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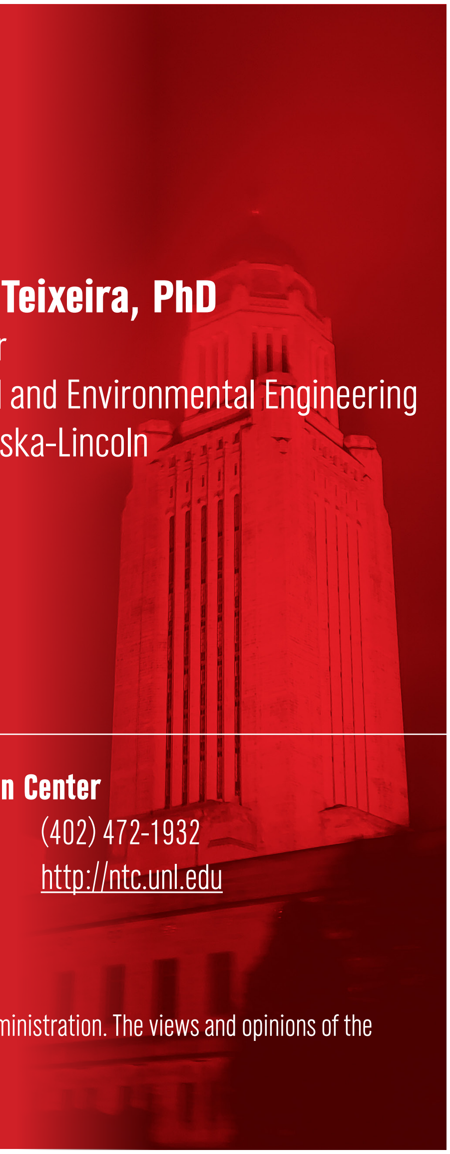
Effect of Antioxidant Additives and Recycling Agents on Performance of Asphalt Binders and Mixtures - Phase I



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16. Abstract

The use of reclaimed asphalt pavement (RAP) in asphalt mixtures has notably increased in recent times. Nevertheless, the inherent stiff and aged characteristics of RAP materials have consistently raised concerns regarding cracking performance. The use of recycling agents (RAs) has gained popularity in recent years since they can effectively modify the engineering properties of the aged asphalt binder. Besides that, the combination of RA with antioxidant (AO) additives has shown promise in enhancing the long-term performance of RAP mixtures. This research aims to investigate the effect of various RAs and one AO additive on performance of asphalt binders and high-RAP mixtures. Five RAs (paraffinic oil, naphthenic oil, aromatic extracts, triglycerides/fatty acids, and tall oils) and one AO (zinc diethyldithiocarbamate - ZnDEC) were selected. Initially, the effects of RA and AO were analyzed at the binder level considering chemical (SARA, FT-IR, CHNOS) and rheological as well as physical (DSR, BBR, and Wihelmy Plate) testing results. Secondly, following the findings at the binder level, two specific RAs (naphthenic oil and triglycerides/fatty acids) were chosen and utilized in combination with ZnDEC to modify the binder used in producing high-RAP mixtures. The studied mixtures were subjected to semi-circular bending test (SCB) and Hamburg wheel tracking test (HWTT) to evaluate cracking, rutting and moisture damage resistance of the mixtures, respectively. The chemical analysis of the RAs showed that those based on triglycerides/fatty acids and tall oils demonstrated pronounced peaks near the 1740 cm^{-1} region and a greater oxygen content relative to other RAs. As expected, the RAs had a softening effect on the binder blends. Additionally, ZnDEC helped retard the oxidation of the RA-modified binders, and its effectiveness depended on the RAs' susceptibility to aging. At the mixture level, the simultaneous use of RAs and ZnDEC in the high-RAP mixture improved cracking performance and reduced oxidative aging but might negatively affected rutting and moisture damage resistance.

17. Key Words
High-RAP Mixtures, Recycling Agent (RAs), Antioxidant (AO), Aging, Performance-based parameters.

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Chapter 1 Introduction

The use of recycled materials, such as reclaimed asphalt pavement (RAP), recycled asphalt shingle (RAS), glass, and ground tire rubber, in asphalt mixtures has the potential to offer a cost-effective and environmentally friendly solution for the asphalt paving industry. Several researchers have investigated the effects of recycled materials on the performance of asphalt mixtures [1-5]. Regarding the use of RAP in asphalt mixture, the increase in stiffness in RAP mixtures, attributed to the presence of aged asphalt binder in the RAP, leads to a higher cracking susceptibility [1-5]. Oppositely, RAP-mixtures often exhibit improved rutting resistance [4] [6].

Recycling agents (RAs) (i.e., rejuvenators or softening agents) are additives that can be introduced to the RAP-mixtures with the aim of providing a softening effect in the RAP materials and thereby enhancing the cracking resistance of these mixtures [2, 7-11]. The National Center for Asphalt Technology (NCAT) has categorized RAs into five main groups based on their origin and production process: 1) Paraffinic Oils, 2) Aromatic Extracts, 3) Naphthenic Oils, 4) Triglycerides and Fatty Acids, and 5) Tall Oils. Currently, there is general agreement that RAs can improve the cracking resistance and diminish the rutting resistance of the RAP blended mixtures [3]. However, there are some concerns about the effects of RAs on moisture susceptibility and long-term performance. For instance, Haghshenas et al. [12] evaluated the effect of two different RAs including one aromatic extract and one triglycerides and fatty acids combination on the performance of a control binder composed of a blend of 65% RAP extracted binder and 35% virgin binder. The authors reported the control binders modified with triglycerides and fatty acids were more prone to oxidative effects based on the chemical results from saturates-aromatics-resins-asphaltenes (SARA) tests, Fourier transform infrared (FT-IR) spectroscopy, and elemental (carbon, nitrogen, hydrogen, sulfur, and oxygen) analysis. Therefore, the authors raised a concern with respect to the long-term performance of those modified asphalt binders. They also reported the addition of tall oil into the high-RAP mixtures increased the moisture damage sensibility. Similar observations regarding the poor long-term performance of asphalt binders and mixtures modified by triglycerides-fatty acids combinations and tall oils were also reported by Bahia et al. [13], Mohammadafzali et al. [14], and Rathore et al. [12-14]. The effect of paraffinic oils on the performance of asphalt binders and mixtures was examined by Cooper et al. [15] and Zaumanis et al. [16]. The studies indicated that the paraffinic oils were unable to maintain long-term low-temperature fracture resistance [15] and improve the fatigue life of the asphalt mixtures [16]. Even though the modification of aged binders and mixtures using RAs is notably affected by the chemical compositions of these additives, further studies are required to provide a comprehensive understanding of their chemical properties and their impacts on the modification process of aged binders.

Apart from RAs, there are other types of additives that can be used to modify asphalt binders with the aim to retard aging and hardening by trapping or scavenging the free radicals responsible for oxidation, referred to as antioxidant (AO) or anti-aging additives [17]. Recently, researchers carried out several rheological and mechanical tests to investigate the effects of various AOs on the performance of asphalt binders and mixtures [18-22]. For example, Apeagyei et al. [22] studied the effect of an AO—produced by combining aldehyde, thioester, and a catalyst—on the performance of asphalt binder and mixture. The results showed that the AO increased the dynamic modulus and improved the rutting and low-temperature cracking resistance of the studied asphalt mixture under both short- and long-term aging conditions [22]. Haghshenas et al. [23] used zinc diethyldithiocarbamate (ZnDEC) as an AO additive and reported an enhancement in low- and mid-temperature cracking resistance of the studied asphalt binder, while no effect was observed in terms of rutting performance.

A survey of literature reveals there is no guideline for RAs and AO selection and laboratory protocol to examine their effectiveness on performance (especially long-term performance) of asphaltic materials. On the other hand, the possible incorporation of RAs and AO additives in asphalt binders and mixtures can provide huge economical, technical, and environmental benefits; however, the combination of these additives and their long-term effectiveness have not been investigated.

1.1 Research Objectives and Scope

The overarching goal of this research is to investigate the effects of various RAs and one AO additive on the performance of asphalt binders and mixtures. More specifically, the objectives of this study are to:

- Verify the main chemical characteristics of the studied RAs.
- Evaluate how RAs and AO affect the chemical and rheological properties of binders.
- Verify if there is a correlation between chemical characteristics of the additives and the rheological properties of the binders.
- Assess the effects of selected additives on cracking, rutting and moisture susceptibility of asphalt mixtures.

1.2 Organization of the Report

This report is organized into five chapters. The first chapter presents an introduction to the project, the research objectives, and outlining the report's structure. Chapter 2 provides a literature review on the use of RAP, RAs and AOs in asphalt binders and mixtures. In Chapter 3, the materials used in this study are described, along with the protocols for sample preparation and the experimental testing procedures. Chapter 4 presents the main test results on both binder and mixture levels and includes an in-depth discussion of these findings. Chapter 5 summarizes the major findings of the study and proposes recommendations for future research.

Chapter 2 Background

The pavement industry is a promising sector poised to contribute significantly to construction sustainability by integrating various waste materials, such as reclaimed asphalt pavement (RAP), into asphalt concrete and binder formulations. Among these, RAP can be considered one of the most frequently utilized materials for constructing pavements, sourced during the resurfacing, reconstruction, and rehabilitation of existing, unserved pavement structures [24]. With intensified ongoing research efforts, there has been a rapid increase in the use and percentage of RAP in asphalt mixture production [25]. The incorporation of RAP in mixtures can bring economical savings and environmental benefits due to the reduced need of virgin materials (aggregates and binder). These advantages make RAP one of the most recyclable materials. However, the high percentages of RAP in asphalt pavements can raise several concerns regarding performance.

The Federal Highway Administration (FHWA) classifies mixtures with over 25% RAP content as high-RAP mixtures [26]. The use of RAP beyond the FHWA limit has both positive and negative effects on pavement structures, as the literature indicates. Positive impacts are mostly reported as improvements in rutting resistance, while the negative effects are often related to premature cracking and failure of asphalt mixtures. In some transportation agencies, the use of high-RAP contents has been limited because of the concerns regarding the uncertainty in the quality of RAP materials, inappropriate mix design methods/procedures, and the unexpected negative performance of high-RAP mixtures [27-31].

Researchers have been investigating different strategies to enhance the performance of high-RAP asphalt mixtures [2, 3, 32]. In general, five different strategies have been developed to overcome the negative effects of the high-RAP mixtures and are presented below [32]:

- Imposing a cap on the maximum RAP content (usually less than 20%).
- Increasing design density (lowering design air voids) or reducing N_{design}.
- Incorporating soft virgin binder into the blend.
- Using RAs to alleviate the stiffness of the RAP binder.
- Employing Warm Mix Additives (WMA) to minimize aging effects and enhance workability.

Among these strategies, the use of RAs as additive in RAP-mixtures has gained attention since one of the major effects of RAs is the softening of highly stiff aged binders existing in RAP materials. However, there are some concerns regarding the long-term performance of RAP mixtures containing some RA additives. In this regard, it is critical to develop a solution that combines RA incorporation and still be able to retard the aging process of RA-modified RAP mixtures. Anti-aging additives, often known as AOs, are considered an important technology in managing the aging phenomenon in asphalt, warranting extensive research[33].

2.1 Use of RAs in RAP- Mixtures

As previously stated, the main function of recycling agents (RAs) in the RAP mixture is to soften the aged binder present in RAP. This results in a RAP mixture with cracking performance comparable to that of a non-RAP mixture at its initial stage (before aging). RAs function differently due to their chemical compositions, leading to variations in the behavior of asphalt binders and mixtures modified with different RAs. A common feature associated with most Ras is that they are composed of a high percentage of maltenes, which is defined as the sum of saturates, aromatics, and resins fractions [34]. In fact, an RA restores the aged binder’s asphaltene to maltene ratio, which is altered over the service life of the pavement due to aging [35]. Another important characteristic of RAs is their dispersibility and diffusivity into the surface of the RAP. These are critical parameters that govern mechanisms related to RAs efficiency, as described by Carpenter and Wolosick [36]. In sum, the mechanisms of RA dispersibility and diffusivity into RAP can be outlined as follows: first, when RA is added to RAP, a lower viscosity layer is formed around the aged asphalt binder; then the RA starts to penetrate the aged binder layer, initiating softening. As this process continues, the RA keeps penetrating the aged binder layer, resulting in the softening of the aged binder outer regions. This mechanism leads to a decrease in the viscosity of the inner layer and an increase in the viscosity of the outer layer. Equilibrium is eventually achieved after the RA fully peneterates the aged binder. Figure 2.1 shows how the diffusion mechanism of the RA occurs in an aged asphalt binder.

