EVALUATION AND CHARACTERIZATION OF RECYCLING AGENTS FOR ASPHALT

CONCRETE

A Thesis

by

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ABSTRACT

The increasing use of recycled materials such as reclaimed asphalt pavements and /or recycled asphalt shingles in pavement construction has led to an overall increase in demand for recycling agents in the market. Currently the only method for their classification is ASTM D4552 that uses viscosity and percentage of saturates to differentiate between different products. This method has proven to be incomplete as the chemistry of the recycling agents plays a very important role along with viscosity. This study was conducted to investigate the differences between various types of recycling agents used in the field today. Chemical as well as rheological properties were taken into consideration to evaluate these products.

Binder and mixture materials were collected from a Delaware field project and different recycling agents available in the market were selected. Analyses were conducted at three different levels – (a) Recycling agents themselves, (b) Rejuvenated binder blends {base binder + asphalt from recycled material + recycling agent}, and (c) Rejuvenated mixture. For the recycling agents and the binder blends, a rheological analysis using a dynamic shear rheometer was conducted alongside a chemical analysis using Fourier transform infra-red spectroscopy. The mixtures were evaluated by performance tests including the Hamburg wheel tracking test for rutting and the Illinois flexibility index test for cracking.

The results indicate that testing of recycling agents themselves might be misleading as their interactions with asphalt binder can alter their chemistry. The differences between just the softening agents that only reduce the modulus and true "rejuvenators" that alter the blend to reduce the stiffness and increase the phase angle were established by exploring the rejuvenating mechanism for the various recycling agents. The challenges faced by some traditional tools for

binder characterization were also made apparent when used for rejuvenated blends. A new parameter, called Binder Embrittlement Parameter (BEP), that includes both chemical and rheological changes was developed to better identify good recycling agents. The effect of dose and type of recycling agent was analyzed again for mixture blends by analyzing rutting and cracking data obtained. Finally, the recycling agents were ranked according to their effectiveness using binder as well as mixture results.

DEDICATION

Firstly, I would like to thank my parents for allowing me to take the opportunity to pursue my education thousands of miles away from my home and my family for being a constant support for my two and a half years here. I would not have been able to complete my education without their continuous encouragement during the ups and the downs of my life here. My entire family has been there as my North Star, helping me guide this journey we call life to their fullest capacity.

I would also like to dedicate this the friends I have made here in the States. They have proven themselves nothing short of a second family to me for the entire time I have been here. We have all come from different backgrounds and formed bonds that will last a lifetime hopefully. I couldn't have gone through these two and a half years without these people keeping a sense of work-life balance intact for me.

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Contributors

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NOMENCLATURE

BEP	Binder Embrittlement Parameter
CA	Carbonyl Area
CAg	Carbonyl Area Growth
δ	Phase Angle
DOT	Department of Transportation
DSR	Dynamic Shear Rheometer
FI	Flexibility Index
FTIR	Fourier Transform Infra-Red Spectroscopy
G*	Complex Shear Modulus
G-R	Glover-Rowe Parameter
G-R/CAg HS	Glover-Rowe versus Carbonyl Area Growth Hardening Susceptibility
HWTT	Hamburg Wheel Tracking Test
I-FIT	Illinois Flexibility Index Test
LMLC	Laboratory Mix Laboratory Compacted
LSV	Low Shear Viscosity
LTOA	Long Term Oven Aged
NCHRP	National Cooperative Highway Research Program
PAV	Pressure Ageing Vessel
PG	Performance Grade
PGH	High Temperature PG
RAP	Reclaimed Asphalt Pavement

RAS	Recycled Asphalt Shingles
RBR	Recycled Binder Ratio
RTFO	Rolling Thin Film Oven
SARA	Saturates, Aromatics, Resins and Asphaltenes
STOA	Short Term Oven Aged
TOAS	Tear Off Asphalt Shingles
ZSV	Zero Shear Viscosity

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1. INTRODUCTION

1.1 History and Use

Use of recycled materials for construction of new pavements has become commonplace. Not only does it make sense financially as the more expensive virgin materials are substituted by cheaper recyclables but it also provides environmental benefits, such as reducing use of virgin materials and therefore reducing energy consumption and greenhouse gases, and providing a use for the older materials instead of putting them in landfills. Including these recycled materials may also improve the performance of pavements in some cases which leads to additional engineering benefits. These factors have led to a steady rise in use of recycled materials for pavement construction especially asphalt pavements.

Asphalt pavements make up over 90% of the pavements in the United States. Being recycled at a rate of almost 99%, these asphalt pavements constitute the number one recycled material in US. Reclaimed Asphalt Pavement (RAP) and Recycled Asphalt Shingles (RAS) constitute the majority of the materials recycled in the construction of asphalt pavement. Around 76.2 million tons or RAP and 950,000 tons of RAS which includes both Tear Off Asphalt Shingles (TOAS) and Manufactured Waste Asphalt Shingles (MWAS) was recycled in 2017, saving more than 2 billion dollars as a result. The use of RAP have generally been increasing over the past seven years (NAPA Recycling 2017).

Recycled materials have certain limitations along with the benefits. These materials have been out in the field for a long time usually and have undergone significant aging. This causes the stiffness to increase and therefore mixtures with recycled blends, i.e. binder blends that contain just recycled materials, have a higher stiffness than virgin blends. This higher stiffness leads to a

higher resistance to rutting distresses that may occur during the early years of pavement. However, this stiffness also leads to a reduced resistance to cracking, both thermal and fatigue, in the pavement with time. Therefore, the amount of recycled materials in the construction of any new pavement has to be limited to balance short- and long-term performance.

Different methods have been proposed to overcome the high stiffness of recycled mixtures. These include using a base binder with a lower Performance Grade (PG) to compensate for the aged RAP/RAS. These softer base binders can be expensive. Alternatively, the use of recycling agents in these recycled blends is increasing in popularity due to their ability to reduce stiffness of recycled blends when used in small quantities and facilitate the use of larger recycled materials contents. This reduction in stiffness occurs due to the low viscosity of these agents. Oversoftening and subsequent reduction in rutting resistance can also be a drawback of using recycling agents at excessive doses. Both of these methods are being used in the industry currently.

The increase in the usage of RAP and RAS for pavement construction has led to several state Departments of Transportation (DOTs) to develop guidelines for inclusion of recycled materials in their pavement design specifications as large quantities of RAP/RAS can be detrimental to pavement performance while too little will not be beneficial economically or environmentally. Some states have also taken a step further and started to develop specifications for the recycling agents that are used in recycled mixtures as they also significantly affect pavement performance.

1.2 Objectives

The main objective of this study is to evaluate the rejuvenating abilities of different recycling agents that are available in the market. The effect of factors like quality of base binder and aging of the sample on rejuvenation was studied. The rejuvenation mechanism was studied in detail and different recycling agents were classified according to their rejuvenating abilities for recycled binder blends and mixtures. The effect of aging on the recycling agents themselves was also evaluated and correlated to rejuvenating performance. These evaluations were completed using both rheological as well as chemical tools for recycling agents and recycled binder blends and performance testing for the recycled mixtures. Finally, the drawbacks of the current standard for classification of recycling agents was reviewed and possible revisions suggested.

1.3 Description of Contents

This thesis is comprised of the following sections: Section 1 gives a brief history and introduction for the objectives of the study. Section 2 comprises a literature review that presents relevant information from previous research conducted on asphalt binder characterization, recycled materials and recycling agents. Section 3 details the methodology adopted for this study including the materials used and the laboratory tests carried out. Section 4 comprises the test results obtained and discussions regarding the data analysis. Section 5 focuses on the conclusions drawn from the discussions and future research opportunities that can be explored to further this study. An appendix with additional data collected throughout this study was also attached for reference.

2. LITERATURE REVIEW

This section provides a literature review for some of the conceptual aspects that were used in the study. For ease these have been divided into three parts:

- Asphalt Binder Characterization

- Recycled Materials

- Recycling Agents

2.1 Asphalt Binder Characterization

Asphalt binders consist of a whole spectrum of organic compounds having different hydrocarbon chains and molecular weights (Eilers, 1949). As analysis of these compounds individually is difficult, so organic molecules in asphalt binders are usually categorized into four different categories – Saturates, Aromatics, Resins and Asphaltenes (SARA) [Petersen, Corbett]. The asphalt binders are thought of as a colloid where the highly polar asphaltenes act as the dispersed phase and the relatively non-polar saturates, aromatics and resins, collectively called the maltenes, are the dispersing medium. Asphaltenes tend to cluster due to their polar nature and can be responsible for the increased viscosity of the asphalt binders. The maltenes disperse these clusters and hence prevent larger clusters from being formed, hence preventing a continuous network of asphaltenes. The purpose of this categorization is to relate the composition of binders to physical properties needed for pavements (Kandhal, 1977). The balance between the SARA fractions can be used to explain the ductility of binders, with binders having large amount of asphaltenes having low ductility. Asphaltenes, if present in large quantities, form larger clusters and can increase the viscosity of the binder leading to a higher stiffness and hence a lower ductility.

So binders with lesser asphaltenes molecules or maltenes with a higher dispersive power usually perform better in the field (Altgelt & Harle, 1975; Petersen, 2009).

Glover et al. (2005) proposed a new asphalt binder parameter using a Dynamic Shear Rheometer (DSR) to correlate with field aging instead of ductility. This DSR parameter was reformulated by Rowe in the discussion of Anderson, King, Hanson, & Blankenship (2011) to the Glover-Rowe (G-R) parameter at 15°C and 0.005 rad/s. This parameter takes both the elastic and viscous parts of binder behavior into account. Binders with a lower G-R parameter value were found to be better than those with higher values. The thresholds developed by Kandhal (1977) were used by Anderson et al. (2011) to calculate new thresholds for this parameter with 180kPa signaling the onset of cracking and 600 kPa representing significant cracking. The complex shear modulus (G*) and phase angle (δ) of a binder can also be combined in a Black space diagram. These diagrams are effective analysis tools for binders, with softer binders being more towards the lower right corner and stiffer binder being towards the upper left corner.

Carbonyl compounds are highly polar compounds found in asphalt. These compounds can be detected with the use of Fourier Transform Infrared (FTIR) spectroscopy, usually between the wavenumbers of 1650 to 1820 cm^{-1}. A semi-quantitative comparison can be made between binders using the Carbonyl area (CA), defined as the area under the FTIR absorbance spectrum from 1650 to 1820 cm^{-1} wavenumbers with a slanted base from 1524 to 1820 cm^{-1} as modified by Epps-Martin et al. (2017), to represent the stiffness of binders (Lamontagne, Dumas, Mouillet, & Kister, 2001; Lu & Isacsson, 2002).

2.2 Recycled Materials

As binders undergo aging they become stiffer. This can be attributed to the maltenes slowly losing their volatiles and formation of more polar compounds like benzylic carbonyls (Yut & Zofka, 2011). This leads to an overall increase of asphaltenes and a decrease in aromatics as noted by Liu et al. (1998) and Siddiqui & Ali (1999) , decreasing the overall mobility in the binder by forming larger polar networks. This process increases the G* and decreases the δ of the binder (Lu & Isacsson, 2002; Petersen, 2009; Y. Wang, Wen, Zhao, Chong, & Wei, 2015). Hence aging leads to movement in the Black space Diagram from the lower right to upper left direction and an increase in the G-R parameter value for the binder, which in turn influences its ductility and therefore field performance. Because aging leads to the formation of polar carbonyls compounds, it also leads to an increase in the CA for a binder. The more aged a binder, the higher the CA (Lu & Isacsson, 2002). Hence CA can be a useful tool for characterizing a binder, in addition to rheology.

To study the effect of aging on binders, artificial aging protocols in the laboratory are used. These procedures have been developed and studied previously and are able to simulate both short-term and long-term aging in field using the Rolling Thin Film Oven (RTFO) and Pressure Aging Vessel (PAV), respectively (King, Anderson, Hanson, & Blankenship, 2012; Lamontagne et al., 2001).

Use of recycled materials such as reclaimed asphalt pavement (RAP) and/or recycled asphalt shingles (RAS) introduces stiffer materials to softer base binders. These produce asphalt mixtures having a higher stiffness than mixtures produced using only the base binder. This makes these mixtures less workable and more difficult to compact along with having a higher susceptibility to raveling and cracking (Kaseer, Yin, Arámbula-Mercado, Epps, & Kaseer, 2017;

Kim, Byron, Sholar, & Kim, 2007; Mogawer et al., 2012). If the recycled materials are present in a lower quantity, then the use of a softer base binder without a recycling agent can offset the increased stiffness of the mixture (Willis & Marasteanu, 2013). However, incorporating a larger amount of recycled materials or highly aged materials like Tear Off Asphalt Shingles (TOAS) makes the mixture too stiff, and the use of softer base binders cannot alone lower the stiffness of the resulting mixture to acceptable levels (Shen, Amirkhanian, & Miller, 2007). Therefore, many State Departments of Transportation (DOTs) limit the amount of recycled materials allowed during the construction of a new pavement. However, the use of recycling agents has increased recently and incorporation of these in blends with high recycled materials contents can help in restoring the stiffness to acceptable levels (Dunning & Mendenhall, 1978; Epps, Little, Holmgreen, & Terrel, 1980).

2.3 Recycling Agents

Recycling agents are naturally occurring or engineered products that can help partially restore the rheological properties of aged binders to levels where it can be used in the field again. They can accomplish this through many rejuvenating mechanisms like softening the mixtures due to their low viscosity (Ongel & Hugener, 2015), replenishing the aromatics lost during aging (Peterson, Davison, Glover, & Bullin, 1994) or reducing the asphaltene cluster size. In all cases the molecular mobility of the binder is partially restored and hence the viscosity and stiffness decrease making the mixture more workable during construction. The Performance Grade (PG) reduction of these recycled materials also takes place with the addition of recycling agents due to a decrease in G* and increase in δ (Zaumanis, Mallick, & Frank, 2014). Additionally, the use of recycling agents can significantly cut down the cost of the project by encouraging the use of more

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recycled materials in place of more expensive base binder (Im, Zhou, Lee, & Scullion, 2014; Martin et al., 2015).

These agents usually don not react chemically with the binder, but instead are responsible for rearrangement of the different compounds to increase molecular mobility (Cavalli, Zaumanis, Mazza, Partl, & Poulikakos, 2018). The rejuvenating mechanism generally accepted in the literature consists of the following steps as detailed by Carpenter & Wolosick (1980):

- Formation of a low viscosity layer of recycling agent on the surface of the aged binder.
- Diffusion of recycling agents into the outer layer of the aged binder, softening it. This depletes the amount of recycling agent on the surface.
- Continued diffusion of recycling agents, with the inner layers getting less viscous and the outer layers getting more viscous.
- Equilibrium is approached in the process after certain time.

This diffusion process can be affected by factors like mixing and compacting temperature, method of addition, etc. (Tran, Taylor, & Willis, 2012; F. Wang et al., 2017).

Recycling agents have been traditionally classified using their viscosity by ASTM D 4552 "Standard Practice for Classifying Hot-Mix Recycling Agents". This classification was developed to be used for traditional petroleum-based agents. However, the newer engineered products in the market often have similar viscosities but their performance varies. Newer classifications to be able to satisfactorily categorize recycling agents are therefore being developed. NCAT (2014) classification for recycling agents is based on the chemistry of the agents themselves. Some

researchers (Tabatabaee & Kurth, 2017; Zaumanis, Mallick, Poulikakos, & Frank, 2014) have categorized the recycling agents according to their effectiveness in the recycled mixtures and their mechanism of rejuvenation. The effectiveness of recycling agents can vary due to factors including recycling agent type and dose, base binder type, recycled material source, temperature and recycling agent addition method.

Previous studies (Im et al., 2014; Kaseer et al., 2017) have evaluated the effect of recycling agents on mixture performance. It was seen that the inclusion of recycled materials increased the rutting resistance while simultaneously lowering the cracking resistance. The addition of recycling agents can improve this cracking resistance but would in turn lower the rutting resistance. Therefore, the dose of recycling agent chosen for rejuvenation should be such that it strikes a balance. Arámbula-Mercado et al (2018) compared different methods to find this optimum dose of recycling agent. The best method was to match the continuous PG High (PGH) of the binder with recycled material to that required by climate and traffic conditions. Since the relationship between the dose of recycling agent and PGH is generally linear, grading the binder blend (base binder + recycled asphalt binder material + recycling agent) at specific doses, the optimum dose is found using interpolation.

