRM concentration, the better the intermediate-temperature performance of the asphalt-rubber binder. The asphalt-guayule-rubber blends provided a good indication in terms of intermediate-temperature grades. The higher the asphalt (with or without CRM) concentration, the better the intermediate-temperature performance of the asphalt-guayule-rubber blend. The AGR(5:5:2)-4h resulted in 16.5℃, whereas the AGR(5:5:1)-4h resulted in 19.8℃. Increasing the interaction time of AGR(5:5:1) to 6 h (AGR(5:5:1)-6h) negatively influenced the intermediate-temperature grade (22℃), rationally stiffer. The effect of asphalt concentration could be depicted by comparing AGR(7.5:2.5:1)-6h to AGR(2.5:7.5:1)-6h, which resulted in 14.6℃ and 21℃, respectively.
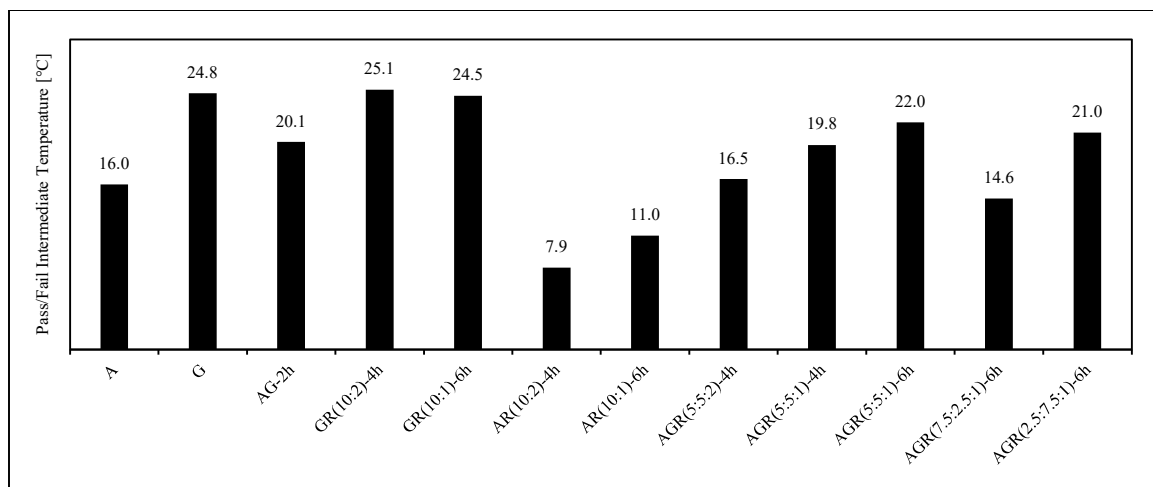

**Figure 4 Pass/fail intermediate temperatures of all designated binders**

3.4 Thermal Cracking Resistance

Figure 5a and **Figure 5b** illustrate both creep stiffness (S) and m-value, respectively, with test temperature. It seems that CRM negatively affected the performance of guayule-rubber (GR) binders. The GR(10:2)-4h and GR(10:1)-6h resulted in worse test temperatures (-6℃ and -3.7℃, respectively) compared to the virgin guayule (-6.4℃). It was noticed that CRM enhanced the low-temperature grade of asphalt-guayule-rubber binders. For instance, the performance was better with AGR(5:5:2)-4h (-15.5℃ P/F low temperature). In contrast, Peralta et al. (*17*) showed that the lower concentrations of CRM in bio-binders led to a better performance at low temperatures. Since the virgin asphalt had a much significant lower P/F temperature (-18.7℃) compared to the virgin guayule (-6.4℃), a higher asphalt concentration led to enhancing the binder performance (e.g., AGR(7.5:2.5:1)-6h > AGR(5:5:1)-6h > AGR(2.5:7.5:1)-6h, which had P/F low temperatures of -17.9℃, -12.4℃, and -12.1℃, respectively). From this, we may conclude that two binders (AGR(7.5:2.5:1)-6h and AGR(5:5:2)-4h) were close to the virgin cement P/F low temperature, which had -17.9℃ and -15.5℃, respectively, but the AR binders (AR(10:2)-4h and AR(10:1)-6h) yielded a much better performance (-27.7℃ and -24.6℃, respectively). As expected, a half asphalt to half guayule blend (AG-2h) led to a P/F low temperature of -12.7℃, almost the average of asphalt and guayule P/F low temperatures. Such a behavior indicated the simplicity of guayule influence when blended with asphalt