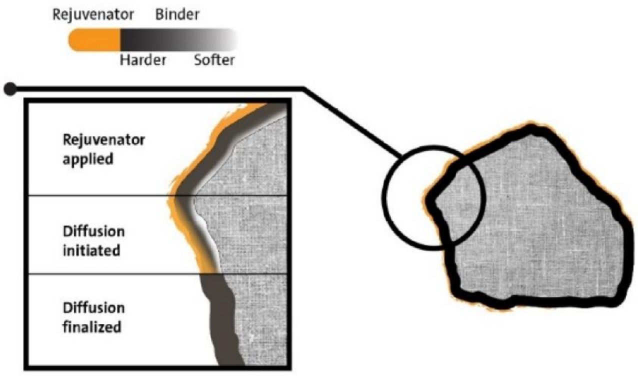


Figure 2.1 Diffusion process between RA or rejuvenator and aged binder [16, 37].

As mentioned in Chapter 1, different types of RAs are utilized in the pavement industries. In most cases, these additives are categorized based on their extraction sources. A classification system of paraffinic oils, aromatic extracts, naphthenic oils, triglycerides and fatty acids, and tall oils, has been established by NCAT [38]. The following section provides a brief discussion on the use of each RA type and their effects on the performance of asphalt binders and mixtures.

2.1.1 Paraffinic Oils

Paraffinic oil is a lubricating oil obtained through crude oil refineries, typically containing C_p (branched saturated chains like iso-octane) in concentrations greater than 50%. The most notable examples are re-refined engine oil bottoms (REOB) and waste engine oil (WEO). Researchers have been utilizing paraffinic oil to enhance the performance of asphalt binders and mixtures. For instance, Zauamanis et al. [16] utilized WEO as an RA and found an improvement in the low-temperature cracking resistance of the asphalt mixtures. However, the mixtures containing WEO showed the lowest fatigue life compared to those with other types of RAs. In another study, Guduru et al. [39] investigated the effects of WEOs in the performance of both binders and mixtures containing 60% RAP materials. The results showed that the addition of WEOs resulted in a decrease in fatigue cracking resistance of both asphalt binders and RAP mixtures compared to virgin ones. Zhang and Bahia [40] recently studied the effect of REOB on two high-RAP mixtures (with 30% and 50% RAP contents) and one combination of 30% RAP and 5% RAS. They reported the rutting and moisture susceptibility of all mixtures modified by REOB increased.

2.1.2 Aromatic Extracts

The aromatic extracts are composed of polar aromatic components and are readily available on the market. The C_a (benzene rings) in these RAs is typically greater than 35%. The application of aromatic extract as an RA for binder and mixtures has been reported in many studies. Zaumanis et al. [16] used aromatic extracts in their mixtures, which resulted in significant improvement in the low-temperature cracking resistance. Similarly, Kaseer et al. [8] and Haghshenas et al. [2] reported that the utilization of aromatic extracts in asphalt mixtures resulted in improved cracking resistance without significantly influencing the rutting performance. However, despite these benefits, the use of aromatic extracts is often discouraged due to their potential carcinogenic properties [16].

2.1.3 Naphthenic Oils

Naphthenic oils are specially designed for asphalt modification. They typically have C_n (saturated rings like cyclohexane) ranging from 30 to 40%. Several researchers have investigated the effects of naphthenic oils in asphalt binder and mixtures. For instance, Cooper et al. [41] evaluated the effect of naphthenic oils in the cracking, rutting, and moisture resistance of RAP mixtures. Their results showed a superior fracture resistance in mixtures modified by naphthenic oil in comparison with a control mixture (without RA); They also indicated that the incorporation of naphthenic oil reduced the RAP mixture rutting resistance significantly compared to the control mixture. Regarding the effect of the RA in the RAP mixture moisture resistance, the authors reported there was no significant difference among the studied mixtures. In another study conducted by Ali et al. [42], asphalt binders modified with naphthenic oil showed improved cracking resistance; however, they were less effective in altering the performance grade (PG) of the extracted binder from RAP materials.

2.1.4 Triglycerides and Fatty Acids

The fourth group of RAs is composed of vegetable-based oils with different chemical elements referred to as triglycerides and fatty acids. In many studies, this type of RA has been used to produce mixtures that exhibit better cracking resistance than those without RA [16, 43]; however, the long-term performance of the modified mixtures with triglyceride and fatty acids is a concern, as shown by Haghshenas et al. [44] [45], Bahia et al. [13], and Mohammadafzali et al. [14]. There is no consensus in the literature on the effects of triglyceride and fatty acids on moisture susceptibility of RAP mixtures. While Cooper et al. [41] showed that the use of triglyceride and fatty acids did not adversely affect moisture susceptibility of the mixtures, Haghshenas et al. [2] and Zhang et al. [40] reported that mixtures produced with this class of RAs were more susceptible to moisture.

2.1.5 Tall Oils

Tall oils are byproducts of the paper industry, and have often been associated with improved cracking resistance [39, 46]. Cooper et al. [47] showed that the addition of tall oil to the RAP mixture resulted in a poor rutting performance while there was no change in the low temperature cracking resistance and moisture susceptibility of asphalt mixtures. The early rutting failure associated with the use of tall oil is also reported by Mercado et al. [43]. Like triglycerides and fatty acids, the durability of modified binders and mixtures with tall oils can be of concern [12].

2.1.6 Summary

Table 2.1 summarizes the effect of each type of RA on stiffness, cracking, rutting, and moisture susceptibility in asphalt binders and mixtures. As shown in Table 2.1, RAs have a softening effect on asphalt binders and mixtures that can improve their cracking resistance. However, the long-term performance of these mixtures, modified by certain classes of RAs (e.g., triglycerides and fatty acids), might be a concern. Also, some of the RAs can decrease rutting resistance and increase moisture susceptibility of modified asphalt binders and mixtures, while others cannot. This suggests the modification of aged asphalt materials (binders and mixtures) using RAs is influenced by the type of additive. However, it should be noted that other factors such as RA dosage, RAP homogeneity, the distribution of RA and its diffusion into the RAP binder, and blending procedures (time, temperature, etc.) of all materials also affect the overall performance of asphalt materials containing RAP treated with RAs [48].

Table 2.1 Effect of RAs on performance of asphalt binders and mixtures.

Study	RAs	Significant Findings
		Stiffness
Asli, Ahmadinia [49]	Waste cooking oil	➢ The stiffness of aged asphalt binder was restored by the waste cooking oil.
Lee, Li [50]	Aromatic extract (maltene)	➢ The dynamic shear modulus decreased while phase angle values increased after addition of aromatic extracts.
Huang, Qin [51]	Emulsion, aromatic extract (maltene), and vegetable oil	➢ Recycling agents interacted with the asphalt binders differently. ➢ The vegetable oil and aromatic extracts provided similar improvement to flow properties of the highly aged binders. ➢ The vegetable oil improved thermal behavior the most compared to the other two rejuvenators.
Kaseer, Yin [52]	Tall oil and aromatic extract (maltene)	➢ The stiffness of asphalt mixtures blended with recycled materials decreased significantly by recycling agents. ➢ The recycled mixtures with an optimum dosage of recycling agents exhibited similar stiffness as that of the virgin mixture.
Oldham, Hung [53]	Bio-oil	➢ The test results indicated the addition of bio-oil decreased the stiffness of aged materials.
Abdelaziz, Epps Martin [54]	Vegetable oil	➢ The addition of the recycling agent reduced stiffness.
		Cracking Resistance
Tran, Taylor [55]	Naphthenic oil	➢ The cracking resistance of mixtures improved by introducing the recycling agent. ➢ Although the average number of cycles to failure for the RAP/RAS blended mixtures compared to virgin mixture increased, the differences in the number of cycles to failure were not statistically significant.
Mogawer, Booshehrian [55]	Bio-oil and naphthenic oil	➢ The addition of the recycling agents improved the cracking performance of all mixtures. ➢ The degree of improvement was dependent on the type of recycling agents.
Tran, Taylor [56]	Tall oil	➢ The recycling agent improved intermediate-temperature cracking resistance of asphalt mixtures, though not to the level of the virgin mixture by the average values. ➢ The low critical temperature of asphalt mixtures with recycling agent was similar to the virgin mixture.
Xinxin, Xuejuan [57]	Vegetable oil	➢ The fatigue life and low temperature cracking of restored asphalt binders was better than aged ones.
Abdelaziz, Epps Martin [54]	Vegetable oil	➢ The addition of the recycling agent improved the low-temperature properties of the binder blends.

Table 2.1 Effect of RAs on performance of asphalt binders and mixtures. (continued).

Study	RAs	Significant Findings
		Rutting Resistance
Zaumanis, Mallick [16]	Vegetable oil, aromatic extract, paraffinic oil, tall oil	➢ The recycling agents did not reduce the high-performance grade of asphalt binder to the level of virgin oil. This indicated that the recycling agents did not affect the rutting resistance of aged materials.
Jia, Huang [58]	Paraffinic oil	➢ The addition of recycling agent decreased the rutting resistance of mixtures containing recycled materials.
Im, Karki [28]	Tall oil and bio-oil	➢ The rut depth of all asphalt mixtures modified by recycling agents increased.
Arámbula-Mercado, Kaseer [43]	Tall oil	➢ The rutting of mixtures increased after addition of the recycling agent.
Kaseer, Arámbula-Mercado [8]	Tall oil aromatic extract, vegetable oil	➢ Laboratory test results demonstrated that adding the recycling agent did not affect the rutting resistance of mixtures after short-term aging if the dosage was selected based on the continuous high-temperature performance grade of the target binder.
		Moisture Susceptibility
Tran, Taylor [55]	Naphthenic oil	➢ The addition of recycling agent to the mixtures did not affect the moisture damage resistance of the mixtures.
Hajj, Souliman [59]	Tall oil	➢ The moisture damage resistance of the RAP mixtures modified by recycling agent improved after three freeze-thaw cycles.
Nazzal, Mogawer [60]	Organic oil and paraffinic oil	➢ Addition of recycling agents led to a decrease in moisture damage resistance of RAP mixtures.
Haghshenas, Nabizadeh [3]	Tall oil, aromatic extract (maltene), and vegetable oil	➢ Recycling agents compromised moisture damage resistance of the high RAP mixture. ➢ The tall oil recycling agent showed the highest detrimental effect out of the three recycling agents.
Tran, Taylor [56]	Tall oil	➢ The RAP blended mixture with recycling agent did not show signs of stripping in the Hamburg test.
Zhang and Bahia [61]	Paraffinic oil and bio-oil	➢ The addition of recycling agents may significantly increase moisture susceptibility potential and the relative effect was specific to the type and composition of the recycling agent.

2.2 Use of AOs

Aging, or oxidation, of asphalt binder is a chemical reaction that occurs when oxygen from the air interacts with the binder molecules over time. This reaction leads to changes in the chemical structure of the binder, causing it to harden and become more brittle. This mechanism is also referred to as age hardening. As asphalt binders are exposed to oxygen, UV radiation, and high temperatures, the oxidation process progresses, altering the binder's engineering properties (such as stiffness) and leading to aging. As a result of the aging stiffness, the cracking resistance of asphalt mixtures decreases, ultimately leading to failure of the flexible pavement surface layer.

Oxidation occurs during asphalt mixture production (short-term aging) and service life of pavements (long-term aging). To minimize the oxidation, researchers have examined when additives are incorporated into the binder by scavenging and trapping free radicals [23, 62, 63]. These additives, known as AO agents, are classified into four different groups, primary AOs, secondary AOs, metal chelators, and light stabilizers based on the mechanism of controlling oxidation [64].

The primary AOs are mainly composed of OH or NH groups that break the chain of oxidation reactions by accepting and donating electrons. The secondary AOs are composed of phosphorous and sulfur compounds, which can easily form peroxide and hydroperoxide for stabilizing oxidation reactions [21, 65]. Metal chelators trap metallic compounds, which are found in trace amounts in asphalt binders and can accelerate the formation of free radicals [66]. The light stabilizers can help asphalt binders to combat UV-induced aging and increase photostability [17].

Many studies have been performed to understand the effect of AOs in enhancing the performance of asphalt binders and mixtures. Table 2.2 summarizes significant findings in literature based on the use of different AOs in improving the performance of the asphalt binders and mixtures. As can be seen, most of the AOs improved the cracking resistance of asphalt binders and mixtures by slowing the aging process [33, 63].

Haghshenas et al. [23] and Reyes [19] reported that rutting resistance of asphalt binders was not significantly affected by AOs. The studies used with ZnDEC and Vitamin E, respectively. However, Dessouky and Diaz [18] found that another AO, a copolymer's solution ethylene-butylene/styrene (SEBS), improved rutting and moisture resistance while compromising fatigue performance. Overall, different AOs can have different effects on asphalt mixture performance. Most of the AOs, however, have demonstrated an increase in the aging resistance of asphalt binders and mixtures.

Table 2.2 Summary on the use of different AOs.