3. METHODOLOGY

This section gives a brief description of the materials used in this study. It also details the testing plan developed in order to achieve the objectives along with giving an abbreviated description of all the tests performed.

3.1 Materials

For this comparative study, seven different recycling agents were selected for testing. Different types of recycling agents were chosen to represent the products available in the market. Both petroleum-based agents as well as bio-based agents were selected for the study. Modified products were also chosen to assess the differences and advantaged they might provide. One aromatic extract (A1), two reacted bio-oils (B1, B2), one paraffinic oil (P), one tall oil (T1) and two modified vegetable oils (V2, V3) were chosen for this experiment. The reacted bio-oils, tall oils and modified vegetable oils can be grouped in a larger category of bio-based agents and paraffinic oils and aromatic extracts can be classified as petroleum-based products. Many of the recycling agents chosen are known industry wide, some performing well in the field to date while others would be expected to perform poorly in the field.

The remaining materials were chosen from the Port Penn/Pole Bridge road overlay project by DelDOT constructed in Fall 2016. The base binder used was a PG 64-28 unmodified binder, common in the region. The virgin aggregates were obtained from an asphalt mix plant located on the southeast side of Wilmington, Delaware. RAP obtained from several different sections of highway was used as the recycled material in this study. No RAS was utilized to limit the number of variables. A high Recycled Binder Ratio (RBR), defined as the percentage by weight of total

recycled binder from RAP/RAS to total binder weight of binder blend or mixture, of 0.5 was chosen to incorporate a high recycled material content in the blends and corresponding mixtures.

3.2 Testing Plan

Table 1. Testing Plan shows the experimental plan. The testing was split into three parts – (a) Recycling agents themselves, (b) Rejuvenated binder blends, and (c) Rejuvenated Mixtures.

Recycling agents chosen were fluid at room temperature, thus traditional rheological tools such as master curves used for binders and binder blends could not be used. Complex viscosity was used instead as a rheological parameter, measured by using a Dynamic Shear Rheometer (DSR) at a specific temperature of 15°C and frequency of 10 rad/s chosen to represent field conditions. For chemical characterization, Fourier Transform Infra-Red spectroscopy (FTIR) was used to obtain an absorbance spectrum from 600cm^{-1} to 2000 cm^{-1} wavenumber according to ASTM E1252 "Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis".

Both analyses were conducted at several aging levels. Short term aging was simulated using the Rolling Thin Film Oven aging (RTFO) according to AASHTO T240 "Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test)" by rotating the samples in the RTFO oven at 163°C (325°F) and 4000ml/min airflow for 85 minutes. Long term aging in the field was simulated using the Pressure Aging Vessel (PAV) for 20 hours according to AASHTO R28 "Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)" at 100°C (212°F) and 2.10 MPa. Since PAV for 20 hours can simulate aging in the field for only 7-10 years (Newcomb et al., 2015), PAV aging was also conducted for 40 hours to simulate longer aging time in the field. These time durations were

selected based on previous research on binder rheology by (King et al., 2012; Mensching, Rowe, Daniel, & Bennert, 2015; Zhou, Im, Morton, & Lee, 2015) .

Binder blends were prepared with the base binder of PG 64-28 and RAP binder extracted from the aged materials in accordance with ASTM D2172 "Standard Test Methods for Quantitative Extraction of Asphalt Binder from Asphalt Mixtures" using a centrifuge and recovered from the solvent trichloroethylene using ASTM D5404 "Standard Practice for Recovery of Asphalt from Solution Using the Rotary Evaporator". As shown in Table 1, nine different binder blends were prepared. The first blend was just the base binder used as a reference for other rejuvenated blends. The recycled blend has an RBR of 0.5 with no recycling agent added. Seven rejuvenated blends were prepared with the different recycling agents at a dose which restores the PGH of the blend to that of the base binder (i.e. PG 64-28). When preparing the blends, the recycling agents (if used) were added to the base binder, preheated at 160-170°C, and stirred by hand using a spatula. The required amount of RAP binder was added to the resulting combination and again hand stirred by a spatula at the same temperature to maintain the fluidity of the blend for complete mixing. These blends were aged at four different aging levels – (a) Unaged, (b) RTFO aged, (c) RTFO + PAV aged for 20 hours, and (d) RTFO + PAV aged for 40 hours to simulate both short-term and long-term aging in field. The DSR was used to perform both PG grading for the blends [AASHTO T315 "Standard Method of Test for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)"] and to obtain the dose of recycling agents (Arámbula-Mercado et al., 2018) as well as frequency sweeps on the recycled, Base binder + RAP binder, and rejuvenated blends, Base Binder + RAP binder + Recycling agent. The blends were also tested using FTIR spectroscopy to obtain an absorbance spectrum from 600cm^{-1} – 2000

cm^{-1} wavenumber. Lastly the binder blends were subjected to the following two separate conditioning sequences to explore the effects of rejuvenation prior to and after aging.

- Conditioning Sequence #1: The rejuvenated binder blend was prepared by combining base binder (PG 64-28) with RAP at 0.5 RBR, and one of seven recycling agents at doses to match continuous PGH. Each blend was then subjected to 20-hour PAV aging.

- Conditioning Sequence #2: The recycled binder blend was prepared by combining base binder (PG 64-28) and RAP at 0.5 RBR. This blend was then subjected to 20-hour PAV and then back-blended with one of the same seven unaged recycling agents at the same doses used in conditioning sequence #1.

This was only completed at one aging level (20-hour PAV) due to time and equipment constraints. Both rheological and chemical analyses similar to the ones described previously were also completed on these blends.

Laboratory mix- laboratory compacted (LMLC) specimens were prepared for the study using the materials identified previously. Virgin aggregate was air dried at room temperature overnight and then mixed with RAP kept at a mixing temperature of 154°C (310°F) for 2 hours along with the base binder to be used. The recycling agent (if used) was added to the base binder first as a replacement of some of the base binder (Arámbula-Mercado et al., 2018), and then the combination was added to the heated aggregates and RAP and then mixed thoroughly using a mechanical mixer. The resulting blend was aged as loose mix at 135°C (275°F) for 2 hours to simulate short-term aging in the field. Compaction of specimens using a Superpave Gyratory Compactor (SGC) was done to create the required eight different mixtures. Long-term aging was simulated for the specimens by oven aging the compacted specimens at 85°C (185°F) for 5 days.

Both the short-term and long-term aging was done in accordance with AASHTO R30 "Standard Practice for Mixture Conditioning of Hot Mix Asphalt (HMA)"as modified by Newcomb et al., 2015. The mixtures were evaluated for resistance to rutting and fatigue cracking. Rutting resistance for the mixtures was tested using the Hamburg Wheel Tracking Test (HWTT) after short-term oven aging (STOA) as rutting occurs in the early life of a pavement when the stiffness is low. The test was performed according to AASHTO T 324 "Standard Method of Test for Hamburg Wheel-Track Testing of Compacted Asphalt Mixtures" in wet conditions at 50°C (122°F). Fatigue cracking resistance was measured after both STOA and long-term oven aging (LTOA) using the Illinois Flexibility Index Test (I-FIT) according to AASHTO TP124 "Standard Method of Test for Determining the Fracture Potential of Asphalt Mixtures Using Semicircular Bend Geometry (SCB) At Intermediate Temperature" at 25°C (77°F).

Table 1. Testing Plan

Materials Combination				Recycling Agent Characterization		Binder Blend Characterization*				Mixture Characterization*	
Base Binder	RAP	RBR	RA Type	Rheology	Chemistry	Conditioning Sequence #1		Conditioning Sequence #2		Rutting Resistance	Cracking Resistance
						Rheology	Chemistry	Rheology	Chemistry		
				DSR[1]	FTIR[1]	DSR[1]	FTIR[1]	DSR	FTIR	HWTT[2]	I-FIT[2,3]
PG 64-28	No RAP	---	No RA			✓	✓				
	RAP	0.5	No RA			✓	✓			✓	✓
			A1	✓	✓	✓	✓	✓	✓	✓	✓
			B1	✓	✓	✓	✓	✓	✓	✓	✓
			B2	✓	✓	✓	✓	✓	✓	✓	✓
			P	✓	✓	✓	✓	✓	✓	✓	✓
			T1	✓	✓	✓	✓	✓	✓	✓	✓
			V2	✓	✓	✓	✓	✓	✓	✓	✓
			V3	✓	✓	✓	✓	✓	✓	✓	✓

* At dose to restore PGH
[1] At Unaged, RTFO, PAV20 and PAV40
[2] At STOA
[3] At LTOA

DSR – Dynamic Shear Rheometer
FTIR – Fourier Transform InfraRed Spectrometer
HWTT – Hamburg Wheel Tracking Test
I-FIT – Illinois Flexibility Index Test

3.3 Laboratory Test

DSR Testing

In this study a research grade Malvern Kinexus Pro DSR [Figure 1] was used for rheological testing of both recycling agents and binder blends. Recycling agents were too fluid making it difficult to construct master curves using different frequencies at different temperatures. Hence the complex viscosity of these agents was measured at a set temperature (15°C) and frequency (10 rad/s), used to simulate traffic conditions at an intermediates temperature, for the different aging levels using the 50mm plate setup. The change in these values indicate the stability of the agent to aging itself, and comparison of the complex viscosities across the recycling agents can differentiate them rheologically.

Figure 1 Malvern Kinexus Pro Dynamic Shear Rheometer

For binder blends the DSR was used to perform frequency sweeps at different aging levels for all material combinations. This sweep was performed at three different temperature of 5°, 15° and 25°C with six frequency points per decade across an angular frequency range of 0.1 to 100 rad/s. The rheological parameters Complex Shear Modulus (G*) and Phase Angle (δ) were obtained, and using RHEA^{TM} software [Abatech, 2011] master curves were constructed for the different blends. These mastercurves were used to evaluate the Glover-Rowe parameter (G-R) at 15°C and 0.005 rad/s using the equation:

$$G - R\ Parameter = \frac{G^* Cos^2\delta}{Sin\ \delta}$$

The parameter has a good correlation with the ductility of the binder blend as shown by Glover (2005). The data for G-R parameter was plotted in a Black Space diagram along with thresholds for onset of cracking (180kPa) and significant cracking (600kPa). The Black Space diagram plots the G* and δ on the Y and X axis, respectively, and shows the change in these parameters with aging and rejuvenation.

FTIR Testing

For chemical analysis of the blend and recycling agents, a Bruker Tensor 27 FTIR [Figure 2] was used to obtain absorbance spectra for the different samples. A small sample of material to be tested was spread across the ZnSe crystal using a spreading tool, and the OPUS data collection program was run to collect an absorbance spectrum of binder blend or recycling agent from 600 cm^{-1} to 2000 cm^{-1}. This was done for all the different aging levels to track the progress of the spectrum with aging. Carbonyl area (CA), area under the FTIR absorbance spectrum from 1650 cm^{-1} to 1820 cm^{-1} with an inclined baseline from 1524 cm^{-1} to 1820 cm^{-1} as developed by NCHRP 9-58 "The Effects of Recycling Agents on Asphalt Mixtures with High RAS and RAP Binder Ratios", was considered as it has been shown to be associated with important compounds in binders and shows correlation with aging characteristics for binders (Jin, Cui, & Glover, 2013; Petersen, 2009). The absorbance spectrum of the recycling agents themselves were also used to identify the type of the agent by identifying some fingerprint regions.

Figure 2 Bruker Tensor 27

Rutting Resistance

Rutting analyses for the recycled and rejuvenated mixtures was done using InstroTek SmartTracker shown in Figure 3, performed according to AASHTO T-324 "Standard Method of Test for Hamburg Wheel-Track Testing of Compacted Asphalt Mixtures" in wet condition at 50°C so as to include moisture susceptibility and traffic load when calculating rut resistance.

Figure 3 InstroTek SmartTracker Hamburg Wheel Tracker

The HWTT is done only after STOA as stiff mixtures are not as susceptible to rutting. The number of load cycles to reach a rut depth of 12.5 mm was reported. Since DelDOT specifications do not include HWTT thresholds, rutting thresholds developed by the Illinois Department of Transportation,(2016) were used due to the similar climate to Delaware. The minimum cycles till a rut depth of 12.5 mm is 7500 for a PG 64-XX binder.

Cracking Resistance

For cracking resistance of mixtures, the Illinois flexibility index test (I-FIT) was performed according to AASHTO TP-124 "Standard Method of Test for Determining the Fracture Potential

of Asphalt Mixtures Using Semicircular Bend Geometry (SCB) At Intermediate Temperature" at

25°C using a locally manufactured semi-circular test bend system shown in Figure 4.

Figure 4 Semicircular Bend Test System

Previous studies suggest that flexibility index (FI) has a good correlation with field

cracking and can be sensitive to the presence of RAP or recycling agents in the mixture (Al-Qadi

et al., 2015; Kaseer et al., 2018; Zhou et al., 2015). Cylindrical specimens (150 mm × 61 mm)

were fabricated for the mixture blends with air voids of 7.0 ± 0.5% using a Superpave Gyratory

Compactor. These specimens were cut in half to create semicircular samples, and a notch was cut at the axis of symmetry 1.5mm wide and 15mm deep. Using a three-point bending configuration, a load was applied at the rate of 50mm/min along the vertical radius till failure.

$$\text{FI} = \frac{G_F}{m} \times 0.01$$

Where G_F is the fracture energy (Work of Fracture/Ligament Area) in J/m^2 and m is the slope at inflection point of the post peak load vs displacement curve of sample. The FI was calculated from the data obtained for the mixture blends after both STOA and LTOA. Currently there are no thresholds set for this performance test.

4. RESULTS AND DISCUSSION

This section describes the results obtained from characterizing recycling agents, binder blends and mixtures in accordance with the testing plan described previously.

Characterization of recycling agents involved defining the differences between each of the types chosen and how each works towards the rejuvenation of recycled binder blends. The effect of aging on these agents was explored and thus their aging susceptibilities are discussed.

Characterization of binder blends started with defining the dose of each recycling agent required to restore the continuous PGH of recycled binder blends to that of the base binder (PG 64-28). The G-R parameter values as well as Black Space diagrams for the nine different binder blends were examined to compare the rejuvenating abilities of the recycling agents with aging. The absorbance spectrum was inspected, especially in the carbonyl region to ascertain the differences in the peaks from those of the base and recycled binder blends. The conditioning sequence results were also compared to evaluate the effect of factors such as aging on the effectiveness of recycling agents and whether traditional tools for aging characterization of binders are still valid for rejuvenated blends. A new parameter that included both the chemical and rheological results, obtained for binder blends, was used to organize the different recycling agents in order of effectiveness.

Characterization of mixtures first examined results from the rutting resistance tests which reflect the effect that type and dose of recycling agent had on the rutting resistance of the mixtures. Then the results from the cracking test were interpreted to compare the performance of the recycling agents and assess the effect of aging.