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concerning the low-temperature grade, unlike the degradation associated with the guayule-based binders at the high-temperature performance.
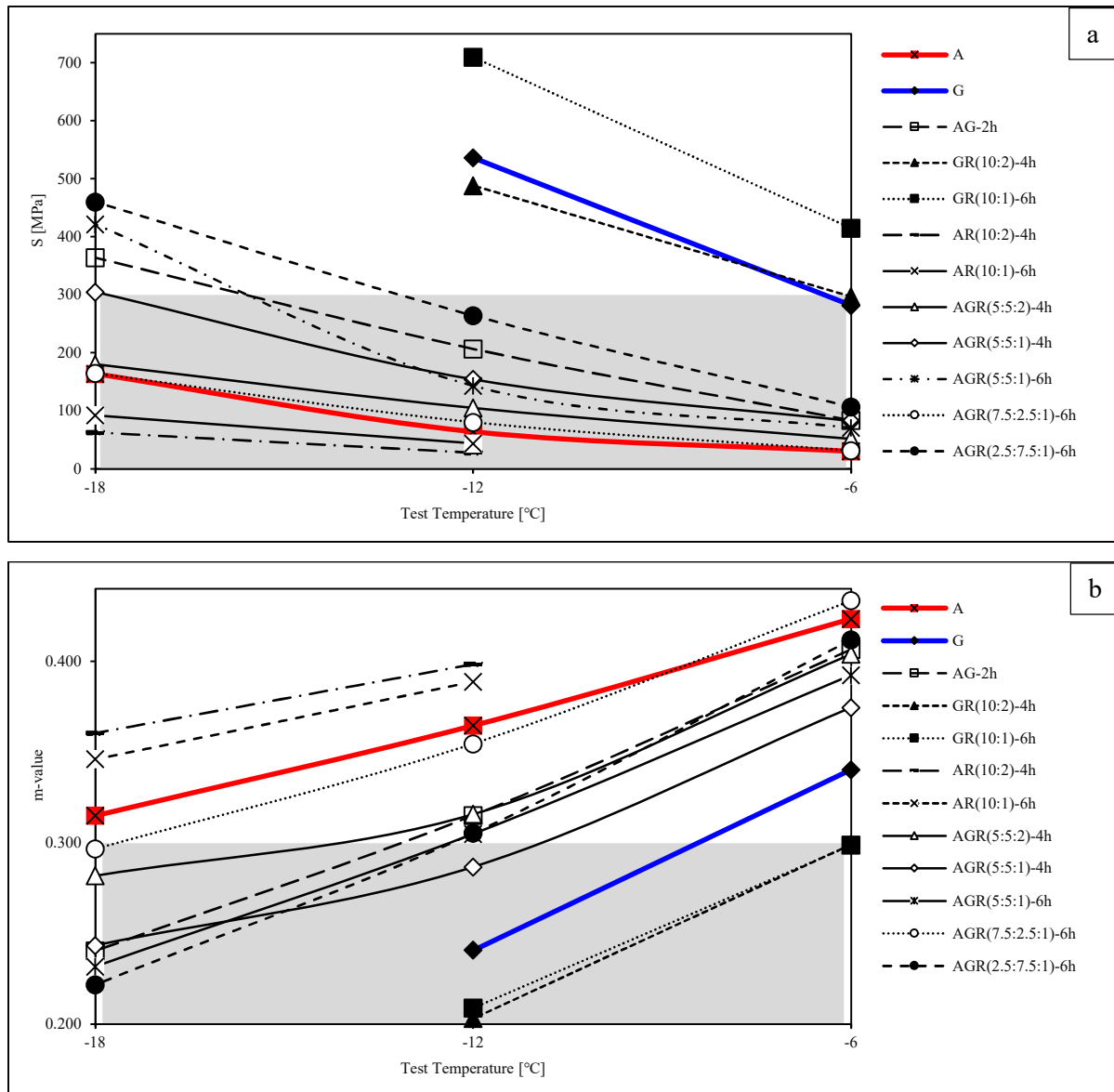
Figure 5 Low-temperature resistance of all designated binders: (a) stiffness (S) and (b) m-value, both with test temperature