Study	AO	Significant Findings
Mohamed [67]	CRABit (CR30 and CR50)	➢ Enhanced resilient modulus, creep, indirect tensile, and fatigue resistances.
Apeagyei et al. [21]	Combination of Furfural and DLTDP; AOXADUR	➢ Increased fatigue resistance as well as better rut resistance with the combination of furfural and DLTDP. ➢ AOXADAUR increased dynamic modulus, improved rut resistance, and increased tensile strength at low temperatures.
Williams [68]	Agriculturally derived lignin-containing ethanol coproducts 3-12%	➢ Improved high-temperature properties of asphalt binder while worsening the low-temperature properties.
Apeagyei [20]	Combination of DLTDP and Furfural, Hydrated Lime, Vitamin E, Carbon Black, Irgafos, P-EPQ, and Irganox 1010	➢ All the tested AOs retarded the aging of the asphalt binder. Notably, the combination of furfural and DLTDP proved to be the most effective in reducing aging.
Reyes [19]	Vitamin E	➢ Decreased viscosity. ➢ Rutting resistance was dependent on dosages, but fatigue cracking resistance was enhanced.
Cong [69]	Zinc-dialkyl dithiophosphate and Carbon Black	➢ Minimal effect to prevent aging was observed with the use of these two particular AOs. ➢ Combination of AOs provided increased aging resistance.
Pan et al. [33]	Coniferyl-Alcohol lignin	➢ Slowed the rate of oxidation and hardening.
Dessouky and Diaz [18]	Copolymer's Solution Ethylene-Butylene/Styrene (SEBS)	➢ Improved rutting and moisture damage resistance. ➢ Decreased fatigue resistance.
Haghshenas et al. [23]	Zinc diethyldithiocarbamate (ZnDEC)	➢ Improved low- and mid-temperature cracking resistance of asphalt binders, with no changes in rutting resistance.
Cong et al. [62]	Tns-(2-4 di-tert-butyl)-phosphate	➢ Increased aging resistance based on ductility, softening point, and penetration tests. ➢ Decreased the formation of carbonyl and sulfoxide.
Kassem et al. [63]	Irganos, Calprene, Solprene, DLTDP, Redicote, Furfural, and Hydrated Lime	➢ All the tested AOs retarded the aging of the asphalt binder. ➢ Solprene, and Calprene maintained the stiffness at high and intermediate temperatures, while Irganox and DLTDP resulted in a soft binder.

Chapter 3 Materials and Laboratory Tests

This chapter presents the selected materials (i.e., RAs, AO, binders, and aggregates), the laboratory used to obtain the modified binders, laboratory-produced RAP materials, and the selected material combinations (modified binders and high-RAP mixtures) used in this study. Furthermore, it details the procedure for obtaining laboratory-compacted samples used in mixture-level performance tests, such as SCB and HWT tests, to evaluate cracking, rutting, and moisture damage resistance of the studied mixtures.

3.1 Selection of Materials

3.1.1 Recycling Agents (RAs) and AO

Five different RAs were selected from the five conventional categories of RAs and are described in Table 3.1. A generic descriptor is used for labeling each RA. It should be noted that the selected RAs are typical materials available in the market.

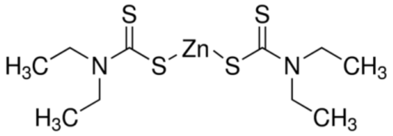
Table 3.1 RAs used in this study.

Category	ID	Physical state and colour	Description	Viscosity (60 °C, Pa.s)
Paraffinic Oil	P	liquid/colourless	refined used lubricating oils	0.019
Aromatic Extract	A	viscose/brown	refined crude oil products	0.120
Naphthenic Oil	N	viscose/yellow	engineered hydrocarbons	0.102
Triglycerides and Fatty Acids	TF	liquid/yellow	derived from vegetable oils	0.012
Tall Oil	T	liquid/reddish Brown	paper industry by-products	0.034

ZnDEC was used as the AO in this study. The AO dosage was selected as 4% by total weight of binder based on the previous study [23].

Table 3.2 summarizes the properties and description of ZnDEC utilized in this study.

Table 3.2 Properties of ZnDEC [23].

Property	**Description/Value**
Linear Formula	$[(C_2H_5)_2NCS_2]_2Zn$
Structure	
Appearance (color / form)	White to off-white / Crystal to powder
Assay (%)	99
Melting Point (°C)	178-181
Flash Point (°C)	204
Specific Gravity	1.48

3.1.2 Asphalt Binders

This study used an unmodified virgin binder with a continuous PG of 67.3-25.9. The virgin binder underwent short- and long-term laboratory aging conditions to simulate field aging, following the procedure suggested by Bowers, Huang [70], and used by other researchers [53, 70] to prepare field-aged binders in the laboratory (i.e., laboratory-produced RAP binder). The aging procedure was as follows: a sample of the virgin binder was conditioned through one standard Rolling Thin Film Oven (RTFO, ASTM-D2872 [71]). Then, the resulting material binder was subjected to two standard Pressure Aging Vessel (PAV, ASTM-D6521 [72]) cycles. The continuous grade of this laboratory-produced RAP binder was assessed, resulting in a determination of PG 89.8-14.4.

To mimic the same proportions of RAP and virgin materials used in a high-RAP mixture containing 65% of RAP, 65% of the laboratory-produced RAP binder was blended with 35% of the virgin PG 64-22 binder to produce the base binder (denoted by CR). This 65% laboratory-produced RAP binder proportion was chosen because the Nebraska Department of Transportation (NDOT) is exploring the use of high-RAP asphalt mixtures containing 50 to 65% RAP materials. The optimum dosage of each RA was selected based on a fixed target PG approach. This dosage was calculated to reduce the base binder (CR) to a target grade classified as PG 64-28, a grade commonly used in the central United States. 4%

of ZnDEC by total weight of binder was introduced to some RA modified binder to examine if ZnDEC can increase the efficacy of these blends. The binder, RAs, and ZnDEC were mixed using a high shear stirrer at 2000 rpm and a temperature of 178 °C. Table 3.3 presents the list of binders tested in this study to evaluate the effects of different types of RAs and ZnDEC AO on the properties and performance of binder.

Table 3.3 Asphalt binders examined in this study.

Binder ID	**Binder Description**
CR	35% PG 64-22+65% laboratory-produced RAP binder
CRZ	31% PG 64-22+65% laboratory-produced RAP binder+4% ZnDEC
CRP	23% PG 64-22+65% laboratory-produced RAP binder+12% P
CRPZ	19% PG 64-22+65% laboratory-produced RAP binder+12% P+4% ZnDEC
CRA	21% PG 64-22+65% laboratory-produced RAP binder+14% A
CRN	21% PG 64-22+65% laboratory-produced RAP binder+14% N
CRTF	29% PG 64-22+65% laboratory-produced RAP binder+6% TF
CRTFZ	25% PG 64-22+65% laboratory-produced RAP binder+6% TF+4% ZnDEC
CRT	27% PG 64-22+65% laboratory-produced RAP binder+8% T
CRTZ	23% PG 64-22+65% laboratory-produced RAP binder+8% T+4% ZnDEC

To examine the long-term performance of RAs with and without ZnDEC during the aging process, the modified binders were further subjected to one cycle of short-term aging (RTFO), and either one, two or five cycles of long-term aging (simulated by PAV) consisting of 20 hrs (1PAV), 40 hrs (2PAV), and 100 hrs (5PAV) of aging at 100ºC under an air pressure of 2.1 MPa. The RTFO+1PAV cycle, RTFO+2PAV cycles, and RTFO+5PAV cycles were referred to as “standard”, “extended”, and “severe” aging, respectively.

3.1.3 Aggregates

An NDOT SPR mixture with a nominal maximum aggregate size (NMAS) of 12.5 mm was designed with the incorporation of 65% RAP combined with 35% virgin aggregates. The blend of aggregates in the control mixture was composed of 14% limestone and 86% gravel aggregates. The laboratory-made RAP was produced using the same aggregate gradation. Figure 3.1 illustrates the gradation of the control blend including the minimum and maximum control points for an SPR mixture according to the NDOT guidelines [73].

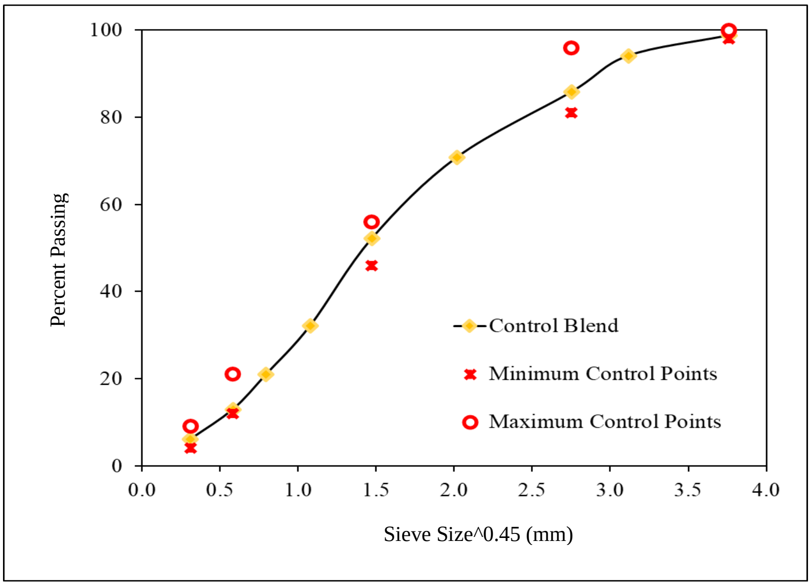


Figure 3.1 Aggregate gradation of asphalt mixtures in this study.

3.2 Asphalt Mixtures

To verify the effect of AO and RA on high-RAP mixtures, a control mixture and five SPR mixtures were produced maintaining the same aggregate gradation and binder content. The binder content for all studied mixtures was fixed at 5.2% to meet the NDOT requirements for SPR mixtures [73], which requires a binder content greater than 5%. For mixtures with AO and RA, the binder content refers to the percentage of virgin binder, RAP binder, and additives, following the same proportions presented in Table 3.3. The design-specific details for the studied mixture are presented in Table 3.4.

Table 3.4 Design details of the studied mixture.

Properties	**Amount**
Binder Content	5.20%
Dust/Binder Ratio	1.16%
Design Air Void	3.00±1.00%
No. of gyrations	65

To produce the laboratory-made RAP materials (R) for SPR mixtures, a blend of virgin aggregates (following the aggregate gradation presented in Figure 3.1) and 5.2% virgin binder (PG 64-22) was prepared. First, the resulting mixture was aged using the short-term aging (STA) conditioning procedure by placing the loose asphalt mixture in an oven at 135 °C for 4 h. After STA, the loose mixture was subjected to the procedure outlined in the National Cooperative Highway Research Program (NCHRP) project 09-54 [74] to simulate long-term aging (LTA), assuming that the resultant mixture is similar to field-aged pavements. According to the NCHRP 09-54 report, a three-day oven aging duration at 95 °C can simulate up to eight years of field aging in Lincoln, Nebraska at a depth of 20 mm below the surface.

Table 3.5 presents the six studied mixtures with corresponding mixture IDs adopted herein. The C and CR mixtures were considered control mixtures. Other mixtures were prepared to assess the effects of selected RAs, based on binder phase testing results, and the studied AO. Mixtures incorporating the two RA types (N and TF) and the AO additive ZnDEC were prepared. The studied mixtures were subjected to STA and LTA conditioning procedures to verify the efficacy of ZnDEC on the long-term performance of the RA-modified mixtures.

Table 3.5 Details of the AC mixtures.

Mixture ID	Mixture Description
C	100 % virgin aggregates and virgin binder
CR	35% virgin aggregates and virgin binder + 65% laboratory-made RAP
CRTF	CR modified by 6% triglycerides and fatty acids
CRTFZ	CR modified by 6% triglycerides and fatty acid and 4% ZnDEC
CRN	CR modified by 14% naphthenic oil
CRNZ	CR modified by 14% naphthenic oil and 4% ZnDEC

3.3 Specimen Fabrication

3.3.1 Semi-Circular Bending (SCB)

To prepare the SCB samples, specimens with a height of 170 mm and a diameter of 150 mm were prepared using the Superpave gyratory compactor, with a target air void of 7% ± 0.5. The necessary cuttings to produce SCB samples were in accordance with AASHTO T 393 [75]. For that, two 10-mm sections from both the top and bottom of each specimen were cut to eliminate the non-uniform air voids found in these areas. The resultant specimens were then sliced and halved, resulting in pieces with a thickness of 50 mm and a diameter of 150 mm. Fracture tests were performed on the specimens after making a notch of 15 mm depth and 2.5 mm width. Figure 3.2 shows the specimen production process and SCB test configuration.