4.1 Recycling Agent Characterization

The complex viscosities for the recycling agents at various aging levels is shown in Figure 5. . The values of complex viscosity are recorded in Appendix for considerations. For additional analysis, an aging index was calculated by dividing the complex viscosity after PAV40 aging by that of the unaged recycling agent. The chemically stable paraffinic oil P as well as the aromatic extract A1 showed little change after oxidation, with aging indexes of 1.09 and 1.15, respectively. Most of the bio-based agents had higher aging indices: 1.85 for V2, 2.60 for B2 and 2.88 for B1. The remaining two agents, V3 and T1, had extremely high aging indices, 1075 and 16285, respectively, suggesting a high susceptibility to aging.
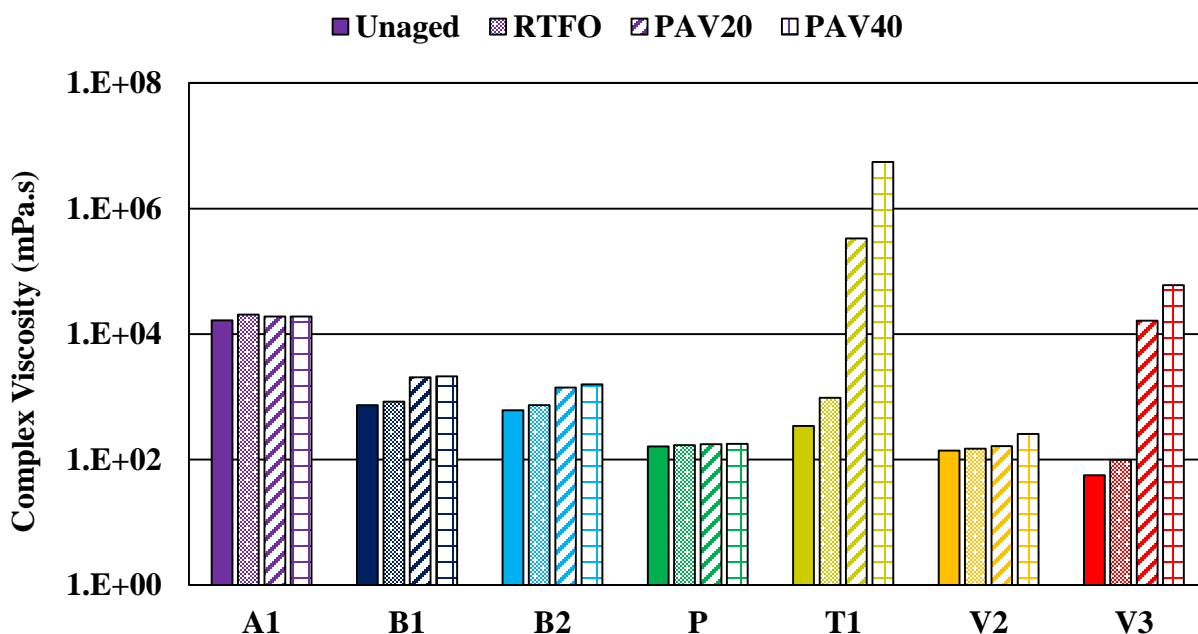

**Figure 5 Complex Viscosity of Recycling Agent with Aging**

The FTIR absorbance spectrum for all recycling agents at four different aging levels are plotted in Figure 6. The chemical data correlates well with the rheological aging indices discussed previously. It can be seen that the petroleum based A1 and P show little to no change with aging owing to a lack of volatiles. The bio-based recycling agents may contain reactive double bonds that can be more easily oxidized or cross-linked. This leads to most of them having a slightly higher index. For V3 and T1 it can be seen in the FTIR spectrum that they undergo major changes with aging, especially around 900-1250 cm^{-1} range with the 1160 cm^{-1} peak showing the maximum change. These recycling agents changed from a relatively fluid state to an almost resin like substance after aging suggesting a more thorough and complete crosslinking. This change was not observed in the other recycling agents used for these experiments, suggesting that these agents to be more age resistant either naturally or due to modifications.

(a) **A1**
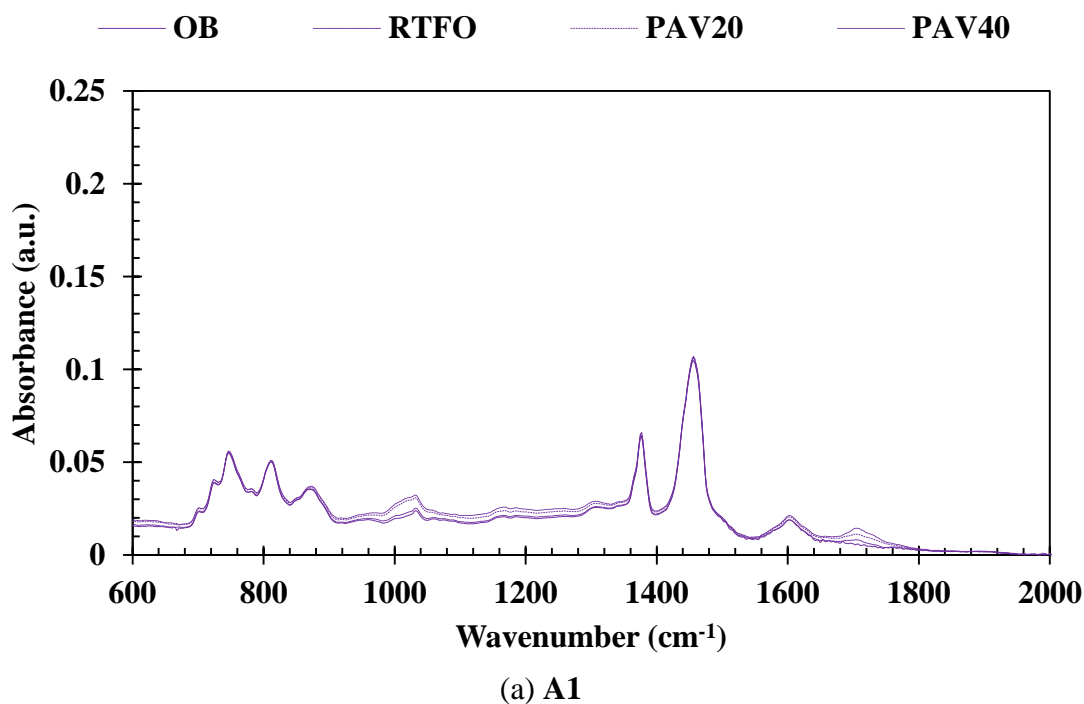
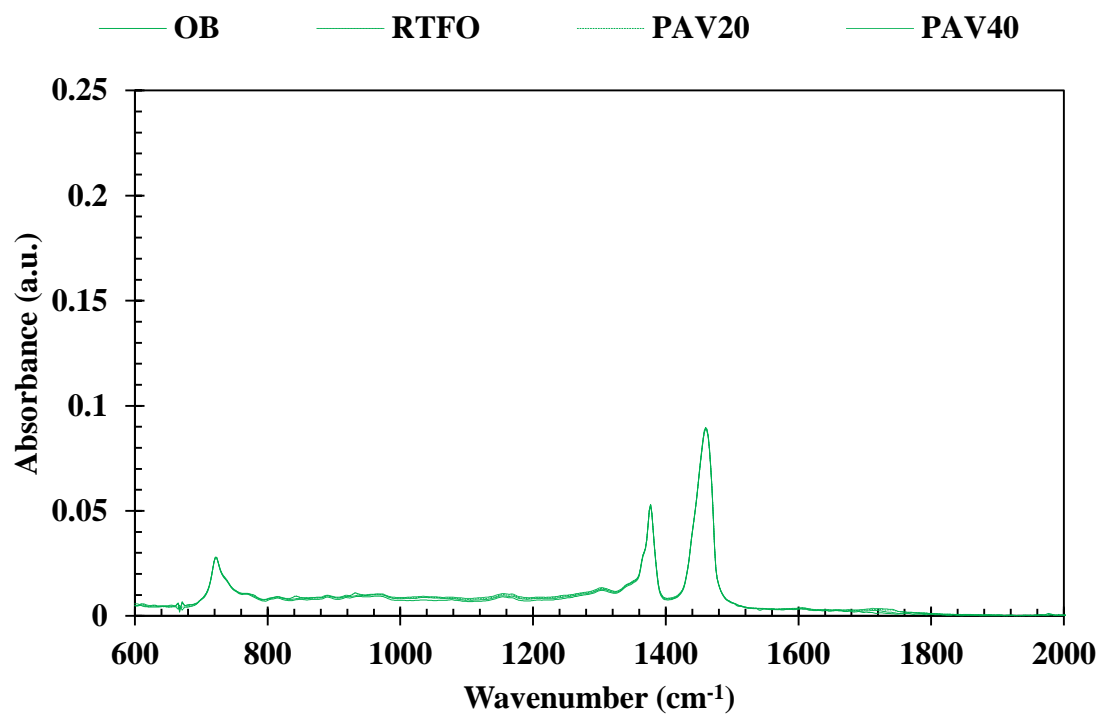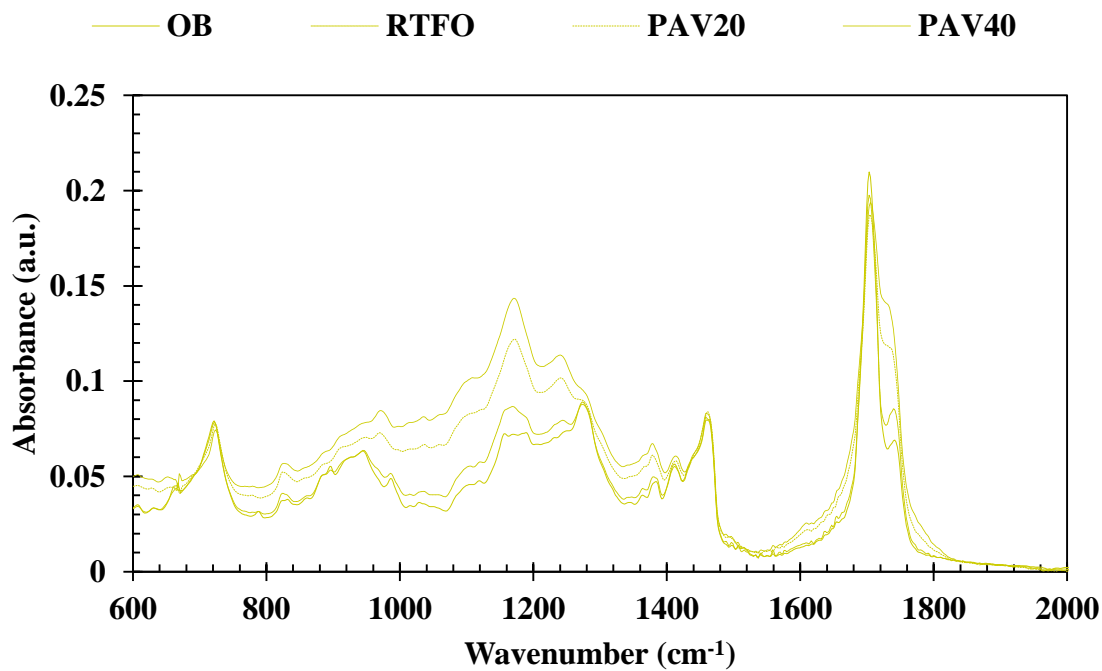**Figure 6 FTIR Absorbance Spectra for (a)A1, (b) B1, (c) B2, (d) P, (e) T1, (f) V2, and (g) V3**
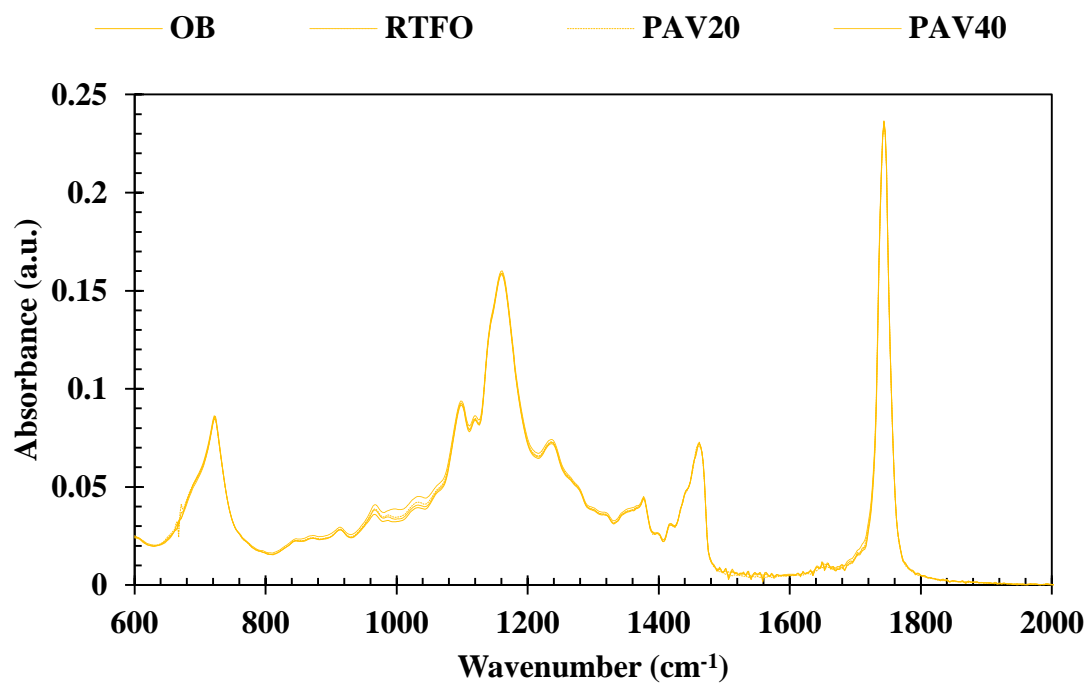
25
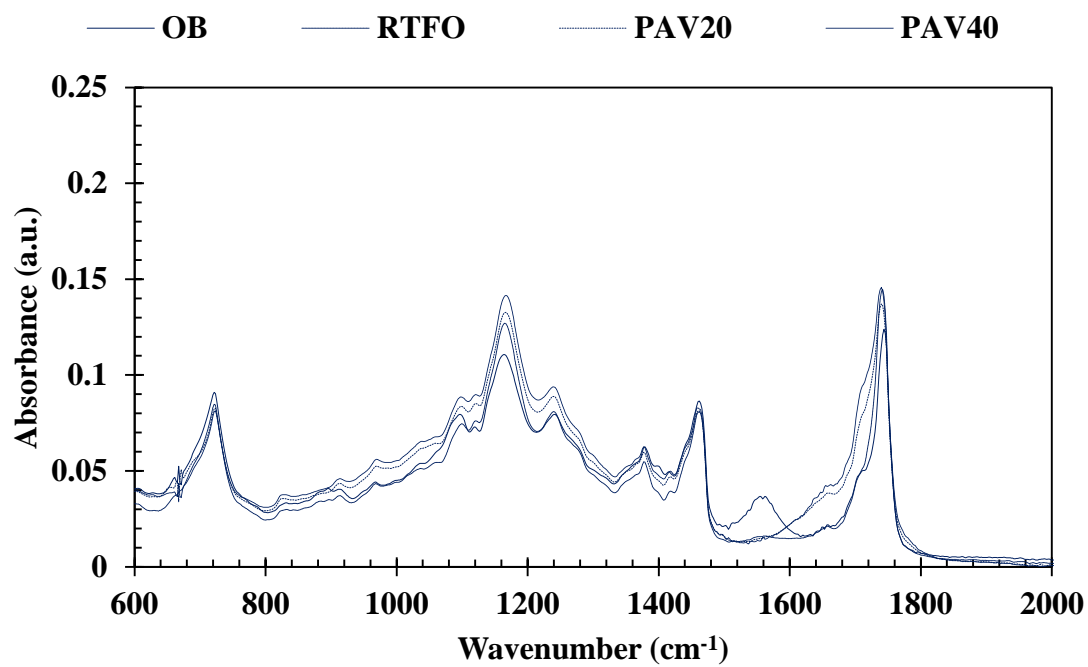
(b) **B1**
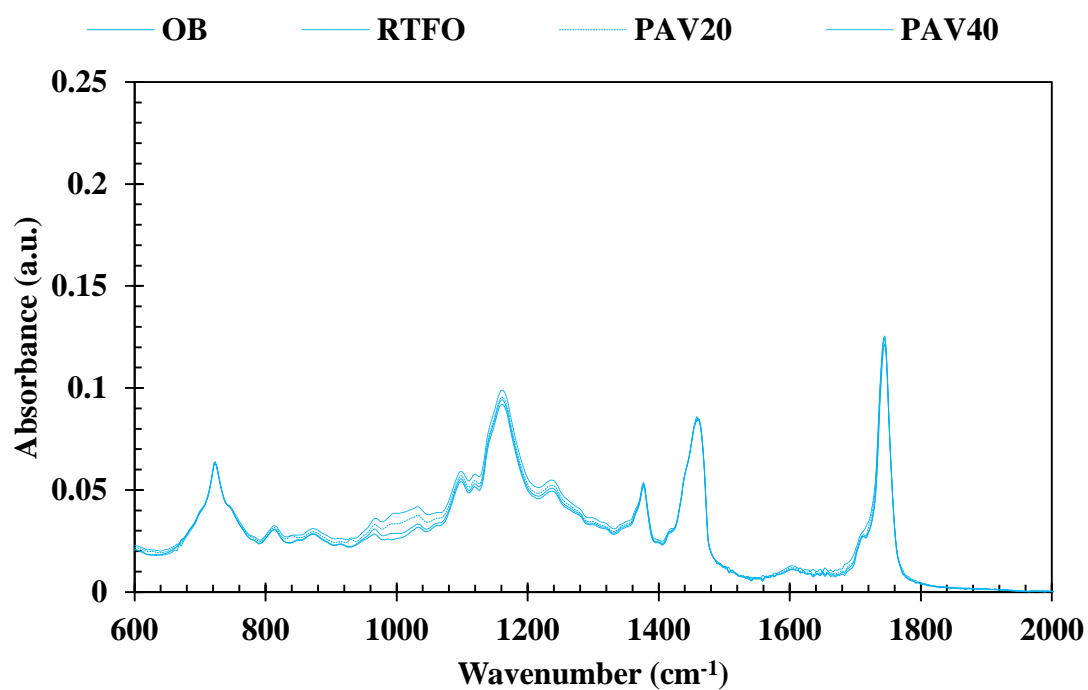
(c) **B2**