3.5 Summary of Performance Grades

Table 2 illustrates the overall rheological performance, required by the Superpave grading system, of all designated binders. In which, one could notice that the most two closest blends to the virgin asphalt cement (control) were the AGR(7.5:2.5:1)-6h and AGR(5:5:2)-4h blends. These blends contained 68.18% asphalt, 22.73% guayule, and 9.1% CRM as well as 41.65% asphalt, 41.65% guayule, and 16.7% CRM, respectively. At these levels of material concentrations, there was a preliminary potential of using guayule resin as a partial replacer of asphalt cement, at the very least, to end up with an equivalent or even better performance in a specific performance grade level (high, intermediate, or low). On the other hand, virgin

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guayule yielded a lower grade (PG54.2-16.4). The CRM enhanced the rheological performance of the virgin guayule at high temperatures, but not intermediate or low temperatures.

Table 2. Temperature Continuous Performance Grade

Binder	Temperature Continuous Performance Grade [°C]		
	High	Intermediate	Low
A	57.3	16.0	-28.7
G	54.2	24.8	-16.4
AG-2h	53.9	20.1	-22.7
GR(10:2)-4h	60.4	25.1	-16
GR(10:1)-6h	56.7	24.5	-13.7
AR(10:2)-4h	77.2	7.9	-37.7
AR(10:1)-6h	66.4	11.0	-34.6
AGR(5:5:2)-4h	60.5	16.5	-25.5
AGR(5:5:1)-4h	59.9	19.8	-20.7
AGR(5:5:1)-6h	59.3	22.0	-22.4
AGR(7.5:2.5:1)-6h	59.7	14.6	-27.9
AGR(2.5:7.5:1)-6h	56.0	21.0	-22.1

3.6 Mass Loss

It was evident that guayule lost high volatile fractions during the RTFO aging compared to the virgin asphalt, as illustrated in **Figure 6**. Multiple volatile fractions might cause such volatilization in guayule, such as α-pinene and β-pinene compounds (*6; 7*). Guayule lost 4.9% by weight. The authors in this research see that such mass loss was in agreement with the volatile fractions' concentration of lightweight compounds mentioned in literature (3–5%) (*1*). In contrast, previous studies reported that the mass loss in bio-oil could be related to further moisture loss (*20; 38*). It seems that guayule lost almost all involved volatile materials mentioned in literature (*1*). Such a mass loss was not associated with either asphalt or asphalt-rubber binders. Instead, it was associated with guayule, asphalt-guayule, guayule-rubber, asphalt-guayule-rubber binders in different percentages. The guayule concentration dominated these percentages.
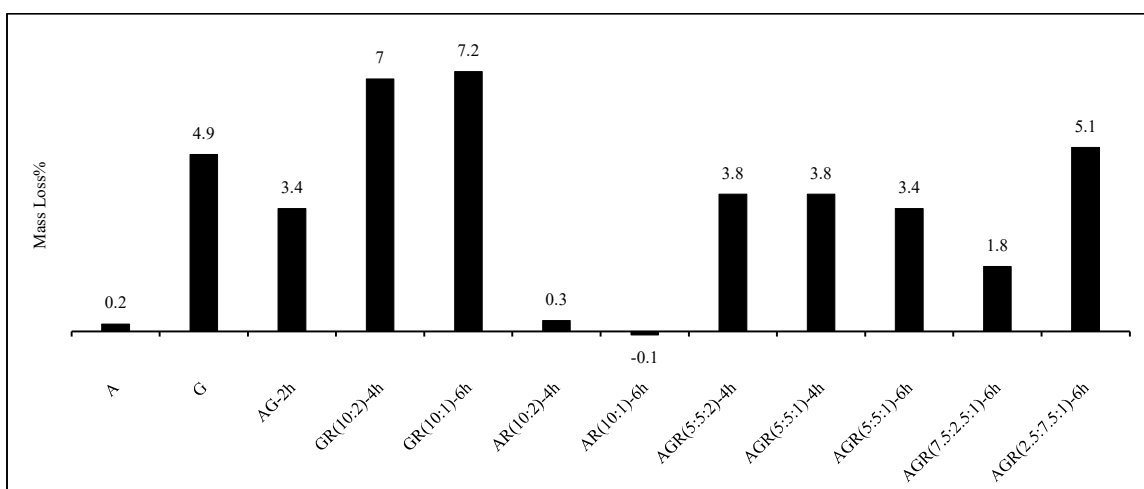
**Figure 6 Mass change of all designated binders**