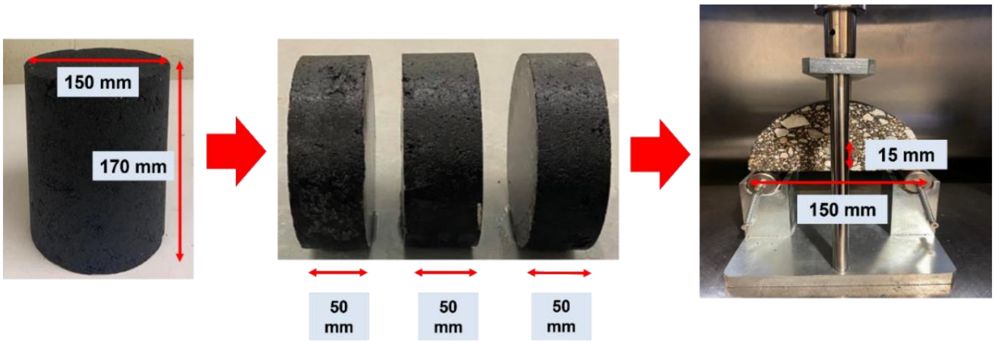
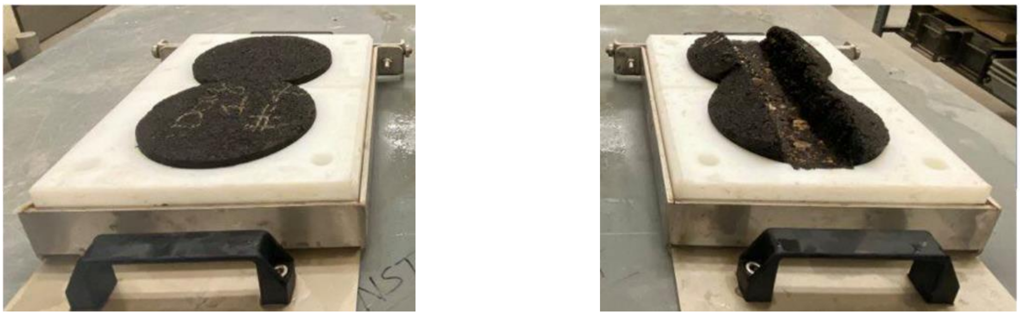


Figure 3.2 Specimen fabrication, slicing and the test setup.

3.3.2 Hamburg Wheel-Tracking (HWTT) Samples

The specimens were given a 62-mm height and a 150-mm diameter using the Superpave gyratory compactor, with a target air void of 7% ± 0.5. The necessary cuttings followed the AASHTO T 324 procedure [76]. Figure 3.3 shows samples positioned inside the testing tray before and after testing.



(a) (b)

Figure 3.3 HWTT test specimens, (a) before testing and (b) after testing.

Chapter 4 Laboratory Tests and Data Analysis

This chapter describes laboratory tests and their results conducted for this study. Various chemical laboratory tests, including Fourier Transform Infrared (FTIR) spectroscopy, Saturates-Aromatics-Resins-Asphaltenes (SARA) analysis, and elemental (carbon, hydrogen, nitrogen, oxygen, and sulfur) analyses are performed on RAs. The rheological of asphalt binders are characterized using Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR), and their chemical properties are characterized using FTIR, SARA, and elemental (oxygen) analysis. Then a linkage between the asphalt binders' rheological properties and their chemical characteristics is explored. In the case of asphalt mixtures, HWTT is carried out for rutting and moisture damage resistance characterization of asphalt mixtures and an SCB fracture test is performed to examine the cracking resistance of asphalt mixtures. Figure 4.1 shows the experimental plan used.

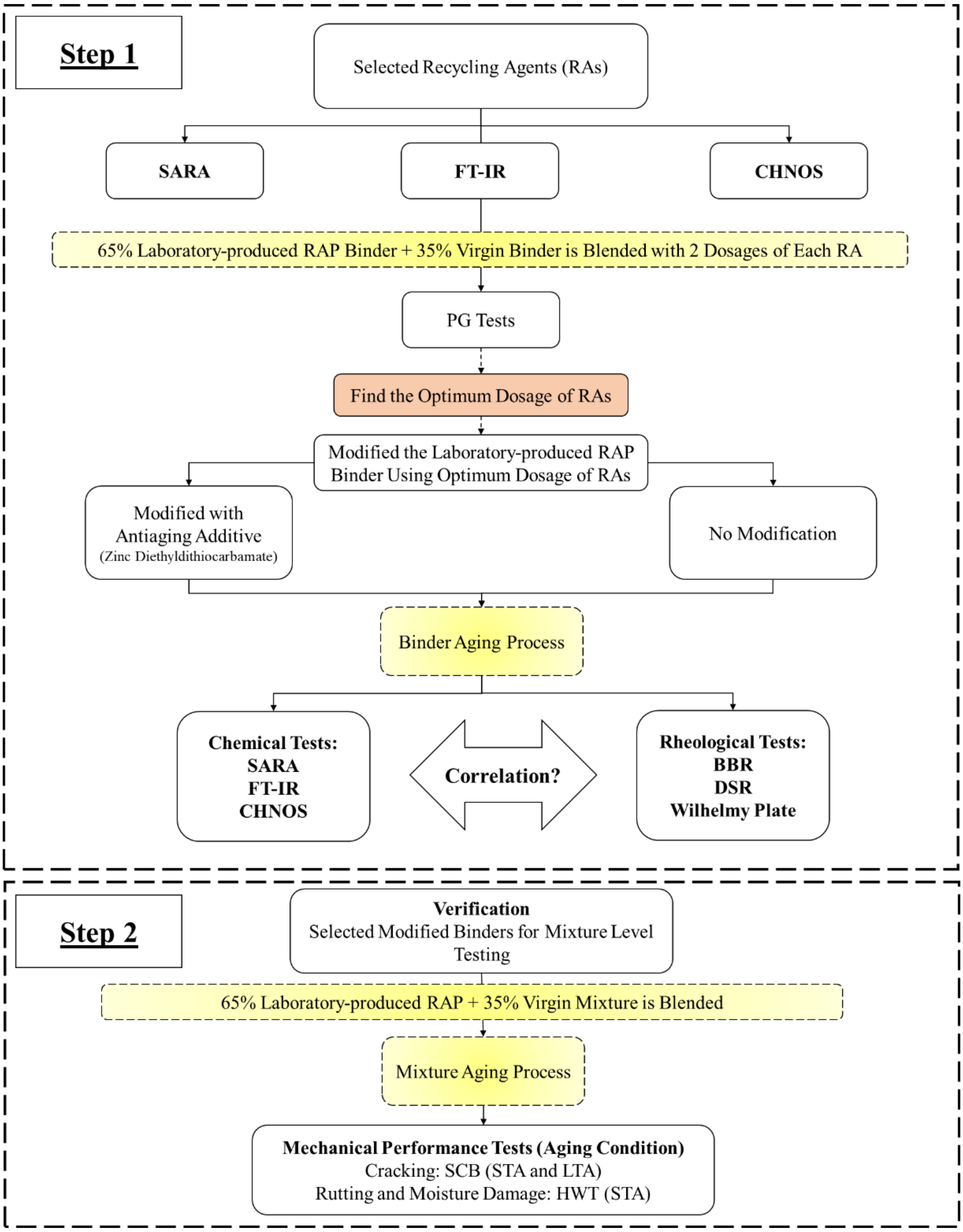


Figure 4.1 Experimental plan.

4.1 RAs Chemical Tests and Results

4.1.1 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectroscopy analysis of the RAs was performed using a Thermo Nicolet Avatar 380 FT-IR spectrometer. The FT-IR spectrum for each RA was captured using the attenuated total reflection (ATR) mode, for which a Smart Performer ATR accessory with a diamond crystal was used. Each spectrum for a given RA was obtained in the range of 500 to 4,000 cm^{-1} wavenumber at a resolution of 4 cm^{-1}. The background spectrum was subtracted from each sample spectrum. The diamond crystal was cleaned after each test.

In this study, RA FT-IR spectra were compared with that of the unmodified virgin binder (PG 64-22) as the reference spectrum, and any differences between spectra were determined. If an RA spectrum showed a peak that does not appear in spectrum of the unmodified virgin binder, the peak was defined as “Present”, while if a peak in the unmodified virgin binder spectrum did not appear in RAs, it was defined as “Absent”. The peaks appearing in both spectra were not reported.

According to the results presented in Table 4.1, all RAs, except for aromatic extracts, did not show a peak at 1602 cm^{-1}. The spectra of paraffinic oil (P), naphthenic oil (N), and aromatic extract (A) were similar to that of unmodified virgin binder, while triglycerides/fatty acids (TF) and tall oil (T) showed several new different peaks (either weak or strong).

The TF had strong peaks at 1162 and 1744 cm^{-1}, which are likely associated with dialkyl/aryl sulfones [77] and esters [78], respectively. These peaks generally increase the aging sensitivity of the binder treated by triglycerides/fatty acids, shown in research conducted by Haghshenas et al [44]. Although the peaks of primary and secondary alcohols are weak, these species, even at a low level, can effectively participate in hydrogen bonding that results in a moisture sensitivity increase. Even when oxidizing primary alcohols to aldehydes or carboxylic acids (depending on the reaction conditions), the moisture sensitivity problem exists regarding the reactivity of aldehydes and carboxylic acids with water [44].

The T showed a similar peaks to the triglycerides/fatty acids spectrum, such as primary or secondary alcohols and a peak around 1740 cm^{-1} assigned to esters. It is known some types of esters degrade in the air while aging. In addition, it is very likely that the existence of carboxylic acids and ketones in T affects the binder performance since they are known to affect aging in the binder system. The carbonyl group (C=O) formed during the binder oxidation process, which can be found in carboxylic acids, aldehydes, amides, anhydrides, esters, and ketones [79]. On the other hand, the tall oils may also participate in hydrogen bonding that results in a moisture sensitivity increase in the asphalt binders/mixtures. More detailed information on hydrogen bonding of the functional groups can be found in research by Haghshenas, Kim [80].

Table 4.1 Functional groups of RAs compared to the unmodified virgin binder.

Wavenumber (cm^{-1})	Assignment	Peaks
	Paraffinic Oil: P	
1602	Conjugated double bonds (C=C) stretching vibration in aromatics	Absent
	Aromatic Extract: A	
	No Peak Absent or Present	
	Naphthenic Oil: N	
1602	Conjugated double bonds (C=C) stretching vibration in aromatics	Absent
	Triglyceride/Fatty Acids: TF	
3008	C-H symmetric stretching vibration of the cis double bonds, = CH	Present
1744	Ester carbonyl (C=O) stretching vibration	Present
1602	Conjugated double bonds (C=C) stretching vibration in aromatics	Absent
1240, 1162 and 1097	C–O stretching vibration of the ester groups	Present
720	cis –CH=CH– bending out of plane	Present
	Tall Oil: T	
3008	C-H symmetric stretching vibration of the cis double bonds, = CH	Present
1737	Ester carbonyl (C=O) stretching vibration	Present
1702	Carboxylic acid or Ketone	Present
1602	Conjugated double bonds (C=C) stretching vibration in aromatics	Absent
1410	Phenol or tertiary alcohol, OH bend	Present
1266	Primary or secondary alcohol, OH in-plane bend	Present
942	Aromatic C-H in-plane bend	Present
720	cis –CH=CH– bending out of plane	Present

4.1.2 Elemental (carbon, hydrogen, nitrogen, oxygen, and sulfur) Analysis

The RA elemental compositions were determined using a Thermo Finnigan FlashEA™ Elemental Analyzer. An infrared absorption technique using SC-632 was used to determine the level of sulfur in the RAs after combustion. The carbon, hydrogen, and nitrogen content of the RAs were estimated using the PerkinElmer 2400 Series II CHNSO Analyzer. More details were described by Haghshenas [81].

Table 4.2 shows the percentage of Carbon (C), Hydrogen (H), Nitrogen (N), Oxygen (O), and Sulfur (S) in each RA. The chemical elements of the RAs were compared with that of the unmodified virgin binder (i.e., C which is PG 64-22). As observed, TF and T contained high percentages of oxygen, while other RAs showed oxygen contents similar to C. The research findings of Haghshenas and Kim [80] suggested that a high oxygen content can negatively affect the long-term performance of binders due to supplying the aging (oxidation) process with oxygen. It is worthy to note that although sulfone was present in TF and increased the level of the aging products before aging occurred, further investigation is required to determine the full impact this chemical has on binder performance.

Table 4.2 Elemental analysis of unmodified virgin binder and RAs.

Sample ID	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)	Sulfur (%)
C*	83.6	10.3	0.5	0.9	4.6
P	86.7	10.5	<0.5	0.5	0.1
A	87.6	10.3	<0.5	1.2	1.0
N	87.6	13.0	<0.5	0.5	0.1
TF	77.6	11.7	<0.5	11.5	0.2
T	77.6	11.7	<0.5	10.8	0.1

*C is a performance grade (PG) 64-22.