Figure 6 Continued

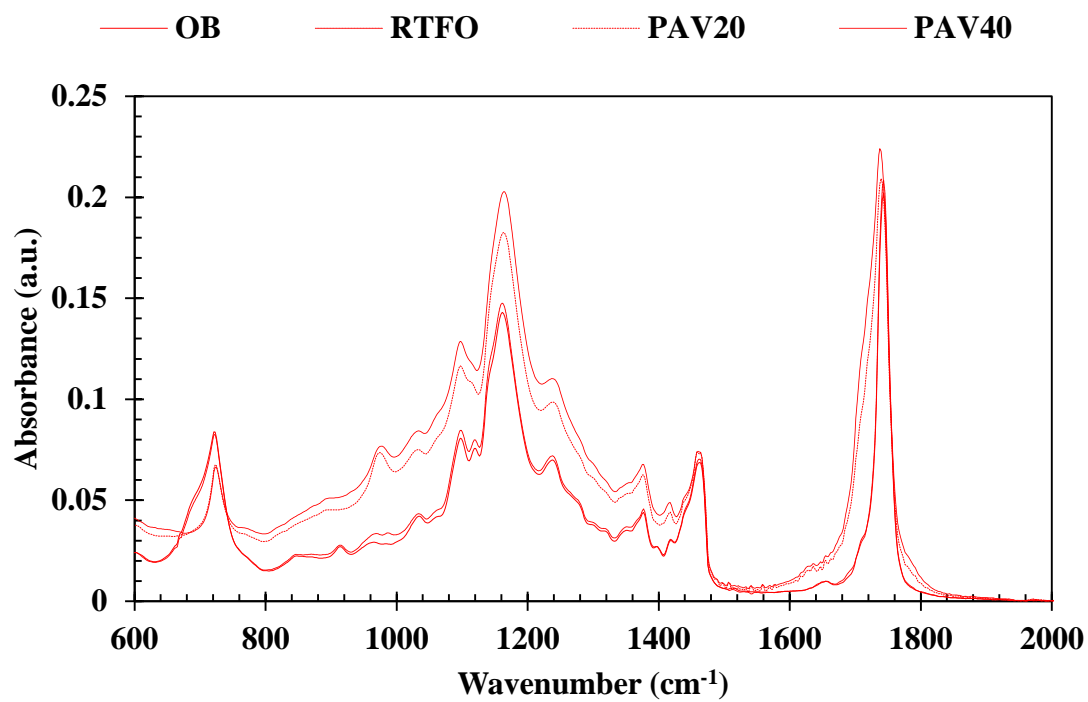(d) **P**

(e) **T1**

Figure 6 Continued

(f) **V2**

(g) **V3**

Figure 6 Continued

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4.2 Binder Blend Characterization

The dose required by each recycling agent to restore the continuous PGH of the recycled binder blend to that of the base binder (PG 64-28) was calculated using the method described by Arámbula-Mercado et al. 2018. The highest dose was required by A1 (13%) followed by P (11%). These were followed by B2 (10.5%), V2 (9%), T1 (8.5%) and B1 and V3 (8% each). The results are in agreement with previous literature by Zaumanis, Mallick, & Frank, 2014 that petroleum-based agents, like A1 and P for this study, require a higher dose for rejuvenation when compared with their bio-based counterparts, which includes the remaining agents in this study.

The results obtained from the DSR testing of binder blends were interpreted in two ways – G-R parameters and Black Space diagrams. The G-R parameter of these blends at various aging levels is shown in Table 2. To be indicative of the field, the value at unaged level was not used for any binder blend for rheological analysis.

Table 2 G-R Parameter for Different Binder Blends

Binder Blends	G-R (kPa)		
	RTFO	**PAV20**	**PAV40**
Base Binder (PG 64-28)	15.23	77.95	225.07
Recycled 0.5 RBR	265.10	1052.66	1741.00
Rejuvenated 0.5 RBR (13.5%) A1	2.68	22.24	54.50
Rejuvenated 0.5 RBR (8%) B1	1.49	12.51	42.56
Rejuvenated 0.5 RBR (10.5%) B2	1.78	13.53	42.44
Rejuvenated 0.5 RBR (11%) P	5.17	53.45	196.92
Rejuvenated 0.5 RBR (8.5%) T1	1.22	16.06	84.10
Rejuvenated 0.5 RBR (9%) V2	1.80	11.15	43.13
Rejuvenated 0.5 RBR (8%) V3	1.90	16.00	45.13

The base binder provided a reference to compare the performance of the other blends with aging. The recycled binder blend {base binder + RAP binder} had a significantly higher value of G-R parameter (1741 kPa) after PAV40 aging, resulting from the use of high recycled material content without the addition of any recycling agents. The binder blend rejuvenated with P was far more brittle when compared with those with the other six recycling agents. The G-R parameter value was 197 kPa for the blend with P, making it the only rejuvenated blend to extend into the transition zone of cracking after PAV40 aging. Blends rejuvenated with T1 had a low G-R parameter value at the unaged level but it increased rapidly with aging to 84 kPa at PAV40 which was still significantly lower than the threshold for onset of cracking (180 kPa). The A1 recycling

agent has been traditionally used in rejuvenation in the field, and after PAV40 aging did not reach the threshold for onset of cracking. The same can be said for the reacted bio-oils and modified vegetable oils used in the study. An aging index was calculated for all the binder blends by taking the log of the ratio of G-R parameter value after PAV40 aging level to that after RTFO aging and shown in Figure 7.
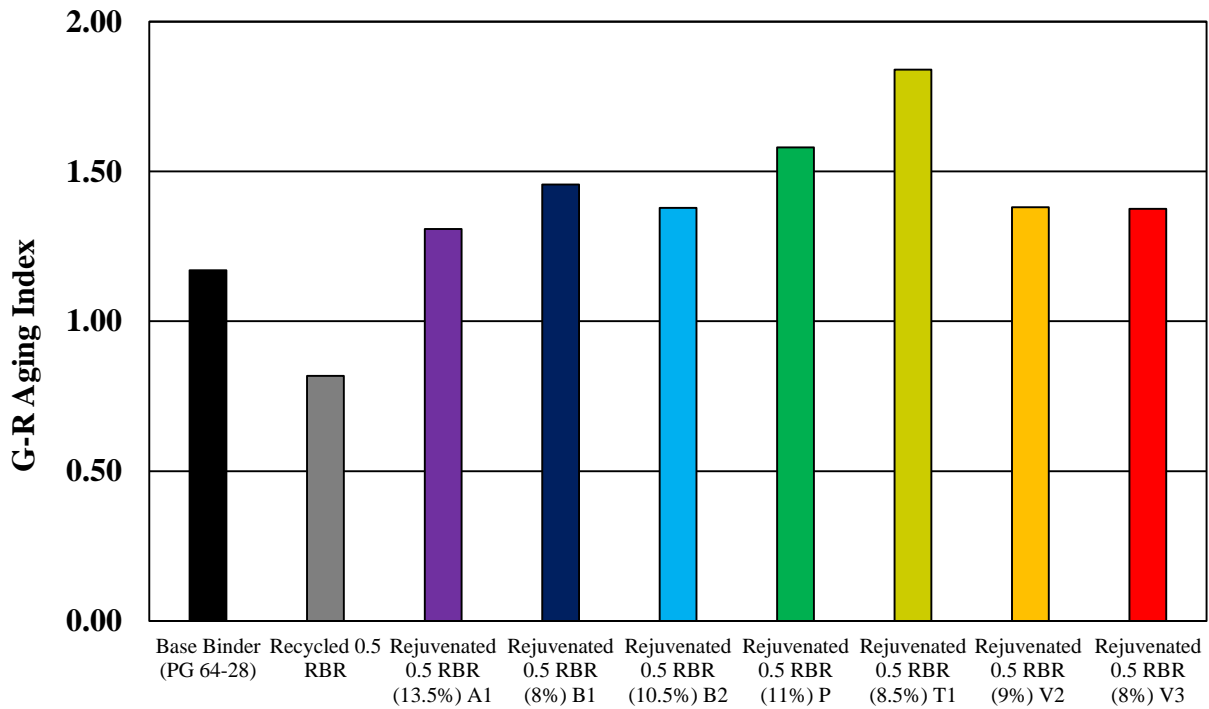

Figure 7 G-R Parameter Aging Index for Different Binder Blends

The blend with T1 showed the highest susceptibility to aging (1.84) followed by the binder blend with P (1.58). This was followed by B1 (1.46), V2, V3 and B2 (1.38 each), and A1 had the smallest index (1.31) amongst the rejuvenated blends. The aging index for the base binder (1.17)

and the recycled binder blend (0.82) were significantly lower showing greater resistance to aging but these had higher initial G-R parameter.

The rheological data was also plotted on a Black Space diagram for analysis in Figure 8. From the Figure 8 it can be seen that aging of a binder blend moves it from the lower right to the upper left in the diagram, which can be correlated to increasing the stiffness or G-R parameter value. The addition of recycled material to base binder moves the state in Black Space significantly, decreasing the phase angle and increasing stiffness. When P is added to a recycled binder blend, a decrease in G* occurs without a sufficient increase in δ. This leads to P being classified as only a softening agent, similar to recycled engine oil bottoms, instead as a true rejuvenator. An absence of polar compounds in the P recycling agent also makes the corresponding blend the least susceptible to aging. This poor effectiveness exhibited by the P recycling agent is generally attributed to problematic compatibility between aromatic asphaltenes and the high concentration of non-aromatic non-polar paraffins in the continuous phase of the binder. Paraffinic oils are not generally used as asphalt additives or recycling agents, and P was chosen specifically as a control agent for comparison. This result makes a clear case supporting the concerns that excess paraffin concentrations may accelerate cracking even when aliphatic molecules might be non-crystalline at low temperatures.
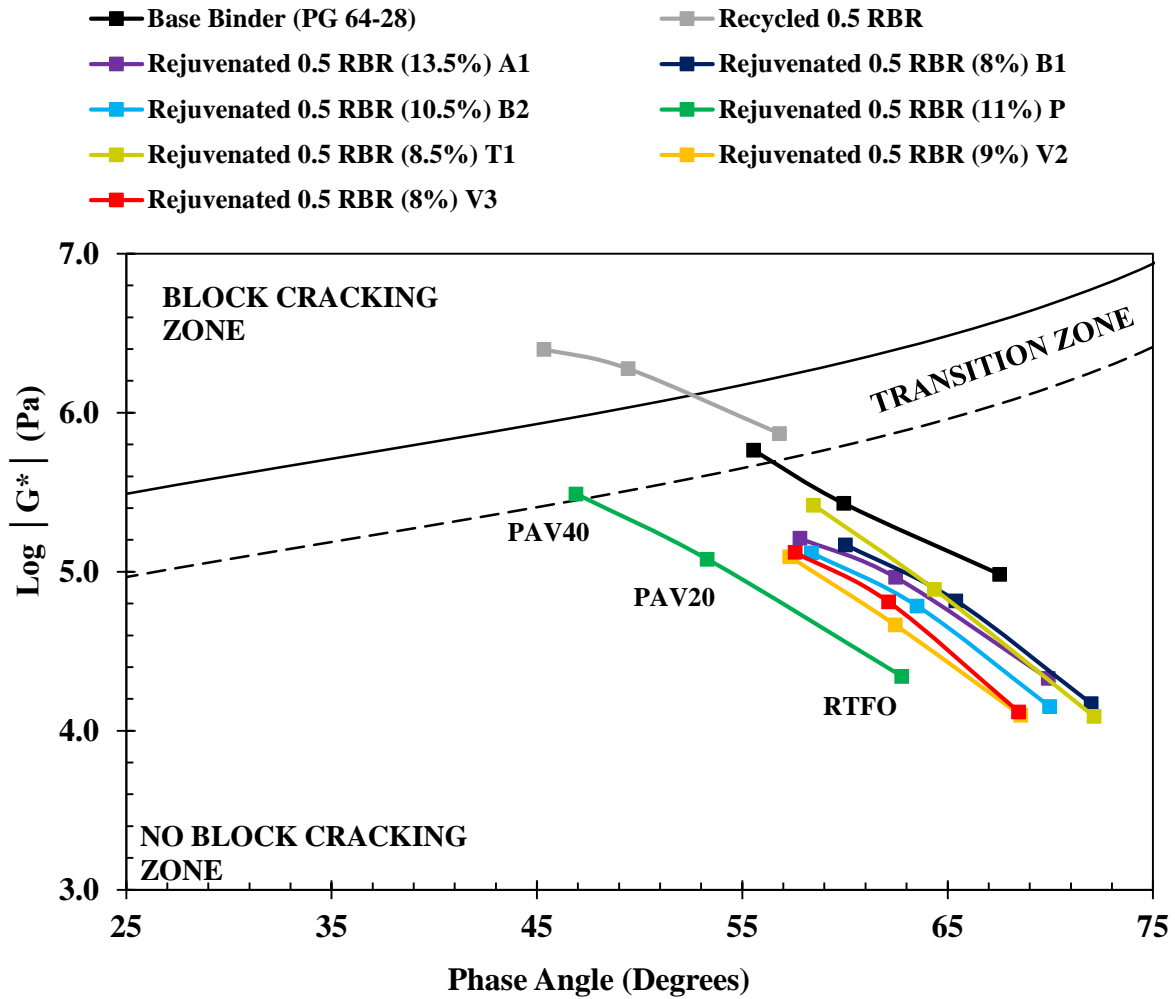
Figure 8 Black Space Diagram for Different Binder Blends

The aromatics as well as bio-based agents used reduced the G* as well as increased the δ of the blend. The basic rejuvenation mechanism used by these selected recycling agents is likely the presence of strongly polar compounds that help to break up large asphaltene clusters in recycled binder blends by polarizing them as well as compatibilizing these smaller asphaltene clusters with the maltenes of the binder blend. These polar compounds include aromatics (A1), fatty acids (T1),

a mixture of glycerides for V2 and V3 and glycerides stabilized through ester and amide bonds or cross-linking bonds for B1 and B2 (Epps Martin et al., 2018). These recycling agents act as rejuvenators for the binder blends as they reduce G* and increase δ.

It can be seen that while aging susceptibility remains an issue for the binder blend rejuvenated with T1, the blend rejuvenated with V3 showed no correlating susceptibility to aging that the agent exhibited on its own. One possible explanation might be the presence of antioxidants. Branthaver et al., 1993 suggests the high concentrations of some natural antioxidants like phenols in asphalt binder. These antioxidants might not prevent the aging of the binder itself by inhibiting the production of benzylic carbonyls, but they might be potent enough to prevent the oxidation of olefinic double bonds in many bio-based recycling agents. This suggests that evaluation of the effectiveness of recycling agents should be done in binder blends and not on the agent itself.