Lower RTFO temperatures could minimize mass loss. In general, bio-binders seem to provide lower mixing and compaction temperatures, as discussed in Section 3.1 and reported in literature (*14; 17; 18; 32*). That's why previous studies used much lower RTFO-aging temperature (*17; 18; 32*). In this study, guayule-based binders, however, were conditioned with respect to the Superpave requirements (163℃) to mimic the conventional asphalt. Therefore, the mass loss associated with guayule-based binders were relatively high. Nevertheless, guayule seems to provide much lower mass loss than bio-oils reported in literature, even with using (110–140℃) for RTFO aging with such bio-oils (*18; 20; 32*). More details related to mass loss of guayule-based binders against bio-oils investigated in literature are demonstrated by the FTIR analysis in the following section.

3.7 Component Analysis

The rheological performance discussed earlier could be understood by investigating the chemical changes. Therefore, the upcoming discussion addresses the component analysis that could help understand the reasons behind the product performance. Thus, enhancements could be provided in the future concerning guayule applications in the asphalt industry.

Figure 7 illustrates to what extent the similarity between virgin asphalt (PG52-28) and guayule constituents. Nevertheless, guayule did not have a 100% similarity with asphalt. Such variation might be the reason behind the attributed rheological properties. Asphalt and guayule had several same peaks such as 2957, 2924, 2868, and 2853 cm^{-1} (the four distinct peaks of symmetric and asymmetric C−H stretches in CH$_2$ and CH$_3$, aliphatic) (*39; 40*), 1606 cm^{-1} (C=C, aromatic) (*41*), 1452 and 1376 cm^{-1} (symmetric and asymmetric bends of CH$_3$, respectively) (*40; 42; 43*), 1032 cm^{-1} (S=O) (*44*), and 721 cm^{-1} ((CH$_2$)$_n$ rocking absorption) (*40*). The peak intensities varied based on the constituent concentration via asphalt and guayule. On the other hand, guayule had several peaks that did not show up in the investigated asphalt cement, which were around 1311 cm^{-1} (C–O stretching of carboxylic acids (*40; 42*), 1204 cm^{-1} (–C−O stretching, phenols) (*40*), 1167 cm^{-1} (–OH deformation vibrations, tertiary alcohols) (*40*). Such absorption peak intensities indicated a high oxygen content in guayule.

In **Figure 7**, it could be noticed that no new peak or significant peak shift was attributed to the asphalt-guayule blend (AG-2h), indicating no chemical interaction between asphalt and guayule (*45*). Since such an interaction was not chemical, it could be physical, as proven in a previous study by Hemida and Abdelrahman (*9*). In which, no phase separation was associated with the asphalt-guayule blend.
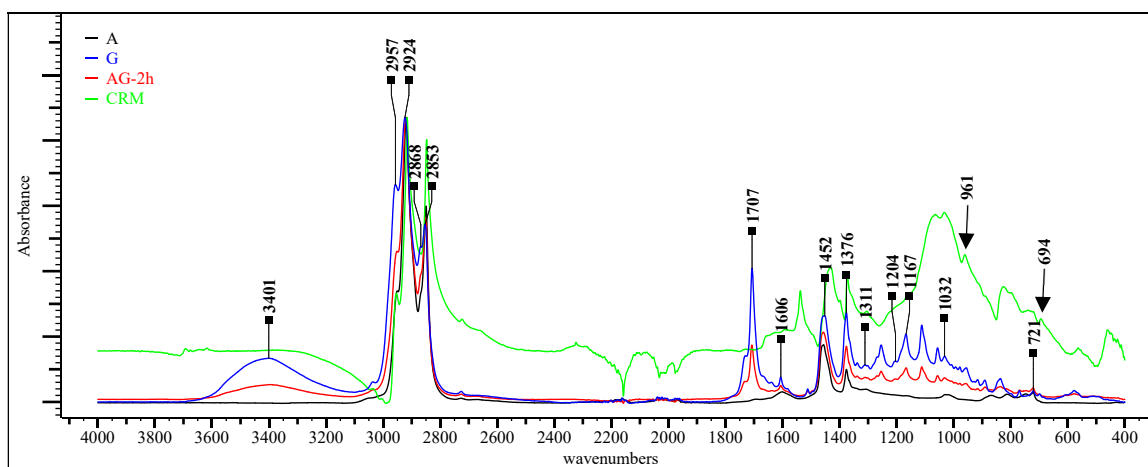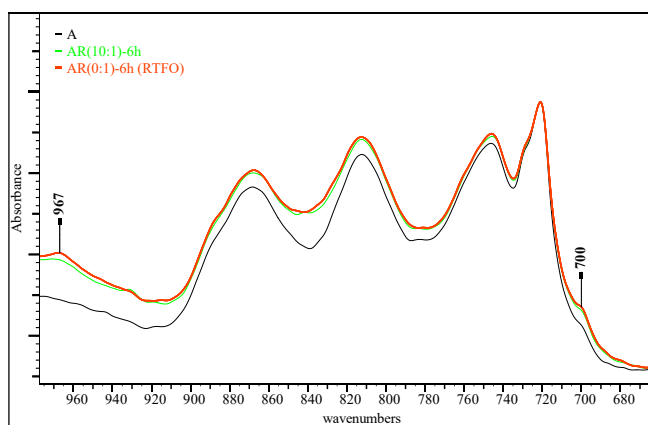