4.1.3 Saturate-Aromatic-Resin-Asphaltene (SARA) Analysis

To estimate the percentage of the RA SARA fractions, Iatroscan MK-6 was employed. The Iatroscan method is based on solubility and polarity. Firstly, the asphaltenes were separated from the bulk RA using normal heptane (n-heptane). N-heptane is a non-polar, linearly saturated alkane solvent and therefore the resin aromatic structures are insoluble. This was a separate test procedure and was not performed by the Iatroscan equipment. Once the n-heptane insoluble material was removed from the RA, the remaining material (generally referred to as maltenes) were further separated based on their relative solubility in different solvents. The detailed procedure on sample preparation and testing has been explained by Haghshenas [81].

The aim of RAs, which contain a high proportion of maltene phase (i.e., saturates, aromatics, and resins), is to restore the balance between maltenes and asphaltenes that is known to fluctuate during the aging process. Although rebalancing the asphaltene to maltene ratio can be achieved by adding only one fraction of maltene phase (e.g., saturate), it is hypothesized the ideal RA is one that can restore all three fractions (i.e., resins, aromatics, and saturates) and results in similar fractions as the maltene phase of the unaged binder. SARA fractions of RAs are shown in Table 4.3. Among all tested RAs, the aromatic extract (i.e., A) had a similar maltene composition to the binders. For instance, the TF contains only the resin fraction whereas T did not have a saturates fraction. The TF and T contain components with similar solubility parameters as aromatics and resins; however, they are chemically different. Paraffinic (P) and naphthenic (N) oils might have a compatibility concern, since they contained a high portion of saturates, which is considered to be the lowest portion of SARA fractions in a binder.

Table 4.3 SARA fractions and elemental analysis of unmodified virgin binder and RAs.

Sample ID	Asphaltenes (wt. %)	Resins (wt. %)	Aromatics (wt. %)	Saturates (wt. %)
C*	13.9	25.8	55.3	5.0
P	0.1	0.0	7.9	91.9
A	0.2	6.4	84.0	9.5
N	0.2	0.0	45.1	54.7
TF	0.3	99.7	0.0	0.0
T	0.6	27.7	71.7	0.0

*C is a performance grade (PG) 64-22.

4.2 Asphalt Binder Rheological Tests and Results

4.2.1 Mid-Temperature Cracking: Dynamic Shear Rheometer (DSR) and Glover-Rowe (G-R) Concept

To determine the performance of an asphalt binder at mid-range temperatures associated with cracking, the Glover-Rowe (G-R) concept was adopted. The G-R concept used 8-mm diameter plates with 2-mm testing gap. The test performed at 45 ˚C and 10 rad/s and records the complex modulus (G^*) and phase angle (δ), along with averages obtained using three replicates. The G-R parameter [82] was determined using the following equation:

$$G - R\ Parameter = G^* \times \frac{(\cos\delta)^2}{\sin\delta} \quad 4.1$$

In the Black Space diagram, if the asphalt binder G-R parameter is less than 180 kPa, the binder does not experience cracking, while an asphalt binder with a G-R parameter above 600 kPa experiences severe cracking. Any G-R parameters between 180 kPa and 600 kPa lines indicate the asphalt binder is in a zone of potential crack damage [82]. This test was conducted on the unaged, standard aged, extended aged, and severely aged asphalt binders.

The results of G-R analysis for binders aged up to RTFO+5PAV are shown in Figure 4.2. The binders were aged to RTFO+5PAV to determine the point at which severe cracking on the G-R diagram would occur. As shown in Figure 4.2, the addition of RAs to the CR binder increased the phase angle and decreased the stiffness, which indicated more fluid-like behaviour and better relaxation behaviour of the binder. Additionally, the results indicated the G-R parameter of the CRA, CRTF, and CRT binders performed satisfactorily up to 40 hrs aging (RTFO+2PAV), falling below the aging onset line after RTFO+2PAV, and an even longer aging time was needed for crack initiation in these binders.

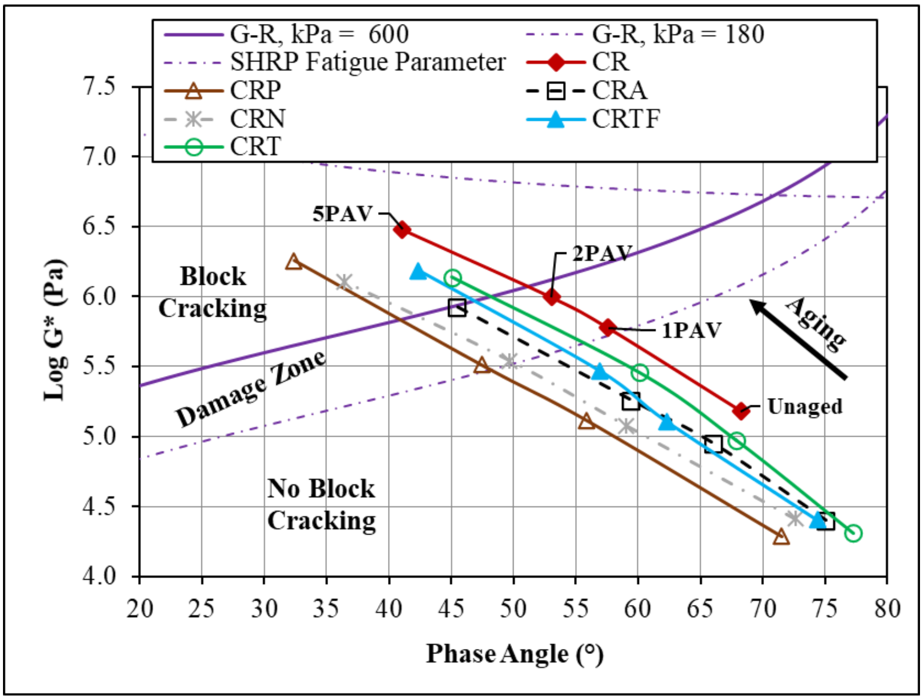
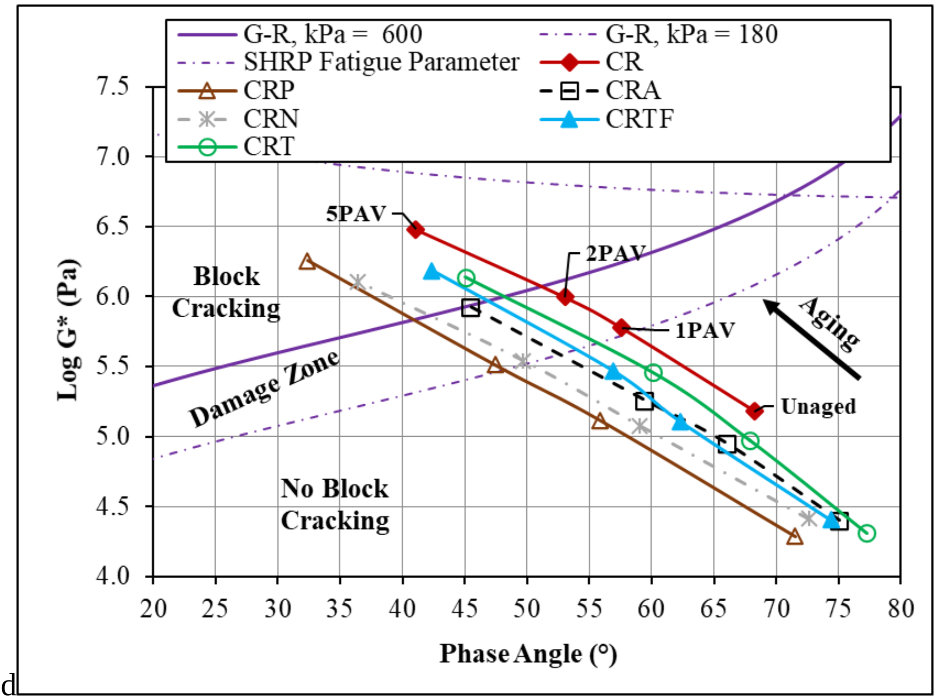


Figure 4.2 Mid-temperature cracking performance for different binder blends.

To measure aging time until onset (initial) and severe cracking, the phase angle of each binder at the intersection of its trend line with G-R lines (G-R = 180 and 600 kPa) was estimated. Also, the phase angles obtained from the G-R test for each binder in unaged, RTFO+1PAV,



RTFO+2PAV, and RTFO+5PAV were plotted versus the aging times (0, 20, 40, and 100 hrs) and the equation of a line of best fit through data points was found. Using phase angles at the intersections and the obtained equations, aging time to induce onset (initial) and severe cracking were determined and summarized in Figure 4.2. The results show that the CR, CRP, and CRN binders experienced onset cracking after 27, 38, and 39 hrs, respectively. These binders did not meet the passing criterion using extended aging (RTFO+2PAV) since the crack initiation in CR, CRP, and CRN occurred before 40 hrs. The binders CRA, CRTF, and CRT passed this RTFO+2PAV criterion and the CRA binder showed the best mid-temperature cracking resistance compared to other RAs.

Table 4.4 Estimated aging time (hr) to induce onset (initial) and severe cracking.

Binder ID	Onset Damage (hr)	Severe Damage (hr)
CR	27	52
CRP	38	70
CRA	55	94
CRN	39	78
CRTF	43	84
CRT	49	90

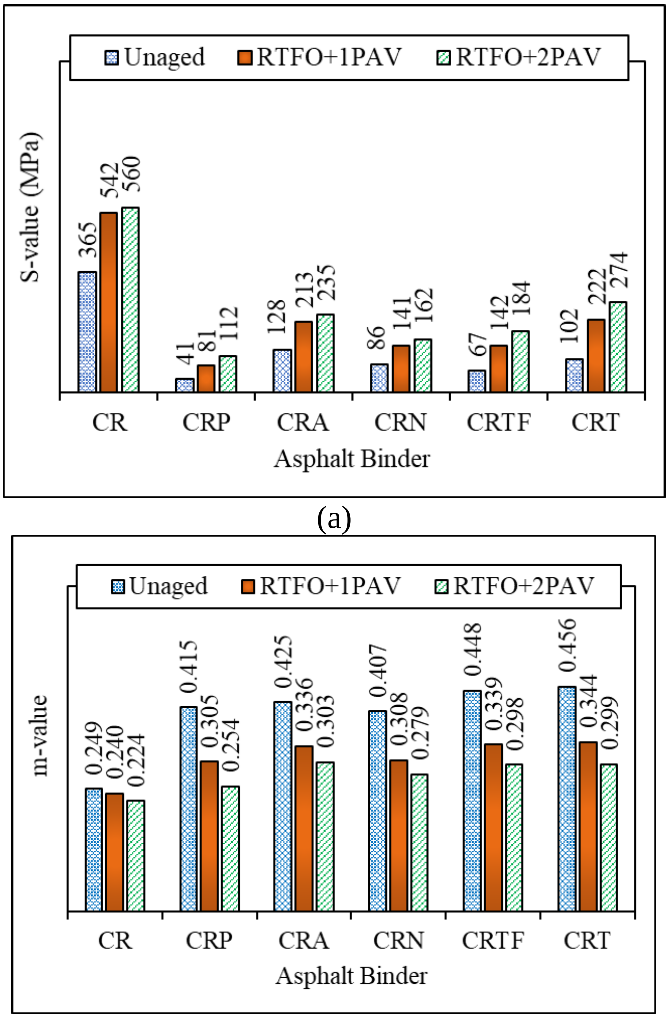
4.2.2 Low-Temperature Cracking: Bending Beam Rheometer (BBR) Analysis

The bending beam rheometer (BBR) was utilized to understand the low-temperature cracking resistance. Binder used for this process was aged with RTFO and PAV procedures. The low-temperature properties were measured at a sub-zero temperature of -18 ºC. Two different parameters were extensively utilized to evaluate the properties of the asphalt binders. The first and second parameters, referred to as relaxation constant (m) and flexural creep stiffness (S), were noted at 60 seconds of loading.

Figure 4.3a shows that all RAs softened the CR binder, and low-temperature performance of the binders modified with RAs was better than that of CR (35% virgin binder+65% aged binder). Moreover, all binders successfully passed the flexural creep stiffness criterion (S-value ≤ 300 MPa) beyond 40 hrs (extended aging: RTFO+2PAV), which is 20 hrs longer than the standard time (RTFO+1PAV) of long-term aging (Figure 4.3a). Although CRA is the only binder to pass the relaxation constant criterion (m-value ≥ 0.300) after extended aging (40 hrs), the m-values of CRTF and CRT of 0.298 and 0.299 would not be considered significantly different in satisfying the criterion (Figure 4.3b). It was reported that binders with a lower m-value at a given low temperature release thermal stress at a slower rate compared to binders with higher m-values at the same temperature, which can be detrimental for asphalt binder performance [83].