The FTIR absorbance spectrum obtained for the different binder blends at different aging levels is shown in Figure 9. A special focus was given with respect to the carbonyl area band from $1650 - 1820$ cm^{-1} wavenumber as typically this region is used to define the oxygen uptake during aging of asphalt binders (Glover et al., 2005; Jin et al., 2013; Lamontagne et al., 2001). The bio-based recycling agents used contain high concentrations of polar compounds like fatty acids or glycerides. The presence of these compounds will lead to high concentrations of carbonyls before aging, and these manifests themselves in the form of peaks in the carbonyl region where none might have existed for base binder or recycled binder blends. The specific chemical functionality causes the absorbance peak for carbonyls to shift somewhat but it still remains in the CA region. This will remain true for all recycling agents even if they have been reacted or modified. Depending upon the source and any chemical reactions used to stabilize or upgrade the recycling agent, the carbonyl functionality may be in the form of fatty acids, esters, fatty anions, or even

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amides or imidazolines. When rejuvenating the recycled binder blend with bio-based recycling agents, differentiation of the different peaks due to recycling agent oxidation and binder oxidation becomes difficult. The oxidized carbonyl ketones in asphalt absorb IR light near 1700 cm-1 and fatty acids absorb near 1710 cm-1, causing peaks to overlap with carbonyl peaks from asphalt oxidation. Ester peaks are formed when the fatty acids from bio-based recycling agents remain attached to glycerin, or when fatty acids are converted to esters through reactions with alcohols. The carbonyl groups in esters should show maximum IR absorbance near 1750 cm-1, making them easier to quantify in the presence of oxidized asphalt than their fatty acid counterparts. Other bands are also valuable for differentiating the presence of bio-based recycling agents from the carbonyls from asphalt oxidation. In particular, carbon-oxygen bonds are present for both esters and fatty acids, but only in small amounts for oxidized asphalt binder. Traditional tools like CA and CA growth (CAg), which deducts the CA value at unaged aging level from the considered CA value, were measured to determine chemical changes due to oxidative aging, however the presence of competing carbonyl peaks from fatty acids and esters from the recycling agents complicated the analysis. The CA and CAg values are recorded in the Appendix for consideration along with the whole FTIR absorption spectrum.
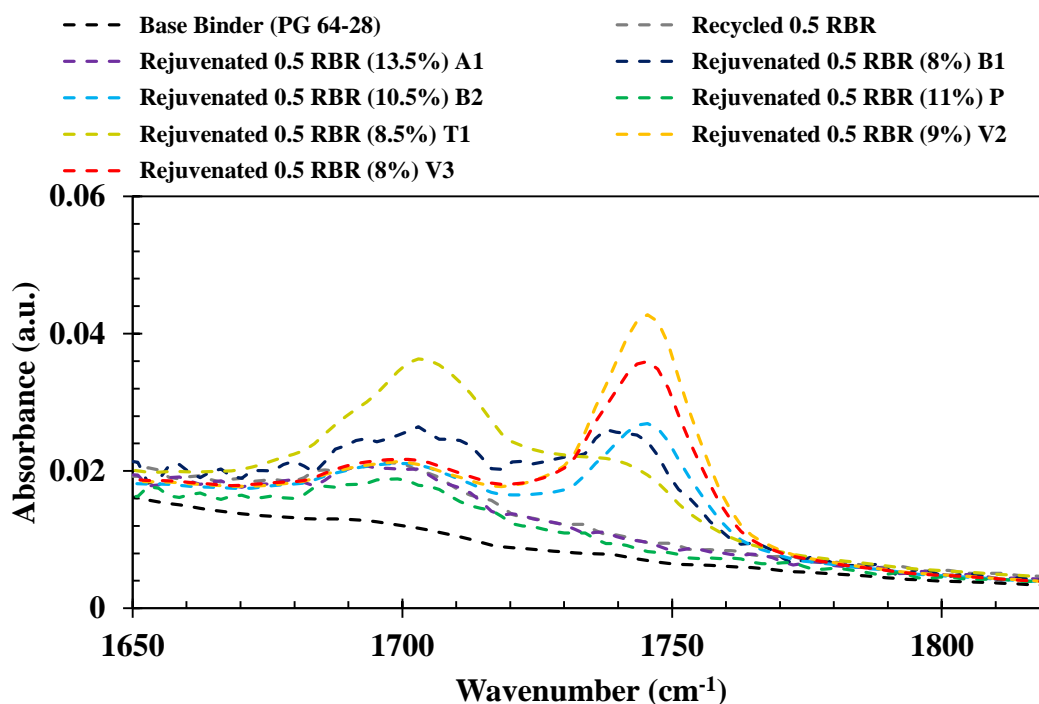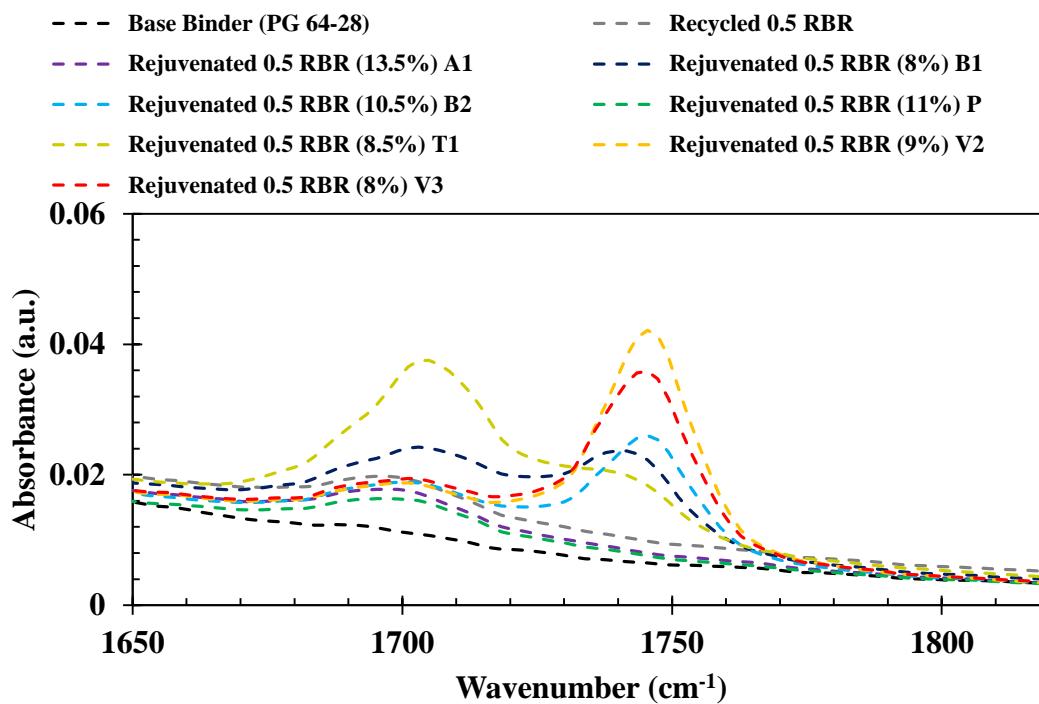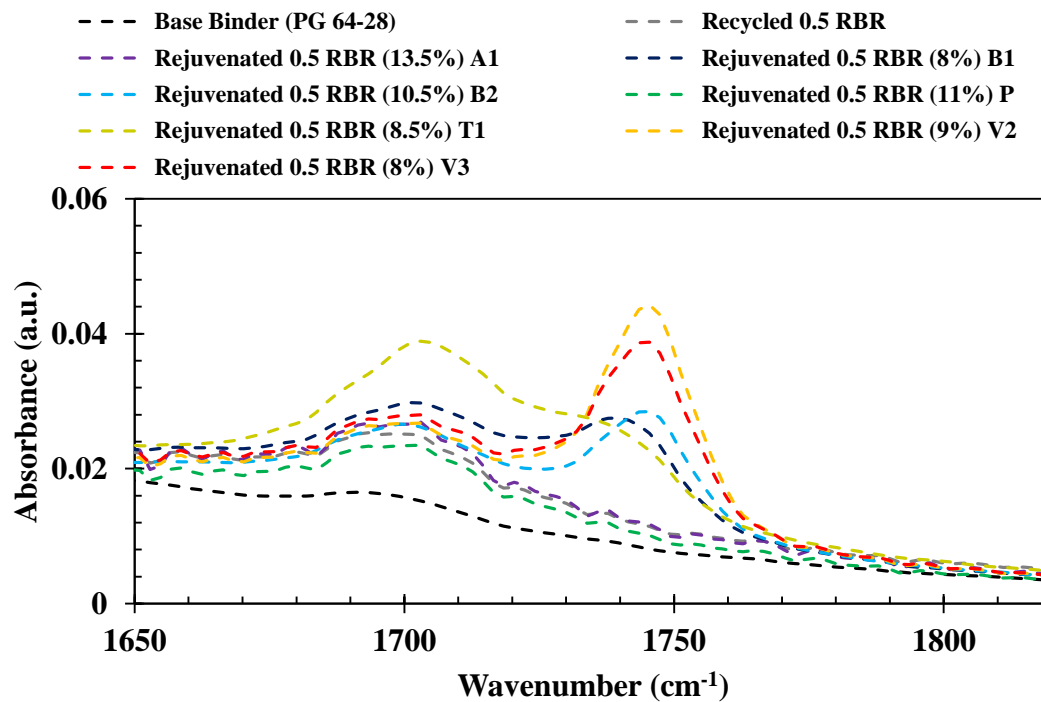
(a) **Unaged**

(b) **RTFO**

Figure 9 Carbonyl Area for Binder Blends at (a) Unaged, (b) RTFO, (c) PAV20, and (d) PAV40 Aging Levels

(c) **PAV20**
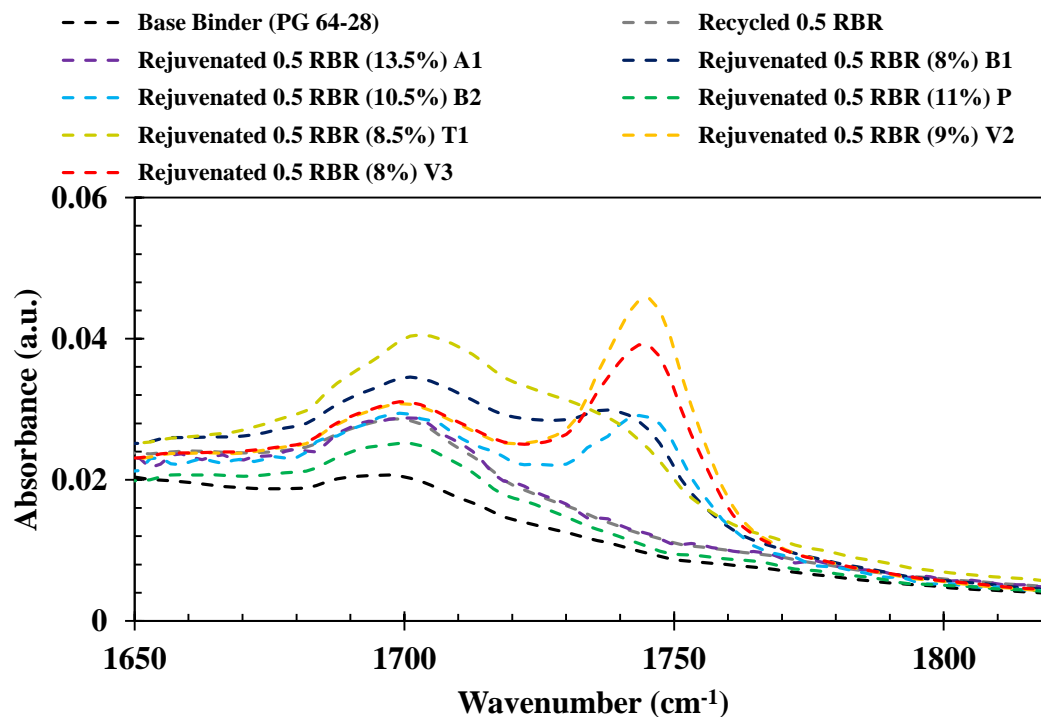
(d) **PAV40**

Figure 9 Continued

The performance of binder blends depends on its rheological as well as chemical parameters. Coupling of these parameters for the binder blends used in this experiment was attempted. For rheology the G-R parameter was utilized instead of Low Shear Viscosity (LSV) (Morea, Agnusdei, & Zerbino, 2011) or Zero Shear Viscosity (ZSV) (Sybilski, 1996) to capture the changes in both G* and δ. Log G-R parameter versus CAg is plotted on a semi-log graph in Figure 10 for the binder blends used with the slopes for the trendlines provided. The slope represents the change in the G-R parameter with unit change in CA growth and can be labeled as a G-R/CAg Hardening Susceptibility (G-R/CAg HS).
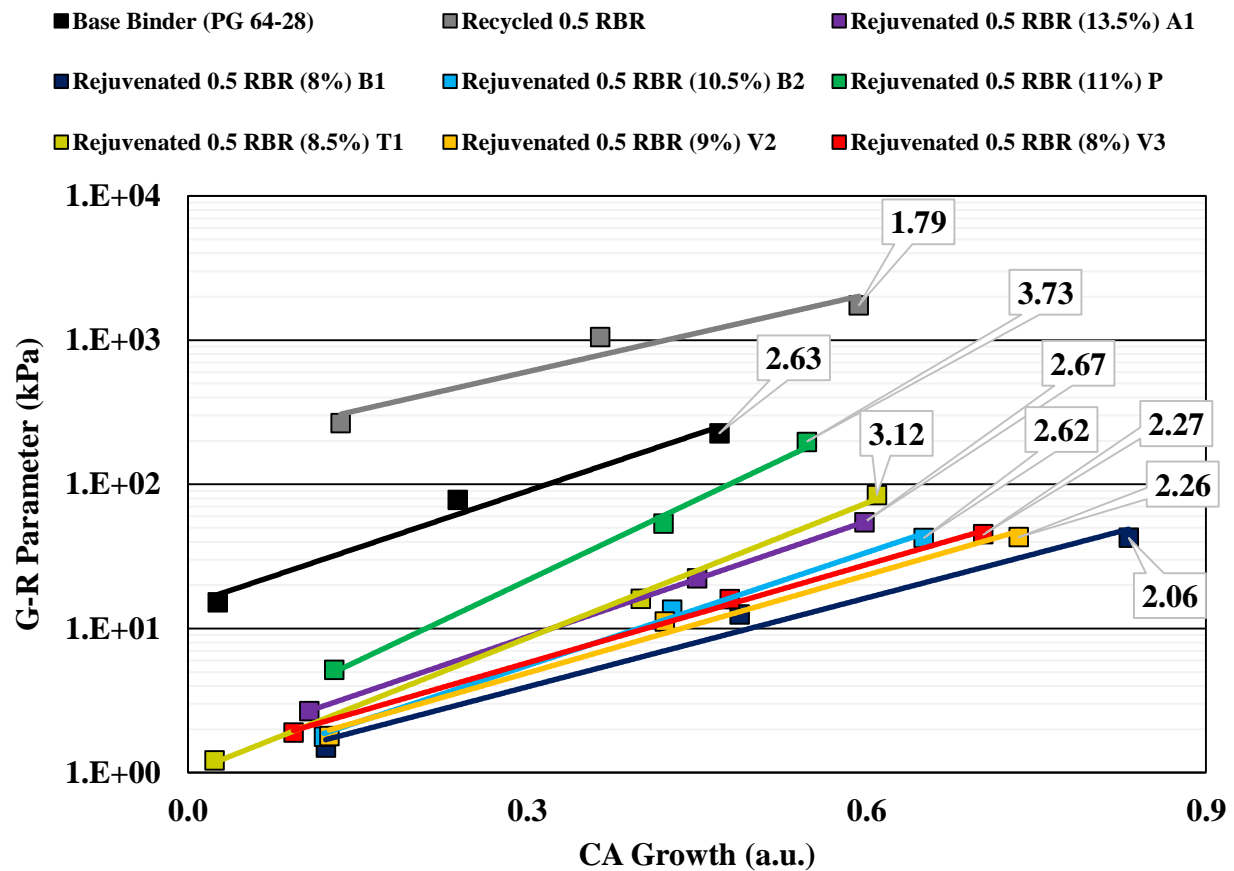
Figure 10 G-R Parameter vs Carbonyl Area Growth for Different Binder Blends with their Slopes

As expected, the rejuvenated binder blend with P had a significantly higher G-R/CAg HS than the blends with all other recycling agents. This finding supports other evidence that the paraffinic oil P was least sensitive to oxidation as measured by CAg, but the blend experienced substantial increases in G-R parameter due to a rapid deterioration in compatibility between a saturate-rich maltene phase and increasingly larger and more polar asphaltenes. The rejuvenated blends with various bio-based recycling agents (including T, V, and B types in this study) contain double bonds, and therefore exhibit considerably more CAg than the blend with P. However, those same double bonds encourage molecular motion, leading to higher phase angles and lower G-R parameter values. For the bio-based recycling agents, the blend with tall oil T1 had a relatively high G-R/CAg HS due to a higher G-R parameter value. The other four bio-based recycling agents (V2, V3, B1, and B2) had almost identical G-R parameter values, but G-R/CAg HS values differed with varying CAg values. G-R/CAg HS provides a necessary, but not sufficient, parameter for evaluating recycling agents as it indicates the rate of rheological change with chemical oxidative aging.