Figure 7 Comparative infrared spectra among asphalt (A), guayule (G), asphalt-guayule blend (AG-2h), and CRM

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Several studies reported that the oxidative aging of conventional asphalt through RTFO and PAV aging was attributed to carbonyl (C=O) and sulfoxide (S=O) bonds (*41; 46; 47*), which identified in ranges of 1740–1690 and 1055–1030, respectively (*48*). However, one could see in **Figure 7** that the unaged guayule had considerable peaks at 1707 cm^{-1} (C=O) and 1032 cm^{-1} (S=O) with little-to-no corresponding peaks attributed to the unaged asphalt. The authors in this study believe that these peaks play a key role in influencing the rheological performance. Guayule seems to have high oxygen content. Literature reported that bio-oils had a high oxygen content, unlike the petroleum-based asphalt that contains relatively more hydrocarbons (*49; 50*). In literature, infrared spectra showed that bio-oils had a high concentration of OH bend, (*17; 18; 20; 49*), which is hydrophilic (*50*). This phenomenon means that bio-oils might encounter problems related to moisture damage resistance (*50*). Nevertheless, it seems that it is not relatively significant in guayule to that extent, as shown in **Figure 7**. This could be due to the process of guayule production against other bio-oils since the guayule used in this study was extracted based on a simultaneous extraction method, which is homogeneous and contains no water-soluble materials, unlike the sequential extraction method (*7*). The high oxygen content contributed to several guayule bends reflects the relatively lower intermediate- and low-temperature performance discussed earlier.

Regarding the AR(10:2)-4h and AR(10:1)-6h blends (unaged and aged), two small peaks were formed at 967 and 700 cm^{-1}. For brevity, these peaks could be shown in **Figure 8** for AR(10:1)6-h. These peaks were reported in literature for asphalt-rubber interaction (*9; 34; 51; 52*). They were attributed to out of plane C−H bends of the aromatic ring for polystyrene and trans component in polybutadiene, respectively, indicating a migration of some of CRM constituents (shown in **Figure 7**) to the liquid asphalt (*51*). Such constituents were most likely responsible for remarkably enhancing the performance at high, intermediate, and low temperatures of the asphalt-rubber blend. These CRM components reported in literature as thermoplastic and rubber characteristics, respectively (*51*), which denoted two significant properties desired for a better binder performance. This enhancement is caused by the swelled polystyrene, which yields swelled entangled network structure connected by polybutadiene that acts as nodes in between (*51*).