Examination of the data in Figure 4.3a shows that the change in S-value in samples containing the aromatic extract RA (A) was less than samples modified with other RAs. For example, the CRA binder experienced 67% and 84% increases in S-value after RTFO+1PAV and RTFO+2PAV, respectively, while CRTF experienced 112% and 175% increases in S-value at the same aging conditions. In addition, Figure 4.3a shows that CRTF and CRT lose the m-value at a faster rate when aging compared to CRA. Even though both CRTF and CRT had higher m-values than CRA after RTFO+1PAV, they both had lower m-values after RTFO+2PAV cycles. The stress relaxation constant of the CRTF binder decreased by 24% and 34% after RTFO+1PAV and RTFO+2PAV, respectively, while CRA showed only 21% and 29% decrease in this parameter in the same aging conditions. The CRT binder exhibited the same trend in the stress relaxation constant, which indicated the binder treated with tall oil loses the m-value faster than the CRA binder. This is not a desirable property in an RA expected to perform well over an extended period of time.

In summary, the rheological behaviours were consistent with the chemical characteristics of the RAs. The A, with SARA fractions and elemental composition similar to a virgin binder, exhibited the best performance even after extended aging (RTFO+2PAV). More importantly, the A did not contain aging functional groups (e.g., carbonyl). RAs like TF and T that had high oxygen content and aging functional groups were more susceptible to long-term aging effects [44, 84]. The P and N RAs were strongly affected by long-term aging and generally contained high amounts of saturates that caused compatibility issues with asphalt binders. The poor performance of paraffinic oils (P) has been reported in many studies [15, 16, 85, 86].



(a)

(b)

Figure 4.3 BBR Tests Results: (a) S-value and (b) m-value at -18 ºC.

4.2.3 Moisture Susceptibility: Wilhelmy Plate and Surface Free Energy (SFE)

To estimate the SFE components of asphalt binders, the contact angles of each binder with different solvents were measured by the Wilhelmy plate method on a Kruss Processor

Tensiometer K100 in triplicate. The method used water as a bi-polar solvent, glycerine as a polar solvent, and formamide as a mono-polar solvent. The SFE of each solvent used was also specified. Each binder used nine prepared slides for testing. Detailed information about the sample preparation and the test procedure can be found in Ghabchi, Singh [87]. All the samples were tested using three replicates, and the final results were reported as an average value. The total surface free energy (SFE) of a system was defined as the required work for the creation of a new unit area of the system [88]. Based on acid–base theory, it was calculated as:

$$\Gamma^{Total} = \Gamma^{LW} + 2 \times \sqrt{\Gamma^{+} \times \Gamma^{-}} \qquad 4.2$$

where Γ^{Total} is the total SFE of the system,

Γ^{LW} is the nonpolar component of SFE,

Γ^{+} is the polar acid component of SFE, and

Γ^{-} is the polar base component of SFE.

In the asphalt mixture system, the work of adhesion between the asphalt binder and the aggregate (W_{BA}), work of cohesion of asphalt binder (W_{BB}), and the required amount of work to detach the asphalt binder from the aggregate in the presence of water (W_{BAW}^{wet}) was obtained using a Wilhelmy plate and a universal sorption device according to the following equations:

$$W_{BA} = 2 \times \sqrt{\Gamma_B^{Lw} \times \Gamma_A^{LW}} + 2 \times \sqrt{\Gamma_B^{+} \times \Gamma_A^{-}} + 2 \times \sqrt{\Gamma_B^{-} \times \Gamma_A^{+}} \qquad 4.3$$

$$W_{BB} = 2 \times \Gamma_B^{Lw} + 4 \times \sqrt{\Gamma_B^{+} \times \Gamma_B^{-}} \qquad 4.4$$

$$W_{BAW}^{wet} = \Gamma_{BW} + \Gamma_{AW} - \Gamma_{BA} \qquad 4.5$$

In these equations, the subscripts ‘A’ and ‘B’ refer to the aggregate and asphalt binder, respectively. The abbreviations ‘BA’, ‘AW’, and ‘BW’ refer to the respective interfaces between asphalt binder and aggregate, aggregate and water, and asphalt binder and water, respectively. The interfacial energy (Γ_{ij}) between materials ‘i’ and ‘j’ were determined as follows:

$$\Gamma_{ij} = \Gamma_i + \Gamma_j - 2 \times \sqrt{\Gamma_i^{LW} \times \Gamma_j^{LW}} - 2 \times \sqrt{\Gamma_i^{+} \times \Gamma_j^{-}} - 2 \times \sqrt{\Gamma_i^{-} \times \Gamma_j^{+}} \qquad 4.6$$

Note that a higher work of adhesion between the asphalt binder and the aggregate (W_{BA}) meant greater resistance of the asphalt mixture to moisture damage, due to the higher energy required to separate asphalt binder from aggregates. Furthermore, a lower value of $|W_{BAW}^{wet}|$ was desirable since it indicated lower moisture sensitivity. Based on these explanations, W_{BA} and W_{BAW}^{wet} were considered in a single parameter that directly indicated the resistance of the asphalt mixture to moisture damage:

$$Energy\ Ratio\ 1\ (ER1) = \left| \frac{W_{BA}}{W_{BAW}^{wet}} \right| \qquad 4.7$$

Another important point regarding the resistance of asphalt mixtures to moisture damage was the wettability of the aggregate by asphalt binder. Thus, a modified version of Equation 4.7 was proposed as:

$$Energy\ Ratio\ 2\ (ER2) = \left|\frac{W_{BA} - W_{BB}}{W_{BAW}^{wet}}\right| \qquad 4.8$$

Higher values of W_{BB}, ER1, and ER2 are desirable and indicated better resistance of a mixture to moisture damage. The details about SFE and the relevant parameters can be found in Bhasin and Little [88]. The calculated surface free energy (SFE) components of the aggregates and asphalt binders are summarized in Table 4.5. Three parameters were used for further discussion: W_{BB}, ER1, and ER2.

Table 4.5 SFE components of aggregates and asphalt binders.

Material	SFE components (ergs/cm^2)			
Aggregate	$\mathbf{\Gamma_A^{LW}}$	$\mathbf{\Gamma_A^{+}}$	$\mathbf{\Gamma_A^{-}}$	$\mathbf{\Gamma_A^{Total}}$
Limestone[1]	51.80	1.80	430.60	107.90
Gravel[1]	54.80	1.30	187.10	86.40
Granite[2]	48.80	0.00	412.00	48.80
Quartzite[3]	60.81	8.86	545.04	200.13
Binder ID	$\mathbf{\Gamma_B^{LW}}$	$\mathbf{\Gamma_B^{+}}$	$\mathbf{\Gamma_B^{-}}$	$\mathbf{\Gamma_B^{Total}}$
CR	12.52	3.54	1.49	17.11
CRP	11.59	3.17	1.37	15.76
CRA	11.50	2.44	1.35	15.13
CRN	11.02	2.63	1.29	14.70
CRTF	9.47	1.97	1.05	12.35
CRT	10.31	2.13	1.17	13.47

Adopted from: [1]Kim and Lutif [89], [2]Bhasin and Little [90], [3]Lytton, Masad [91].

SFE components (Γ^{Total}, Γ^{LW}, Γ^{+}, and Γ^{-}) were used to calculate the cohesion work of the asphalt binder (W_{BB}) and the work required to detach asphalt binder from aggregate in the absence of water (W_{BA}) and in the presence of water (W_{BAW}^{wet}). ER1 and ER2 were determined using Equation 4.7 and Equation 4.8, respectively. W_{BB} provided information about cohesion failure (loss of cohesion within an asphalt binder); ER1 and ER2 quantified the moisture-damage resistance of the mixtures against adhesion failure (binder and aggregate debonding).

According to Table 4.6, the addition of RAs to CR binder resulted in a decrease in W_{BB} (absolute value of this parameter), indicating their negative effect on the cohesive strength of asphalt binder. Among the RAs used in this study, paraffinic oil showed the lowest negative impact on W_{BB} of CR binder (-8%), followed by aromatic extract (-12%), naphthenic oil (-14%), tall oil (-21%), and triglycerides/fatty acids (-28%). In other words, tall oil and triglyceride/fatty acid RAs may increase moisture sensitivity (decrease cohesive strength) of RAP-blended asphalt mixtures more than petroleum-based RAs (i.e., paraffinic oil, aromatic extract, and naphthenic oil).

Table 4.6 Comparison of ER1, ER2, and W_{BB} for asphalt binders.

Binder ID	Source of Aggregate								W_{BB} (*%)
	Limestone		Gravel		Granite		Quartzite		
	ER1 (*%)	ER2 (*%)	ER1 (*%)	ER2 (*%)	ER1 (*%)	ER2 (*%)	ER1 (*%)	ER2 (*%)	
CR	1.722	1.277	3.449	2.342	1.991	1.450	1.403	1.083	34.2
CRP	1.570 (-9)	1.177 (-8)	3.084 (-11)	2.129 (-9)	1.805 (-9)	1.331 (-8)	1.285 (-8)	1.002 (-8)	31.5 (-8)
CRN	1.383 (-20)	1.038 (-19)	2.675 (-22)	1.856 (-21)	1.575 (-21)	1.162 (-20)	1.141 (-19)	0.891 (-18)	29.4 (-14)
CRA	1.340 (-22)	0.993 (-22)	2.599 (-25)	1.776 (-24)	1.517 (-24)	1.103 (-24)	1.111 (-21)	0.858 (-21)	30.3 (-12)
CRT	1.210 (-30)	0.913 (-29)	2.312 (-33)	1.619 (-31)	1.367 (-31)	1.013 (-30)	1.005 (-28)	0.788 (-27)	26.9 (-21)
CRTF	1.136 (-34)	0.870 (-32)	2.149 (-38)	1.534 (-34)	1.283 (-36)	0.966 (-33)	0.944 (-33)	0.749 (-31)	24.7 (-28)

*The numbers in parenthesis indicate the percentage relative change of ER1 or ER2 or W_{BB} with respect to ER1 or ER2 or W_{BB} of CR, respectively.

In Table 4.6, the values of ER1 and ER2 are presented for the six binders used in this research mixed with the four sources of aggregate. Although ER1 was used for the evaluation of moisture sensitivity of the asphalt materials, Bhasin and Little [88] stated the wettability of aggregate by the asphalt binder, which plays an important role in moisture-damage resistance, can be taken into account using the ER2 parameter. The results show that the reduction in the ER1 and ER2 of CR was more pronounced when TF was introduced to the CR binder. CRP shows the best performance regardless of the type of aggregate. For example, when limestone was used as an aggregate in the asphalt mixture, the addition of paraffinic oil to CR binder (CRP) resulted in 9% and 8% decreases in ER1 and ER2, respectively, while ER1 and ER2 decreased 30% and 29% for CRT and 34% and 39% for CRTF, respectively. The same trend in ER1 and ER2 was observed for all asphalt binders modified by RAs, regardless of the type of aggregate: CRP had the highest adhesive strength (lowest sensitivity to moisture) followed by CRN, CRA, CRT, and CRTF.

To sum up, the SFE parameters of RA-modified binders were consistent with the chemical characteristics of the RA modifier. The SFE data showed that triglycerides/fatty acids (TF) and tall oil (T), with several hydroxyl and carbonyl functional groups, resulted in an increase in the moisture sensitivity of the asphalt binders and mixtures compared to other RAs tested in this study.

4.2.4 Relationship of the Colloidal Index with Rheological Parameters

The colloidal index (CI) was used to explain the extent the asphaltene particles were stable within the asphalt binder examined in this study. The CI can be calculated based on SARA analysis explained in section 4.1.3 and is defined as follows [92]:

$$Colloidal\ Index\ (CI) = \frac{Resins\ + Aromatics}{Asphaltenes\ + Saturates} \tag{4.9}$$

In Equation 4.9, a higher CI value was desirable as it indicated the potentially higher stability of the asphaltenes in the binder system [44].

Table 4.7 summarizes the SARA fractions and CI values of all the binder blends. The reported values are presented at various conditioning levels: before aging (original), standard aging (RTFO+1PAV), and extended aging (RTFO+2PAV). It was observed the addition of P and N RAs to CR binder reduced the CI, which may have negatively affected the long-term performance of the binder. Different studies also reported poor long-term performance of paraffinic oils [15, 16, 86]. On the other hand, the CI of CRA, CRTF, and CRT was higher than the CR before and after standard aging (RTFO+1PAV). In addition, the CI of CRA was higher than other binders after extended aging. The SARA and CI results of RA-modified binders are consistent with the rheological properties, the CRA which had the lowest rate of loss of m- and S- value, after RTFO + 2PAV cycles, showed higher a CI value.

Table 4.7 SARA fractions and CI of asphalt binders.