Location in Black space is also important with respect to cracking resistance in corresponding mixtures. For example, the blends with aromatic extract A1 and reacted bio-based oil B2 were almost equivalent to the base binder in terms of G-R/CAg HS, but their locations in Black space and G-R parameter values were different (Figure 8). In addition, the lowest G-R/CAg HS value was exhibited by the recycled blend without recycling agent due to significant previous aging which is also shown by the highest G-R parameter values.

A combined parameter to include both the change due to embrittlement as well as location of the binder blends in the Log G-R versus CAg graph was developed. This parameter was called the Binder Embrittlement Parameter (BEP) and defined as follows:

$$BEP = Log[(G - R_{RTFO} \times G - R_{PAV40}) \times (G - R/CAg\ HS)^2]$$

Where G-R parameters are used for RTFO and PAV40 aged level. This parameter considers both the slope as well as location in Figure 10. G-R parameter value at two separate aging levels also indicate the aging susceptibility of binder blends which is an important factor to consider in itself. The BEP for various binder blends is shown in Figure 11.
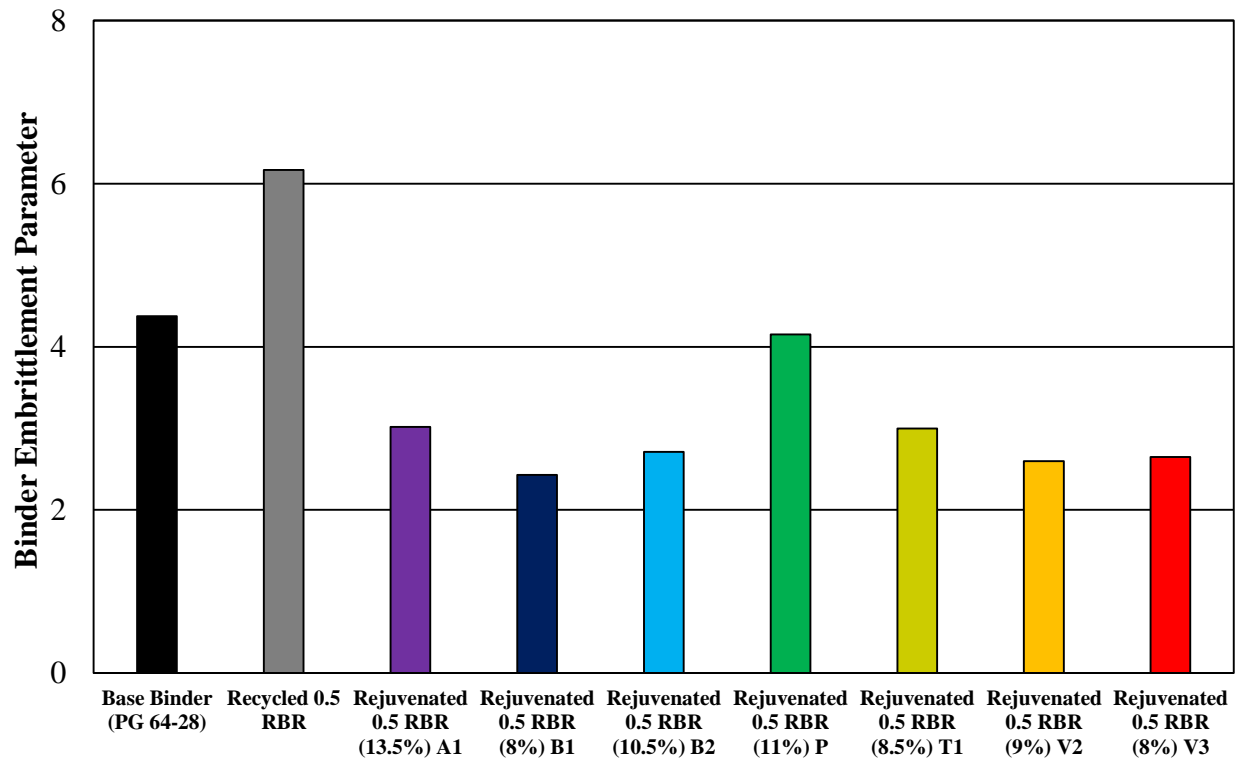
Figure 11 Binder Embrittlement Parameter for Different Binder Blends

A lower value of BEP would indicate a lower stiffness as well as less rheological response due to uptake of oxygen during aging. Both these qualities would be desirable for the binder blend. The recycled blend has a significantly higher value than the rejuvenated blends even though it has a low G-R/CA HS due to an extremely high initial stiffness because of the large quantity of RAP. The base binder serves as threshold to evaluate the other blends. As expected the rejuvenated blend with P did not perform as well as the blends with other recycling agents due to both a higher G-R parameter value and a higher response to oxygen uptake.

Lastly the results for the conditioning sequence experiment were analyzed with both the rheological and chemical data obtained. Figure 12 shows the rheological data obtained by the analysis in the Black Space Diagram for the various blends. Conditioning sequence #1 is depicted by the movement in the lower right of the diagram due to rejuvenation and then the upper left shift due to aging. Conditioning sequence #2 starts with a movement to the upper left in the diagram due to aging and then a lower right shift due to rejuvenation. For all the cases, the binder blends that underwent conditioning sequence #1 had a lower G* and higher δ than the corresponding ones that underwent conditioning sequence #2 even though the aging of recycling agents occurred in sequence #1. This indicates that the loss of effectiveness of recycling agents with aging contributes to a lesser extent when compared to other factors like aging of the binder blend itself.
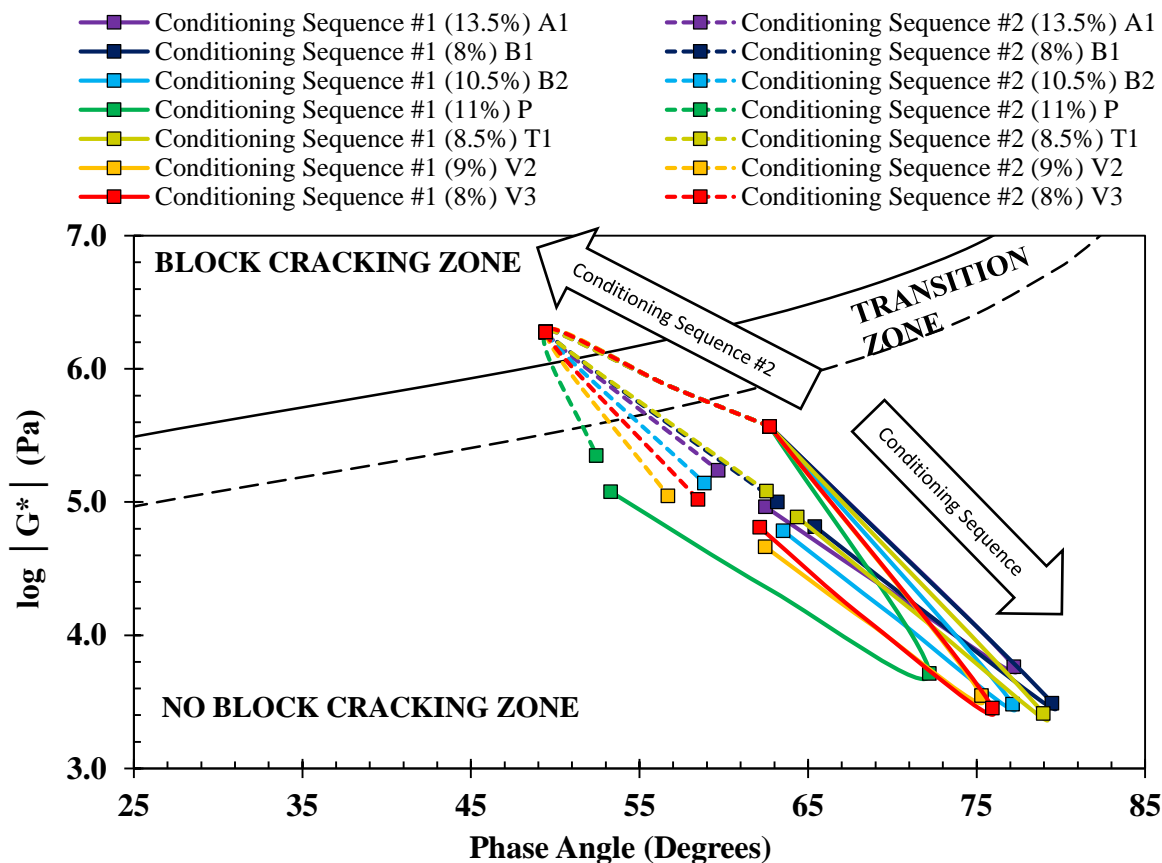
Figure 12 Black Space Diagram for Binder Blends Undergoing Different Conditioning Sequences

Figure 13 plots the G-R parameter of these blends to illustrate the difference between the two conditioning sequences. The G-R parameter values for sequence #2 were much higher than for their counterparts that underwent sequence #1 despite the use of unaged recycling agents throughout the experiment. One explanation for this unexpected behavior could be that the recycling agent is consuming some of the available oxygen during PAV aging, but the rheological consequences of these oxidation products were not as great as forming benzylic carbonyl on highly aromatic asphalt molecules as discussed subsequently. The effectiveness of each recycling agent with aging, represented by low G-R parameter values after conditioning sequence #1 with 20-hour

PAV, is in agreement with the effectiveness rankings after 40-hour PAV discussed previously. After conditioning sequence #1, binder blends with all five bio-based recycling agents had lower G-R parameter values within the range of 11-16 kPa, while the blend with aromatic extract A1 had a higher value (22 kPa), and the blend with paraffinic oil P exhibited an even higher value (53 kPa).
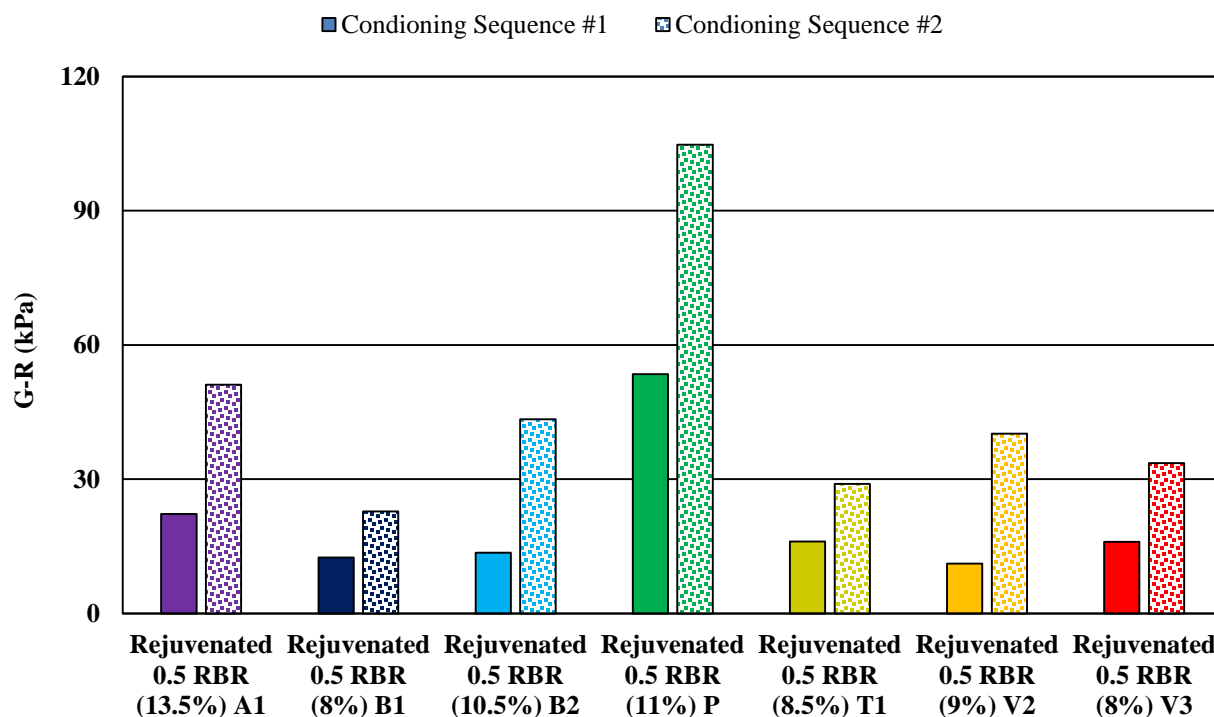
Figure 13 G-R Parameter for Binder Blends Undergoing Different Conditioning Sequences

The CAg measured for the conditioning experiment is reported in Figure 14. These results indicate more oxygen uptake due to higher CAg for blends that underwent conditioning sequence #1. However as seen previously the blends that underwent conditioning sequence #2 had a higher G-R parameter value. These remain true for both petroleum-based agents, that age similarly to binders, as well as bio-based agents. One reason for this disparity might be attributed to the fact

that oxygen diffusion through binder blends might be different for the sequences. Binder blends that underwent sequence #1 were much softer and less brittle hence oxygen diffusion would be higher for these blends. However, this alone would not be able to explain the differences in the rheology between the conditioning sequences. These differences might arise due to the presence of recycling agents during aging of a binder blend. The presence of recycling agents might divert some of the oxygen uptake to reactions where the highly damaging benzylic carbonyl compounds are not formed then this would impact the rheology of the binder blend significantly. These recycling agents would therefore reduce the damaging impact of each carbonyl-based oxygen, which would suggest additional benefits beyond the initial impact of rheology.
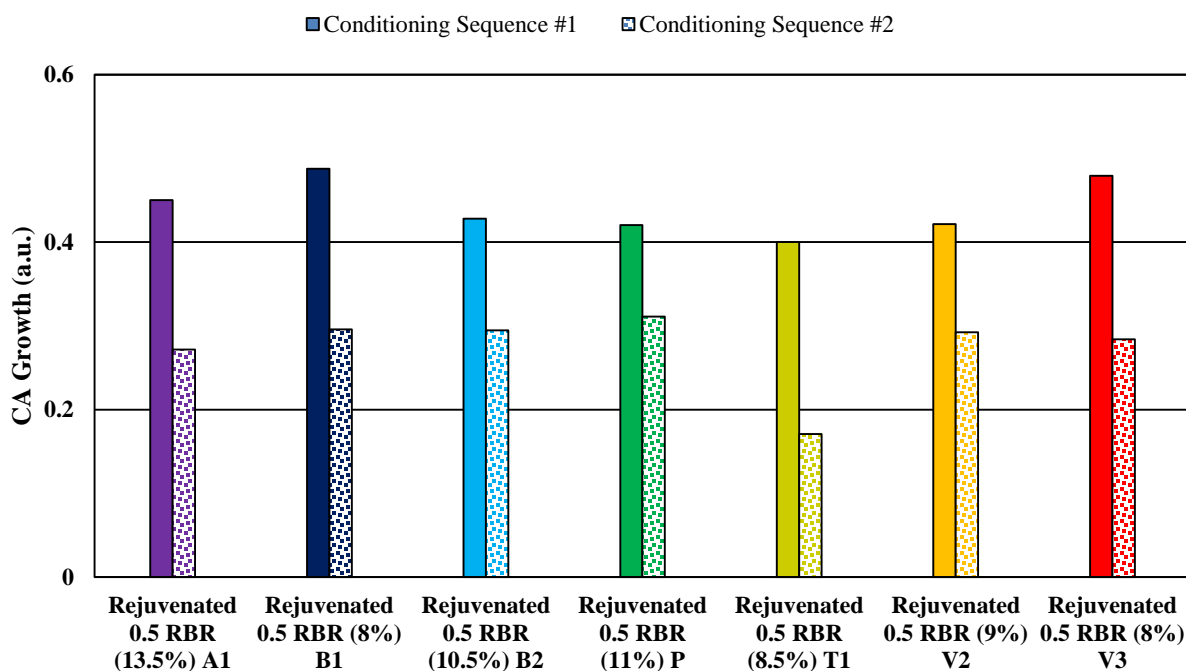