Figure 8 Comparative infrared spectra: migration of CRM constituents to asphalt (A) to the asphalt-rubber AR(10:1)-6h blend (unaged and RTFO-aged)
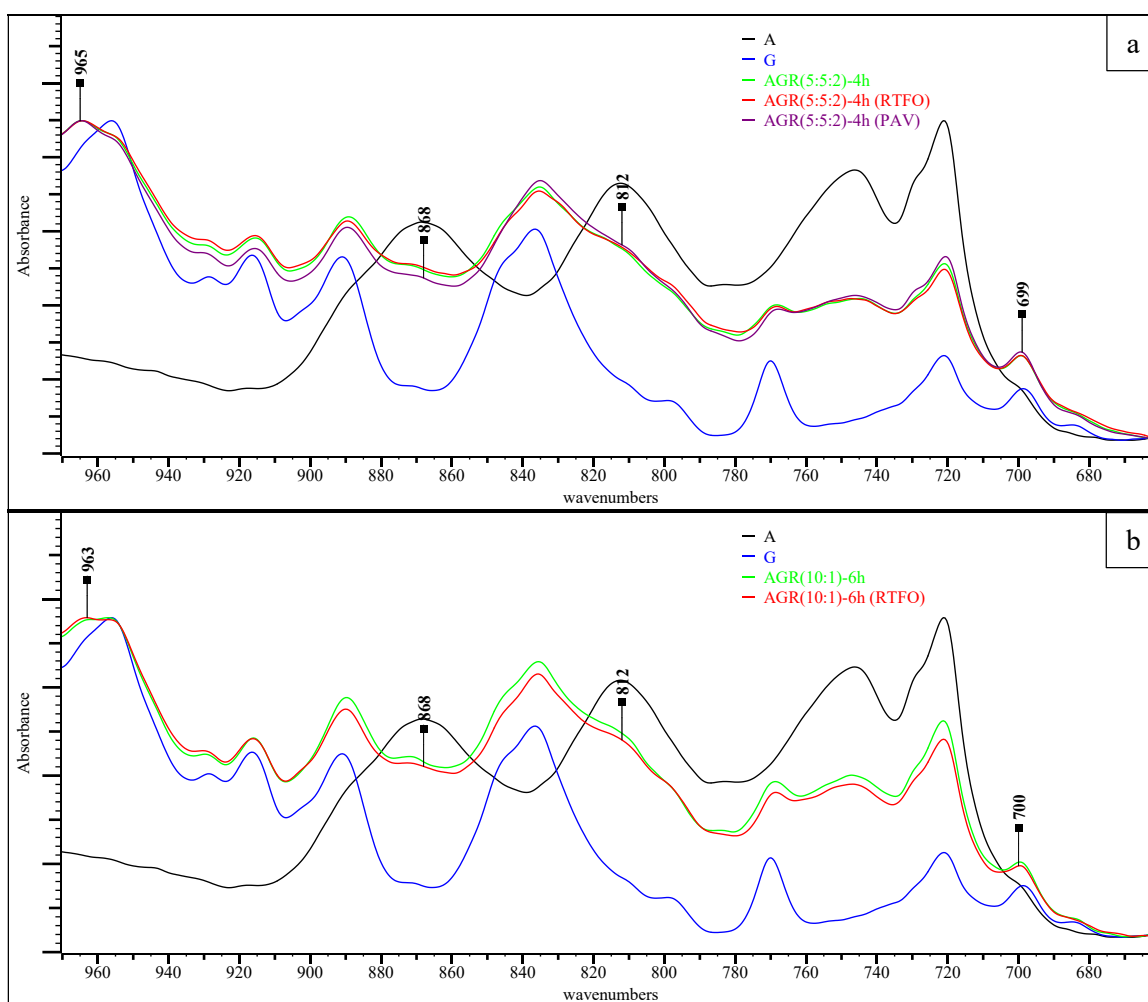
Figure 9a illustrates the comparative infrared spectra of asphalt-guayule-rubber blends: AGR(5:5:2)-4h, unaged, and RTFO- and PAV-aged. To show whether the migration of some CRM constituents into the liquid asphalt-guayule blend, the infrared spectra of virgin asphalt and guayule were added in the figure. A new peak could be noticed around 965 cm^{-1} in all aging conditions of AGR(5:5:2)-4h, indicating a migration of trans component in polybutadiene to the liquid portion. Although a peak was found at 699 cm^{-1} in infrared spectra of all aging conditions of AGR(5:5:2)-4h, one might say that this peak was for guayule as it was present in the virgin guayule. Since the asphalt and guayule proportions in such a binder were fifty to fifty percent, it could be noticed that the guayule peak intensities decreased in the

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blend (e.g., the peak at 721 cm^{-1}). However, the peak of AGR(5:5:2)-4h at 699 cm^{-1} seems to have about the same intensity of virgin guayule (or even higher). Such analysis tends to the concept of migration of out of plane C−H bends of the aromatic ring for polystyrene in CRM to the liquid portion.