Binder ID	**SARA**				**CI**
	Asphaltenes (wt. %)	**Resins (wt. %)**	**Aromatics (wt. %)**	**Saturates (wt. %)**	
Original					
CR	21.5	27	46.8	4.7	2.817
CRP	19.2	27.5	41.1	12.2	2.185
CRA	18.9	27.9	47.5	5.7	3.065
CRN	18.4	27.5	44.0	10.1	2.509
CRTF	20.5	31.6	43.1	4.8	2.953
CRT	19.0	34.3	41.8	4.8	3.197
RTFO + 1 PAV					
CR	26.3	31.7	37.5	4.4	2.254
CRP	24.6	30.7	33.4	11.4	1.781
CRA	25.1	30.8	39.1	5.0	2.322
CRN	23.9	30.1	36.1	9.8	1.964
CRTF	25.6	35.8	34.2	4.4	2.333
CRT	25.3	39.0	31.4	4.4	2.370
RTFO + 2 PAV					
CR	28.3	31.5	35.1	5.1	1.994
CRP	27.3	28.7	31.6	12.4	1.519
CRA	27.8	29.1	39.1	4.0	2.145
CRN	25.2	29.8	34.3	10.7	1.786
CRTF	29.8	36.4	29.1	4.7	1.899
CRT	29.8	38.3	27.2	4.6	1.904

To obtain relationships between chemical and rheological properties and CI of binders, linear empirical correlations between experimental data were derived (Figure 4.4), chosen for its simplicity and straightforwardness. Another advantage of linear correlation was the explicitness, i.e., proportionality between parameters and measurements was clearly defined. According to the results presented in Figure 4.4, there was a strong correlation between the chemical and rheological properties and the CI of all binders. Flexural creep stiffness (S-value), high PG temperature, Log complex modulus (Log (G*)), and Log G-R parameter with CI were inversely proportional while phase angle and the relaxation constant (m-value) were directly proportional. This meant a decrease in the CI of unmodified binder (CR) and modified binders by RAs due to aging led to an increase in high PG temperature, Log (G*), S-value, and G-R parameters and indicated the binder obtained a more solid-like behavior (became more brittle). This decreasing trend in CI consequently decreased both the phase angle and m-value.

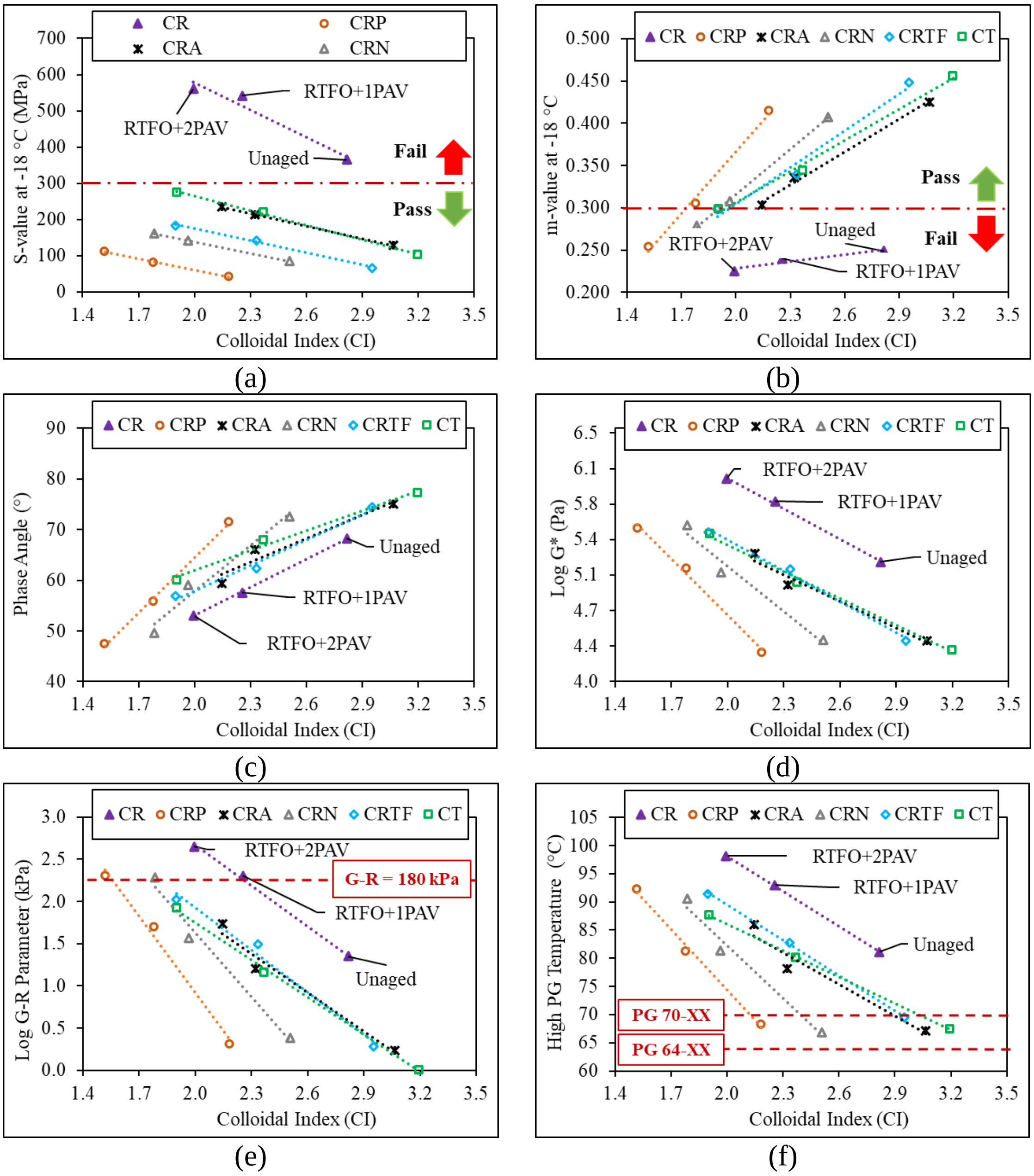


Figure 4.4 Linear correlation between rheological properties and colloidal index (CI) at the unaged, standard, and extended aging conditions.

4.3 Effect of AO on Performance of Asphalt Binders

The results presented in the previous sections showed that some RAs were prone to oxidation, and oxidation rendered them ineffective. Therefore, there was a need to protect RA-modified binders against aging to maintain their effectiveness. The following sections evaluate the effect on asphalt binder performance when using Zinc Diethyldithiocarbamate (ZnDEC) and RAs simultaneously.

4.3.1 High-Temperature Rutting: Dynamic Shear Rheometer (DSR)

A DSR was used to evaluate the rutting resistance of the binders. The complex shear modulus (G*) and phase angle (δ) of binders were recorded at temperatures ranging from 58 to 94 ºC using a 25-mm parallel-plate setup with a 1-mm gap. The G*/sinδ was measured and the temperature at which the value of G*/sinδ was 1.0 kPa was considered as the high-temperature PG.

According to the results presented in Figure 4.5, the addition of RAs softened the CR binder and led to a reduction of high-temperature grade from 81.5 ºC in C binder to 64 ºC-70 ºC in modified asphalt binder. Introducing ZnDEC to the blends slightly decreased high-temperature PG. Although the blends satisfied the requirements for the high-temperature PG grade at 64 ºC, the high-temperature PG of CRPZ and CRTZ implied that a dosage of AO higher than what was required should be avoided to prevent excessive permanent deformation or rutting in pavement.

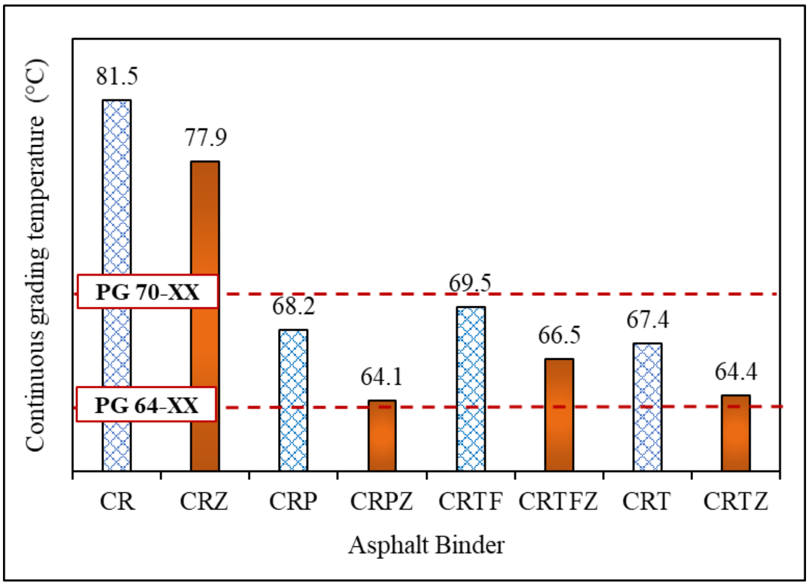


Figure 4.5 High-temperature performance grade of asphalt binders.

4.3.2 Mid-Temperature Cracking: Dynamic Shear Rheometer (DSR) and Glover-Rowe (G-R) Concept

The cracking resistance of binder at mid-temperature is evaluated in Figure 4.6. A comparison between CR and CRZ data shows the rate of change in G* and phase angle, as aging progress, were continuously lower than samples not having ZnDEC. The fact that CR and CRZ lie on the same Log G* as a function of phase angle revealed the impact of aging had not degraded the CRZ binder as much as it degraded the CR binder. In other words, the CRZ binder has been aged at a lower rate compared to CR. In addition, the results presented in Figure 4.6 show that the performance of CRP binder associated with aging was not satisfactory, since the G-R parameter of this binder fell into the damage zone area even before RTFO+2PAVs. However, introducing ZnDEC shifted the crack initiation to well after 40 hrs (2PAV). Although the efficacy of the AO highly depended on the recycling agent, the study results show that the addition of the AO delayed the crack initiation to a longer aging time for all binders.

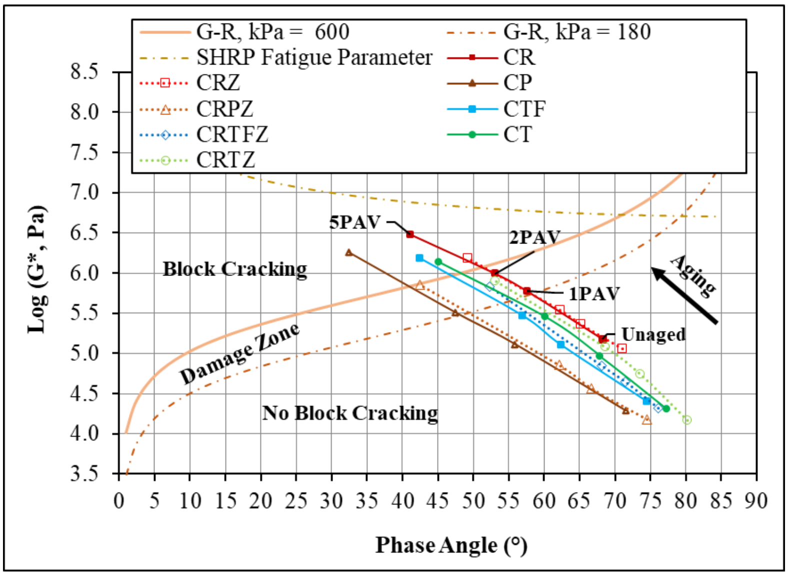
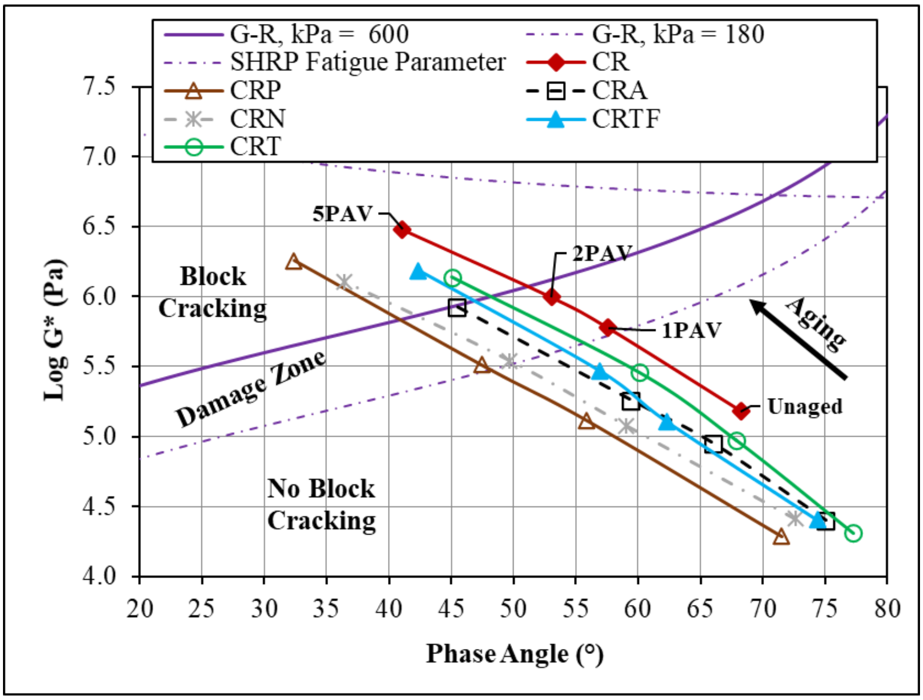


Figure 4.6 Mid-temperature cracking performances of asphalt binder.