Figure 14 Carbonyl Area Growth for Binder Blends Undergoing Different Conditioning Sequences

4.3 Mixture Characterization

The results from the HWTT for rutting are plotted in Figure 15. The recycled blend showed good resistance to rutting, which is expected as the addition of stiffer aged materials like RAP would only increase overall stiffness of a mixture. The addition of recycling agents reduces the stiffness of these mixtures significantly. Most of the rejuvenated mixtures pass the threshold of 7500 cycles to a 12.5mm rut depth. The mixture rejuvenated with P, however, failed this threshold. The incompatible nature of P recycling agents leads to a higher moisture susceptibility of the mixture as seen in Figure 15. This further proves the disadvantages of the use of softening agents for rejuvenation, increasing the rutting susceptibility of mixtures due to their incompatibility. For all the other rejuvenated mixtures, there seems to be a correlation between the dose of the recycling agent and its rut resistance with mixtures rejuvenated with B1 having the lowest dose and the highest rutting resistance. The exception in this case being the A1 rejuvenated mixtures, which show a higher rut resistance than most rejuvenated mixtures. This implies that the high oil contents present in bio-based recycling agents might be affecting the adhesive properties between the binders and the aggregates, which could be leading to early stripping and therefore less rutting resistance as stated by Villanueva, Ho, & Zanzotto, 2008. Since the dose of the recycling agent contributes to rutting resistance, an upper limit on the dose used is needed to preclude failure due to rutting in the field.
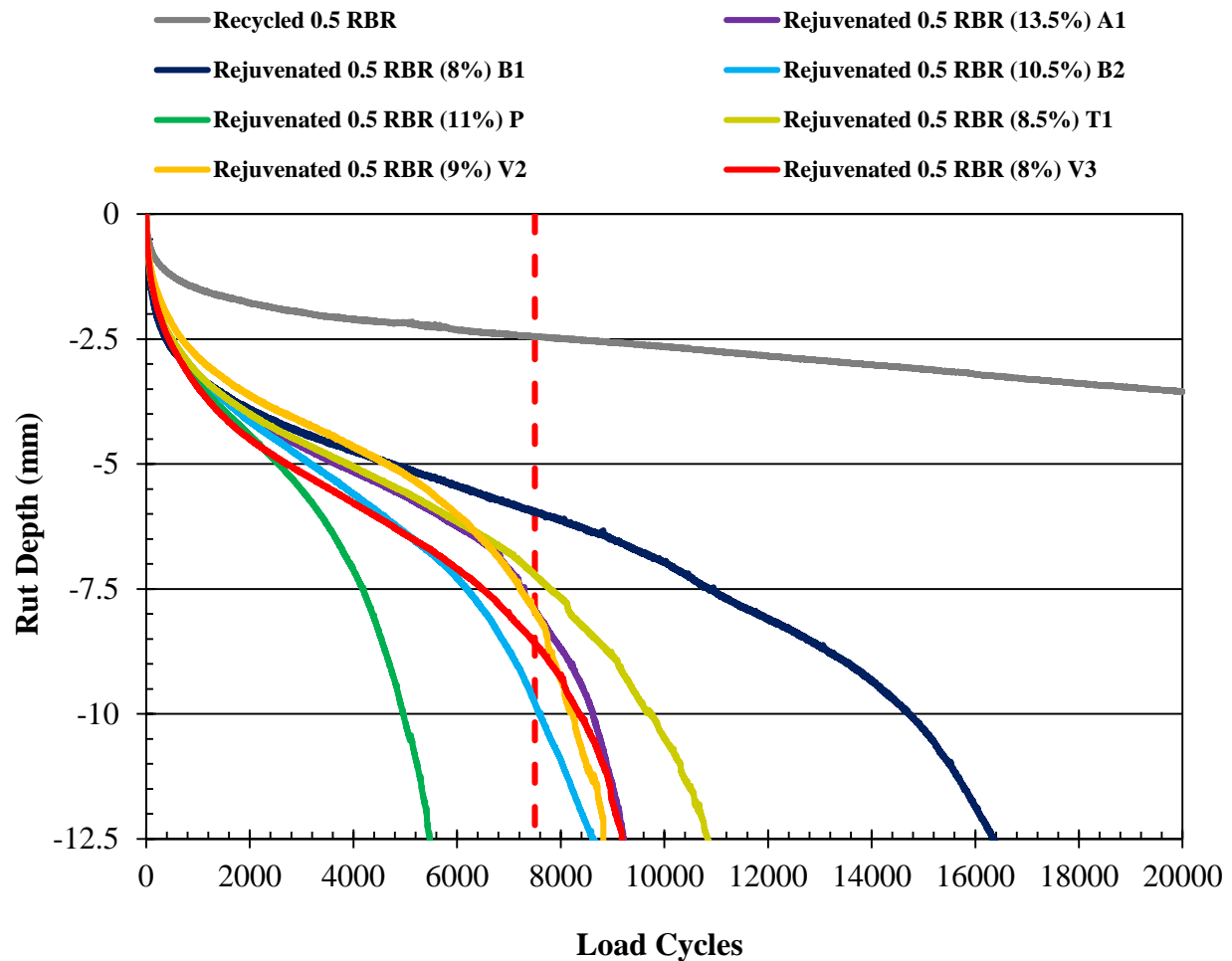
Figure 15 HWTT Results for Different Mixtures

The I-FIT test was performed for the mixtures and the results are shown in Figure 16 along with the error bars to present the variability in the test. The recycled blend, due to its high stiffness, performs the worst as expected. The stiffness of this mixture after LTOA couldn't be measured due to the low cracking resistance. This high stiffness is the major challenge of using recycled materials like RAP in the field in higher quantities. The addition of recycling agents softens these recycled blends to a significant degree as seen in Figure 9. After STOA the reacted bio-oils performed the best with high FI followed by the rest who all perform comparatively the same.

After LTOA of these rejuvenated mixtures, a drop in the FI value is shown as expected. The B1 rejuvenated mixture still exhibited the highest FI values. It was closely followed by B2 and V3. V2, A1, P and T1 rejuvenated mixtures that had FI values in that descending order. The bio-based recycling agents generally performed better than petroleum-based products with the exception of T1. This can be attributed to the aging susceptibility of tall oils.

An aging index similar to recycling agents was calculated by dividing the FI value after STOA by FI value after LTOA and shown in Figure 17. The rejuvenated mixture with T1 had the highest aging index (1.71) which correlates with the results from binder blends and recycling agents rheological testing. It was followed by A1 and P with 1.70 each. These were followed by V2 (1.62), B2 (1.54), B1 (1.28) and V3 (1.23). The high variability for the V3 rejuvenated mixture after STOA might lead to a low aging index.
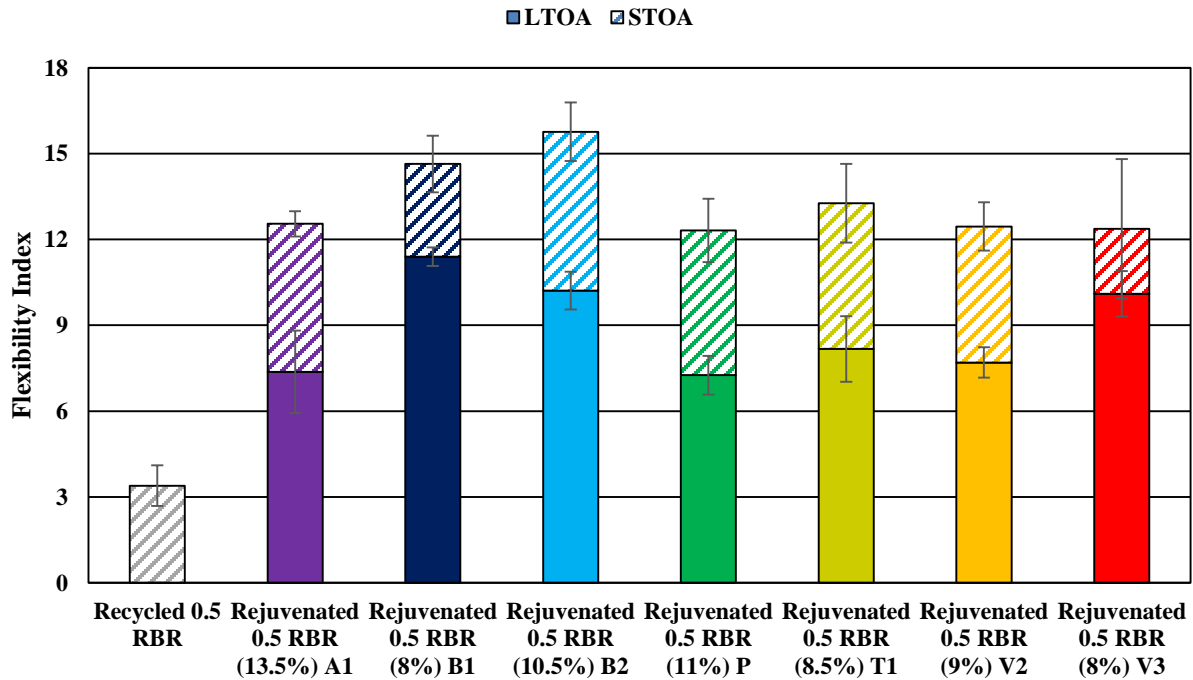
Figure 16 I-FIT Results for Different Mixtures

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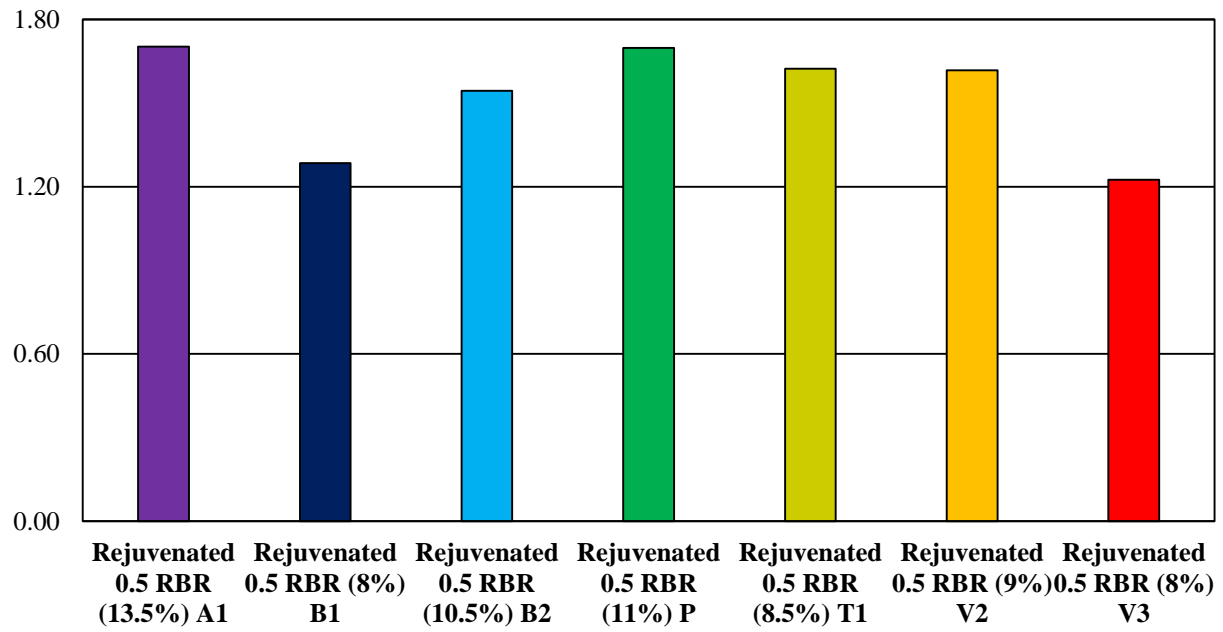
Figure 17 Flexibility Index Aging Index for Different Mixtures

5. CONCLUSIONS AND RECOMMENDATIONS

This study analyzed the effectiveness of recycling agents for rejuvenation of binder blends and mixtures with high recycled materials content at different aging levels. The agents themselves were tested for their rheological and chemical properties using the tools traditionally used in the industry. The same tools were utilized to evaluate the binder blends prepared with these recycling agents and RAP at a high RBR. Performance testing was then utilized to assess corresponding recycled mixtures.

5.1 Observations

The main findings of this study are listed as follows: -

- Testing of recycling agents by themselves may not be representative of their behavior in binder blends. The chemistry of recycling agents can be influenced by that of binders and vice versa, making it difficult to predict their properties if not tested in conjunction with binder and recycled material in a blend.

- Recycling agents included in the experiment interact with the recycled materials in different ways and therefore can be categorized into different groups based on their mechanism of rejuvenation.

  - The paraffinic oil P included in this study was not expected to be a good rejuvenator. It still helps to meet the PG requirements of binder blend when an appropriate dose is mixed with the recycled binder, but it performs poorly based on almost all the rheological testing, placing it in a separate category from the other recycling agents. It performs more as a softening agent than as a rejuvenator, having little compatibility with the oxidized aromatics. Even though oxygen uptake doesn't increase significantly with aging, this

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lack of compatibility can hinder molecular motion, leading to a low δ and high G*.

o Aromatic extract A1 has traditionally performed well in the field when used for rejuvenation. It is thought to replace the aromatics and resins lost in the binder during oxidation while also maintaining higher compatibility with the asphaltenes produced. It also performed well under rigorous aging levels like PAV40 and outperformed other petroleum-based recycling agents like P. However, the quality of the base binder as well as the content of recycled materials used may affect the rejuvenating capabilities of A1, oftentimes requiring high doses that are not likely economical.

o Tall oil T1 is a by-product from the paper production industry that is now used for rejuvenation. Being a bio-based recycling agent, it contains strong polar compounds that can help with rejuvenation in much the same way as reacted bio-oils and modified vegetable oils. It shows a greater amount of cracking resistance when compared with petroleum-based recycling agents due to unsaturated double bonds present in it, however these double bonds are prone to oxidation and make them susceptible to aging. This along with the lower molecular weight makes this recycling agent more volatile than the others, even the other bio-based recycling agents.

o The modified vegetable oils (V2, V3) and reacted bio-oils (B1, B2) seem to be the most effective recycling agents. Even though they lack aromatics, these agents offer a different mechanism for rejuvenation. Acting more like emulsifiers, the highly polar carbonyl groups attach themselves to the polar

asphaltene agglomerates developed due to aging while the olefinic chains remain in the mobile maltenes present in binder. This leads to an increase in the mobility of polar molecules in a non-polar phase and subsequently better performance both in lowering G* and higher δ. Oxidation may lead to decrease in benefits of double bonds, but the same might not be reflected in the rheological parameters. The presence of these agents might alter the oxidation pathways that the binder undergoes with aging as seen with the G-R/CA HS. Some oxidation of the double-bond sites on the recycling agent molecule could even be helpful by creating more compatibility with asphaltenes through polar interactions. Modification of these agents to resist long-term aging also helps retain their effectiveness with oxidation. Pure vegetable oils are usually edible and have a high flash point, so these agents might also perform well from a safety stand point

- o However not all bio-based oils may be suitable for rejuvenation. Pure saturated fatty acids like steric or palmitic acid may behave like waxes due to their high melting points. Even when substituted on lager chains of glycerides these might crystallize, damaging the rheological properties greatly.