With regard to the AGR(5:5:1)-6h binder, a peak might be initiated at 963 cm^{-1} while the binder was unaged (original). When exposed to RTFO conditioning, such a peak was relatively more evident at that wavenumber (963 cm^{-1}), as shown in **Figure 9b**. From **Figure 9a** and **Figure 9b**, the migration of CRM components might be higher with the more involved CRM in the blend (i.e., 20% CRM).

On the other hand, one could see that some asphalt functional groups decreased or disappeared in the asphalt-rubber blends, such as peaks around 868 cm^{-1} and 812 cm^{-1}. These peaks were found in literature to belong to a range of 800–1150 cm^{-1}, which corresponds to linear aliphatic chains migrating from asphalt to CRM and most likely causing rubber swelling (*17; 20*). These components were reported to provide better compatibility with a linear polymeric skeleton of rubber (*20; 53*). The reduction of these peak intensities was not noticed above with the asphalt-rubber blends.
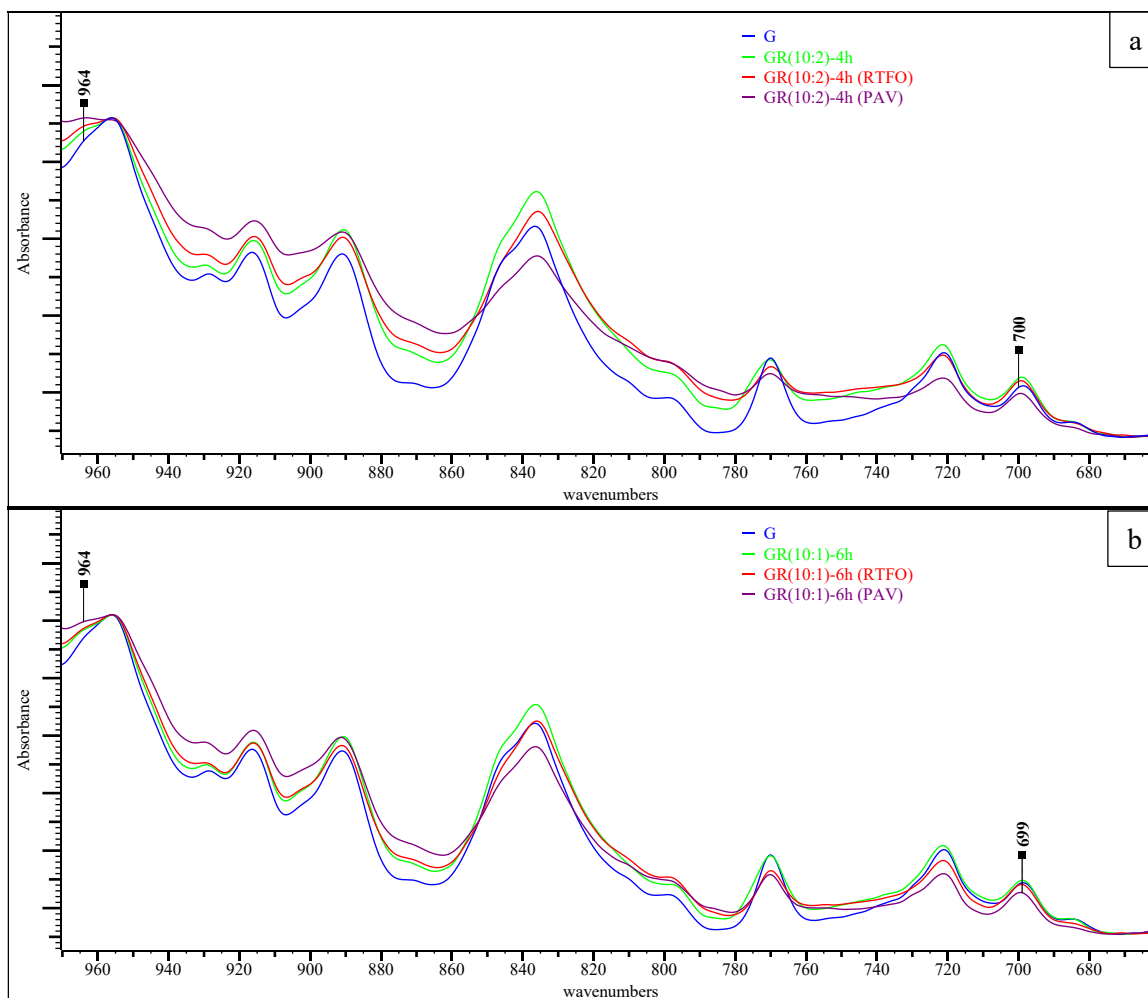

Figure 9 Comparative infrared spectra: migration of CRM constituents to the liquid portion of asphalt-guayule-rubber blends: (a) AGR(5:5:2)-4h (unaged and (RTFO and PAV) aged) and (b) AGR(5:5:1)-6h (unaged and RTFO-aged).

With monitoring the effect of CRM on the sole guayule after the interaction and through RTFO aging and PAV aging in **Figure 10**, the reactivity between guayule and CRM could be discovered. It seems no change in the peak intensity at 700 cm^{-1}. However, a peak was potentially initiated at 964 cm^{-1} after the

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interaction. The same scenario was observed for RTFO, but it was clear after PAV aging. Such an analysis might show the slow gain of CRM dissolution into guayule. In other words, the same CRM components, which might migrate to the conventional asphalt, might migrate to guayule but with more sever interaction parameters such as prolonged interaction time, temperature, or speed that could be investigated in the future.

Figure 10 Comparative infrared spectra: migration of CRM constituents to the liquid portion of guayule-rubber blends: (a) GR(10:2)-4h and (b) GR(10:1)-6h, both unaged and (RTFO and PAV) aged

4. CONCLUSIONS

Outcomes showed a relatively much lower viscosity of guayule in the same high-temperature asphalt grade indicating savings in plant energy consumption and reduced environmental emissions. The CRM interacted with guayule, but not as much as its interaction with asphalt. For instance, the guayule-rubber (GR(10:2)-4h) interaction yielded an 11.4% enhancement of the high-temperature performance, but the enhancement reached up to 34.5% in terms of the asphalt-rubber (AR(10:2)-4h) interaction. Both scenarios could be interpreted by the relative migration of some CRM components, including polystyrene and polybutadiene at the high-, intermediate-, and low-temperature levels. These CRM components represent thermoplastic and rubbery characteristics, respectively (*51*), indicating two significant properties desired for a better binder performance at the high-, intermediate-, and low-temperature levels, as demonstrated by the rheological performance of asphalt-rubber and asphalt-guayule-rubber blends.

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The different behavior of CRM with asphalt against guayule was based on the variant components between asphalt and guayule. Guayule seems to have almost all bonds reported in asphalt. However, guayule had a much more complicated chemical structure. It had a remarkable absorption peak related to alcohol at 3401 cm^{-1} ($-$OH stretch) in addition to its presence at 1167 cm^{-1}. There is a belief that such peaks were most likely contributed to most of the performance at the three levels (high, intermediate, and low temperatures). This alcoholic hydroxyl group is hydrophilic (*50*), although the investigated guayule (which was extracted by the simultaneous extraction method) is entirely insoluble in water (*7*) like bio-asphalts from oil residues (*50*). This functional group might play a key role in presenting a relatively soft binder, high-temperature performance grade of sole guayule. Furthermore, guayule seems to have a relatively higher glass transition point that negatively affects its low-temperature performance. Likewise, guayule appears to possess a considerable amount of oxidative bonds before mimicking the age hardening by RTFO and PAV, such as carbonyl (C=O), sulfoxide (S=O) structures, in addition to groups containing carbon-oxygen single bonds (*35*). However, with monitoring these kinds of peaks, there was almost no change in their intensities after RTFO as well as PAV aging. This could be described as pre-oxidized bio-asphalt that negatively affected the intermediate and low-temperature performance presented in **Figure 4** and **Figure 5**, respectively. However, CRM, beside asphalt, had potential to compensate with partial guayule replacement. Based on the study limitations, the closest overall performance to the virgin asphalt cement (control) could be observed through a blend of 68.18% asphalt, 22.73% guayule, and 9.1% CRM as well as a blend of 41.65% asphalt, 41.65% guayule, and 16.7% CRM, all by weight of blend.

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AUTHOR CONTRIBUTIONS

The authors confirm contribution to the paper as follows: study conception and design: Abdelrahman, Hemida; data collection and lab testing: Hemida; analysis and interpretation of results: Hemida, Abdelrahman; draft manuscript preparation: Hemida, Abdelrahman. All authors reviewed the findings and approved the final version of the manuscript.

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