- The presence of strongly polar groups in recycling agents proves challenging to traditional tools like FTIR. The CA might be greatly increased by the presence of recycling agent but, not all the oxygen uptake leads to an increase in G-R parameter. The aging pathways might be changed due to the presence of recycling agents. Even the uptake of more oxygen during aging might not affect the rheological properties

as thought for binders. Instead oxidative impact on key rheology indicators tied to cracking seem to be ameliorated for all recycling agents. The same challenges can be encountered when using other tools like SARA-AD as demonstrated by (Garcia Cucalon et al., 2017). In this study due to the presence of carbonyl rich agents in the blends, the CA was discarded in favor of CAg which measures the growth between two aging levels instead of a value.

- The type and dose of recycling agents can also affect performance properties of mixtures as seen with rutting in this study. As seen in this study, recycling agents with a lower dose to restore PGH had a higher rutting resistance than those agents that required a higher dose, with the exception of A1. This might be due to high oil contents present in bio-based agents that reduce the adhesion between binder and aggregates.

- Considering all the factors, reacted bio-oils had the best performance followed closely by the modified vegetable oils. Tall oils performed better than the petroleum-based products, but their aging susceptibility casts a doubt on long-term effectiveness in the field. Aromatic extracts, with a higher compatibility with asphalt binders, are more effective than paraffinic oil that just act as softening agents.

- The current classification system for recycling agents is contained in ASTM D-4552" Standard Practice for Classifying Hot-Mix Recycling Agents". This specification is based on kinematic viscosity at 60°C, flash point, saturate content, and viscosity ratio with short-term aging (RTFO). As discussed previously, the aging index based on complex viscosity for the recycling agent itself could be

highly misleading, and this specification for recycling agents does not include critical aged rheological properties for the rejuvenated blend. Based on these results, it may be more appropriate to set specifications for the final rejuvenated binder after long-term aging and leave some flexibility as to the choice of rejuvenator, controlled by a qualified products list.

5.2 Future Research

Many aspects of the evaluation of recycling agents might require a more thorough analysis that was not done in this study. Recommendations for future research include:

- Introduction of different materials for creation of blends. Different base binders, recycled materials like RAS or different recycling agents can be included to further study the effect that these factors on the performance of rejuvenated blends. Long-term aging like PAV for 80 hours can also be done to further assess the effect of aging on performance.

- Use of more mixture analysis tools like resilient modulus and low temperature thermal cracking resistance can be used to perform a more comprehensive analysis of the effect of recycling agents on mixture performance. For binder testing, parameters like ΔTc (numerical difference between the low continuous grade temperature determined from the Bending Beam Rheometer (BBR) S and m-value criteria) can also be measured as it correlates with cracking resistance.

- The FTIR spectra obtained was primarily analyzed in the CA region. Further analyses of the spectra might provide helpful insights into the chemistry of recycling agents and rejuvenated blends.

- Correlation between binder characterization data and the corresponding mixture characterization data is significantly affected by the degree of blending in mixtures between the base binder, recycled materials and recycling agents. Degree of blending in mixtures should be further explored as it has a significant impact on mixture properties.

- Current standards for classification of recycling agents need to be updated to include testing of agents in binder blends, and new specifications need to be adopted to properly distinguish between the performance of good and bad recycling agents.

- The Binder Embrittlement Parameter developed should be further modified by analyses of field data, and thresholds should be developed.

- Utilization of oxidation kinetics for the different rejuvenated blends in pavement oxidation modeling can be explored to better understand the different aging mechanisms that the blends might undergo.

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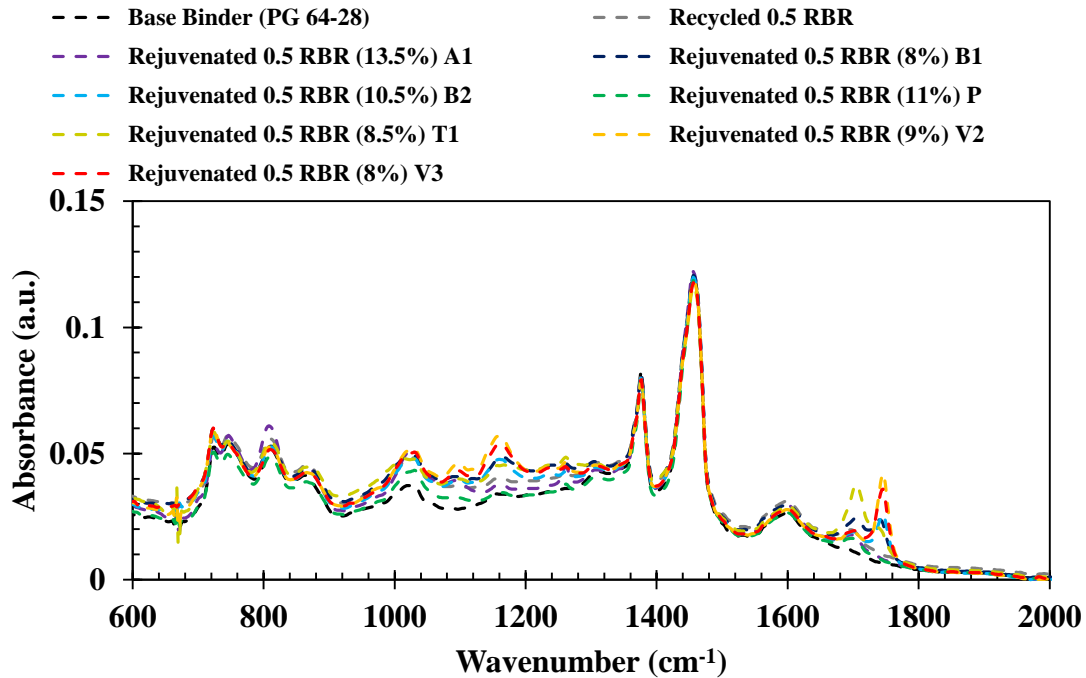
APPENDIX

- Rheological Characterization of Recycling Agents

Table 3 Complex Viscosity for Recycling Agents at 15°C and 10 rad/s

Recycling Agent	Complex Viscosity η* (mPa.s)				Aging Ratio (Pav40/Unaged)
	Unaged	RTFO	PAV20	PAV40	
A1	16440	20315	18945	18965	1.15
B1	732.85	840.35	2034	2110	2.88
B2	608.4	731.9	1408	1583	2.60
P	161.5	170.3	175.3	176.75	1.09
T1	341.25	967.8	332850	5557000	16284.25
V2	138	149.65	163.35	255.4	1.85
V3	55.92	99.235	16290	60110	1074.93

- Chemical Characterization of Binder Blends

- - - Base Binder (PG 64-28)
- - - Recycled 0.5 RBR
- - - Rejuvenated 0.5 RBR (13.5%) A1
- - - Rejuvenated 0.5 RBR (8%) B1
- - - Rejuvenated 0.5 RBR (10.5%) B2
- - - Rejuvenated 0.5 RBR (11%) P
- - - Rejuvenated 0.5 RBR (8.5%) T1
- - - Rejuvenated 0.5 RBR (9%) V2
- - - Rejuvenated 0.5 RBR (8%) V3

(a)

Figure 18 FTIR Spectra for Binder Blends at (a) Unaged, (b) RTFO, (c) PAV20, and (d) PAV40 Aging Levels
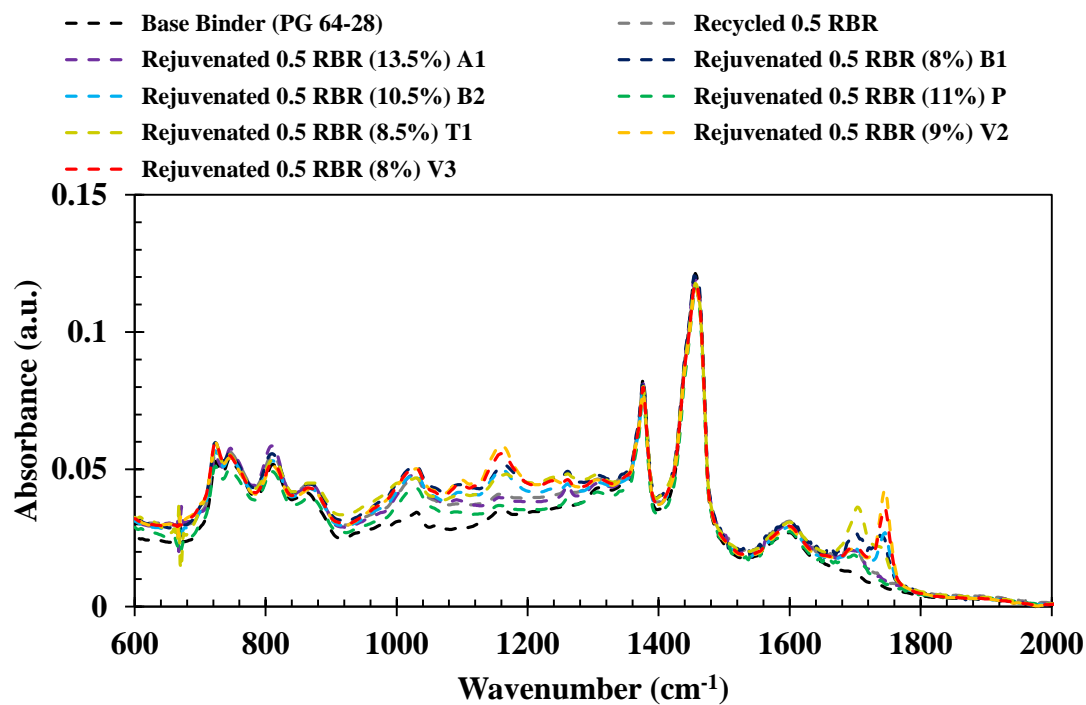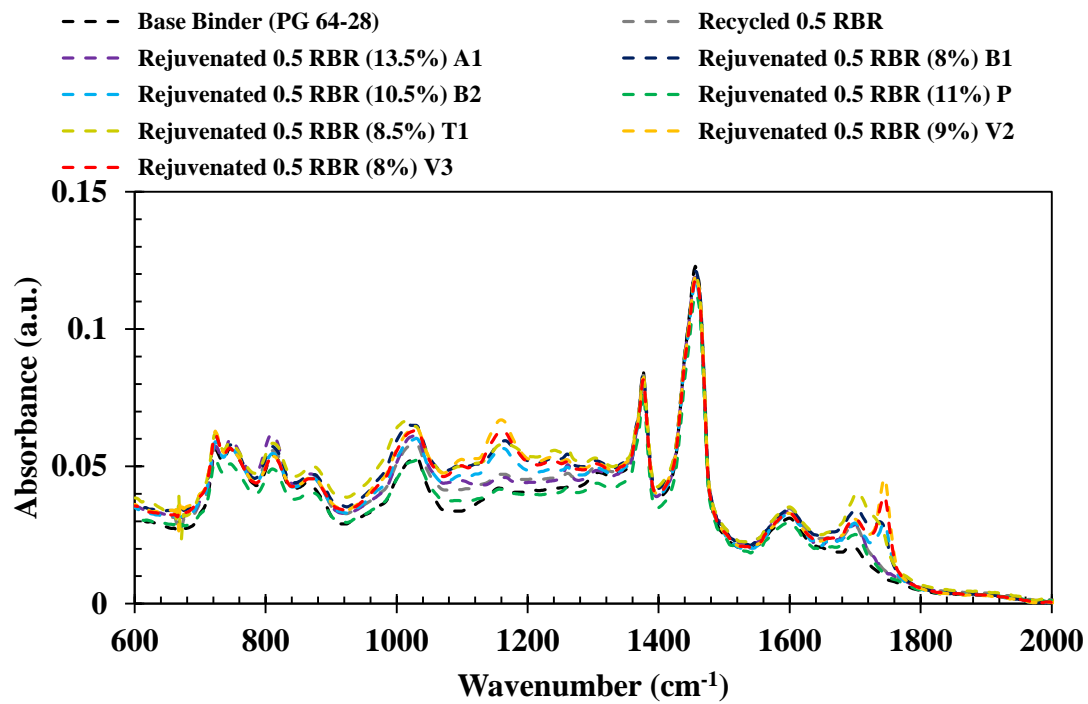
(b)
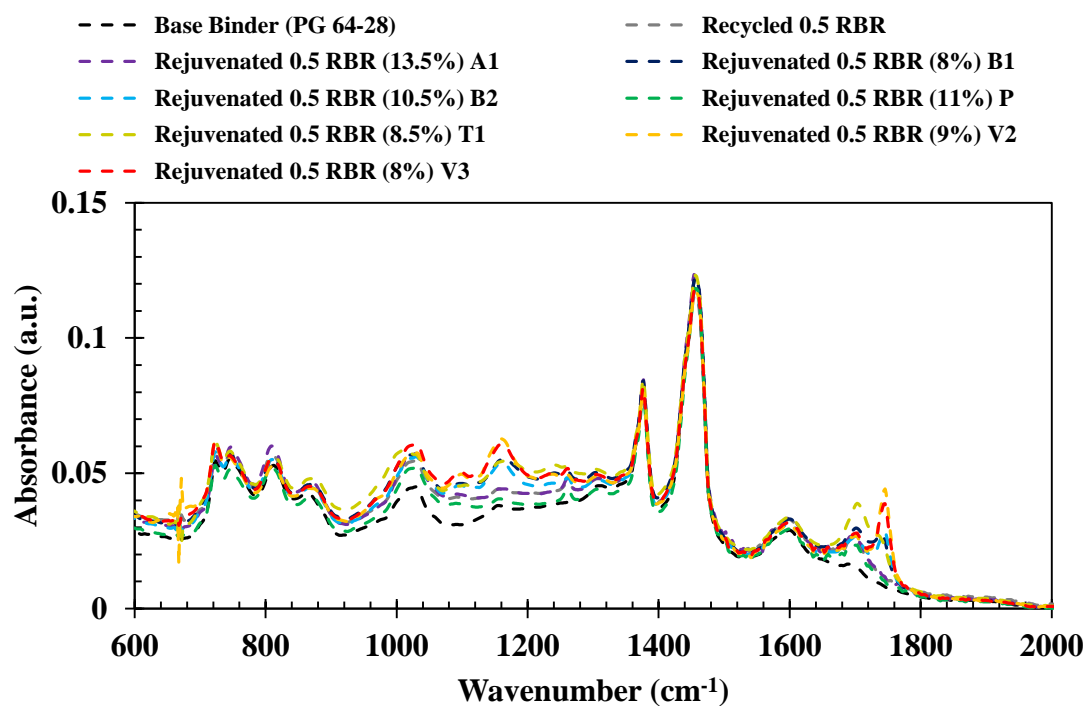
(c)

Figure 18 Continued

63

(d)

Figure 18 Continued

Table 4 CA and CAg Values for Different Binder Blends

Binder Blend	CA Value (a.u.)				CA Growth (a.u.)		
	OB	RTFO	PAV 20	PAV 40	RTFO	PAV 20	PAV40
Base Binder (PG 64-28)	0.171	0.197	0.409	0.640	0.026	0.238	0.470
Recycled 0.5 RBR	0.461	0.596	0.825	1.054	0.135	0.365	0.593
Rejuvenated 0.5 RBR (13.5%) A1	0.474	0.581	0.924	1.072	0.107	0.450	0.598
Rejuvenated 0.5 RBR (8%) B1	1.112	1.234	1.600	1.944	0.122	0.488	0.832
Rejuvenated 0.5 RBR (10.5%) B2	0.975	1.095	1.403	1.625	0.120	0.428	0.651
Rejuvenated 0.5 RBR (11%) P	0.417	0.546	0.837	0.964	0.129	0.420	0.547
Rejuvenated 0.5 RBR (8.5%) T1	1.442	1.465	1.842	2.051	0.023	0.400	0.609
Rejuvenated 0.5 RBR (9%) V2	1.348	1.473	1.769	2.082	0.125	0.421	0.734
Rejuvenated 0.5 RBR (8%) V3	1.254	1.347	1.733	1.957	0.093	0.479	0.703