The aging time to induce onset (initial) and severe cracking were determined using Figure 4.6 and the method explained in section 4.2.1



and summarized in Table 4.8. The results revealed that the ZnDEC can significantly improve the aging related performance of the binders in mid-temperature. For instance, in CRP binder, the crack was initiated after 38 hrs and this binder experienced severe cracking conditions after 70 hrs.

However, addition of ZnDEC to the CRP binder (CRPZ) increased the crack initiation and severe cracking time to 78 and 100 hrs, respectively. The same trend can be observed for other asphalt binders.

Table 4.8 Measured aging time (hr) to induce onset (initial) and severe cracking.

Binder ID	Onset Damage (hr), G-R=180 kPa	Severe Damage (hr), G-R=600 kPa
CR	27	52
CRZ	61	91
CRP	38	70
CRPZ	78	100
CRTF	43	84
CRTFZ	91	116
CRT	49	90
CRTZ	83	103

4.3.3 Low-Temperature Cracking: Bending Beam Rheometer (BBR) Analysis

The properties of each binder at low temperatures were characterized using the BBR test at -18 ºC. The data exhibits change in binder S-values containing ZnDEC was less than those without it. For example, the CRP binder experienced a 98% and 173% increase in the S-value from the original condition after RTFO+1PAV and RTFO+2PAV, respectively. While CRPZ (CP containing ZnDEC) showed only a 24% and 35% increase in the S-value in the same aging conditions. This in turn indicated that ZnDEC retarded the aging process.

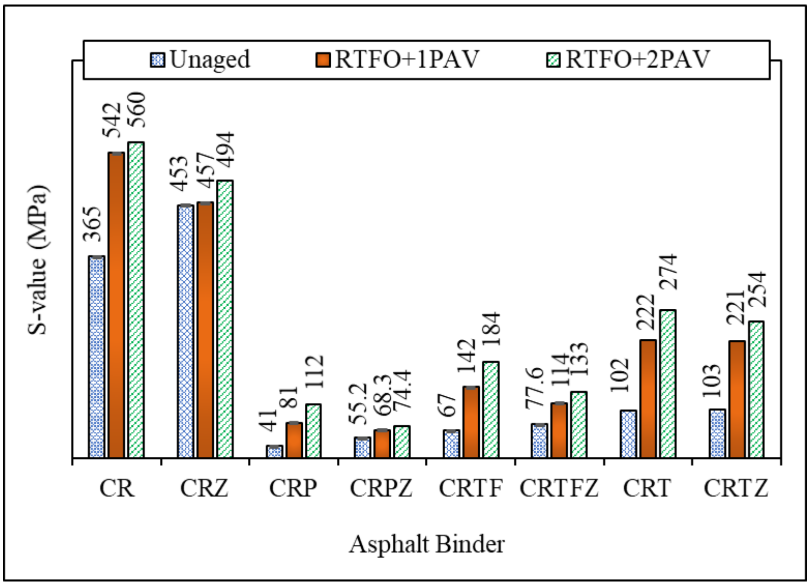


Figure 4.7 S-value of asphalt binders -18 ºC.

Moreover, the results obtained as m-values presented in Figure 4.8 also supported that the use of ZnDEC resulted in passing the criterion of the m-value being greater than 0.300. However, it is to be noted that the binders without ZnDEC could not pass the given criterion. The reasons might be attributed to physical hardening due to the stacking of wax-like molecules [93] and inadequate dispersion of wax [94] after utilizing RAs.

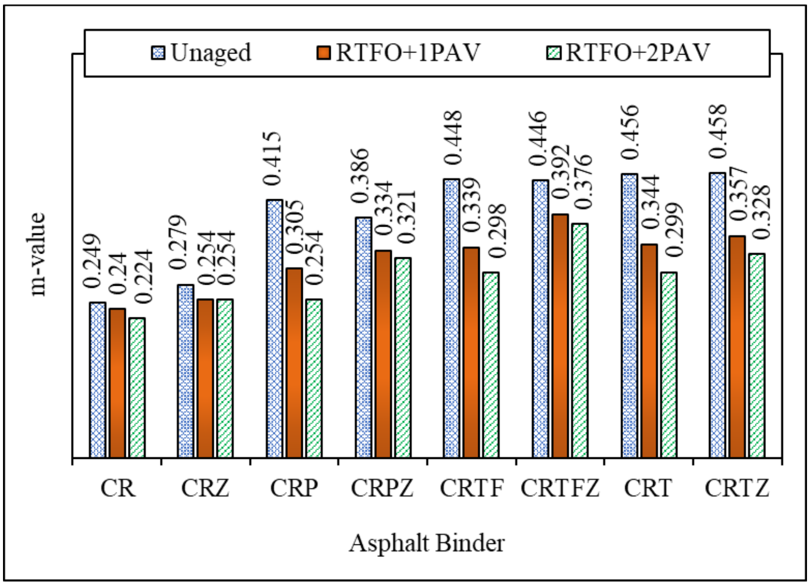


Figure 4.8 m-value of asphalt binders -18 ºC.

4.4 Asphalt Mixture Tests and Results

4.4.1 Mid-Temperature Cracking: Semi-Circular Bending (SCB)

This study followed the AASHTO T 393 [75] testing protocol for SCB. Before testing, specimens were placed inside an environmental chamber of a universal testing machine (UTM) to achieve an equilibrium temperature of 25°C. Subsequently, each specimen was positioned in the loading frame in a three-point bending configuration. A monotonic loading rate of 50 mm/min was applied to the top of the specimen. The load and displacement relationship was recorded and used to measure the cracking performance of the specimens using the Flexibility Index (FI) as shown in Equation 4.10.

$$FI = A\,\frac{G_f}{|m|} \tag{4.10}$$

where G_f, $|m|$, and A are the fracture energy (J/m^2), the absolute value of the post-peak slope, and the unit conversion factor, respectively.

The FI results of mixtures before and after the laboratory long-term aging process are depicted in Figure 4.9.

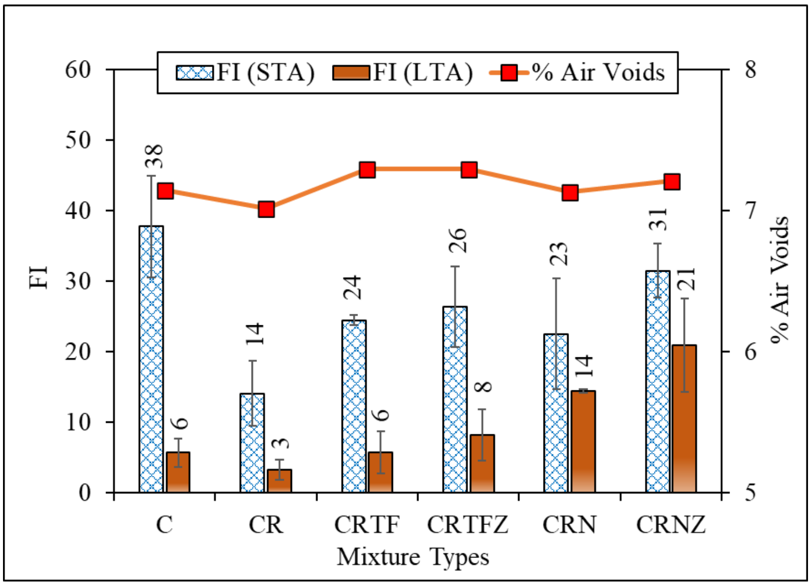


Figure 4.9 FI of specimens.

The FI of the C (i.e., the specimen without 65% laboratory-made RAP) was 38; however, incorporating 65% laboratory-made RAP to the C specimen resulted in an FI decrease to 14. The addition of TF and N to CR increased the FI, indicating the use of RAs improved the cracking resistance of RAP-blended asphalt mixtures. An increase of 42% and 46% was observed, respectively, with the use of TF and N as the RAs in the CR mixture. However, The optimum dosage of each RA was determined at the binder level and then introduced to the CR mixture; these dosages might not be sufficient to enhance the FI of the CR mixture to the level of the C mixture. Furthermore, other factors such as variability in the blending of RAP, RAs, virgin binders, and aggregates might contribute to these differences [16].

On the other hand, after aging, the FI of all specimens decreased. Comparing the FI of CRTF and CRN before and after aging showed a 76% and 35% drop in FI, respectively. The higher aging susceptibility of CRTF than CRN might be related to the chemical characteristics of TF used in this study, which contained aging functional groups and high oxygen content. However, no such functional groups existed for N, and its performance is comparatively higher than that of CRTF after long-term aging.

This study also assessed the cracking performance of asphalt mixtures when simultaneously using ZnDEC and RAs to determine if this approach addressed concerns regarding the aging susceptibility of the RAs, both TF and N, at the binder level. The FI presented in Figure 4.9 shows that using the ZnDEC on asphalt mixtures increased their FI. The addition of ZnDEC to CRTF resulted in an FI increase from 24 to 26. A similar case was observed for the CRN mixture, raising the FI from 23 to 31. The increasing FI value revealed that zinc might have a softening effect on the mixtures. While this effect was not desirable for an AO [95], the high-end PG binder level results indicated that this softening effect was minimal and did not lead to a change in binder grade (see Figure 4.5).

The statistical analysis can offer deeper insights into the differences among each specimen under various aging conditions, such as STA and LTA. To accomplish this, an Analysis of Variance (ANOVA) test was conducted for all the mixtures in each aging condition at a 95% confidence level, and the p-values were assessed and results are presented in Table 4.9 and Table 4.10.

Table 4.9 ANOVA analysis: single factor for the FI values at STA Condition.

Source of Variation	Sums of Squares (SS)	Degree of Freedom (df)	Mean Squares (MS)	F	P-value	F crit
Between Groups	974.52	5	194.90	26.33	4.45E-06	3.10
Within Groups	88.81	12	7.40			
Total	1063.34	17				

Table 4.10 ANOVA analysis: single factor for the FI values at LTA Condition.

Source of Variation	Sums of Squares (SS)	Degree of Freedom (df)	Mean Squares (MS)	F	P-value	F crit
Between Groups	676.40	5	135.28	46.13	2.00E-07	3.10
Within Groups	35.18	12	2.93			
Total	711.58	17				

As shown in Table 4.9 and Table 4.10, the p-values were less than the α-level (i.e., 0.05), indicating that at least one mean was significantly different from the others in each aging condition. Therefore, Tukey's Honestly Significant Difference (HSD) test was utilized for pairwise comparisons among all group means to identify specific groups that exhibited significant differences from each other, and the findings are presented in Table 4.11**Error! Reference source not found.**.

Table 4.11 Summary of Tukey's HSD test results (α=0.05) for FI values.

Mixture ID	Mean FI Value	Tukey's HSD Grouping			
	STA Condition				
C	37.8	A			
CR	14.1				D
CRTF	24.5		B	C	
CRTFZ	26.4		B	C	
CRN	22.5			C	
CRNZ	31.5	A	B		
	LTA Condition				
C	5.7			C	D
CR	3.3				D
CRTF	5.8			C	D
CRTFZ	8.2			C	
CRN	14.4		B		
CRNZ	21	A			

According to Tukey's HSD results in the STA condition, the CR mixture differed from the other mixtures, indicating statistically different results, confirming its worst cracking performance considering the FI parameter. On the other hand, C and CRNZ shared a similar group, suggesting that the FI of CRNZ was statistically similar to the C mixture. Additionally, CRNZ differed from the CRN mixture, confirming that ZnDEC effectively acted as an antioxidant when reducing mixture aging in comparison with CRN in the mixture level, demonstrating that the simultaneous use of N and ZnDEC was positive to enhance STA cracking resistance of high-RAP mixtures. CRTFZ also performed similarly to CRNZ and different from CR, being in the same group B. This indicates a softening effect of the AOs (TF and N) alone. However, CRTFZ sharing a common group C with CRTF indicated that no significant softening effect was attributed to the CRTFZ mixture by ZnDEC.

Moreover, statistical analysis, as presented in Table 4.11, revealed that the effect of AO was observed for the CRNZ mixture after LTA. The CRNZ mixture had a unique group A, different from other mixtures, supporting that it is statistically different, and the effect of ZnDEC was there. Additionally, CRN having another unique group B provided evidence of its superior performance than other RA utilized. For other mixtures (C, CR, CRTF, and CRTFZ), they shared a common grouping of C and D, implying that the performance of these mixtures was statistically similar. Therefore, at LTA, the high-RAP mixtures performed similar to (and in some cases better than) the C mixture. The analysis presented showed that the effect of ZnDEC provided a statistically significant effect with the use of specific RA. However, this phase only tested the interaction between two RAs and one AO. Therefore, further testing is needed to fully understand how various RAs and AOs interact, considering different conditions such as aging time, temperature, moisture, and ultraviolet light.

Furthermore, the use of ZnDEC was known to enhance long-term performance of asphaltic materials by retarding oxidative aging. Therefore, the impact of the drop in the FI index was considered in each case and presented in Figure 4.10.

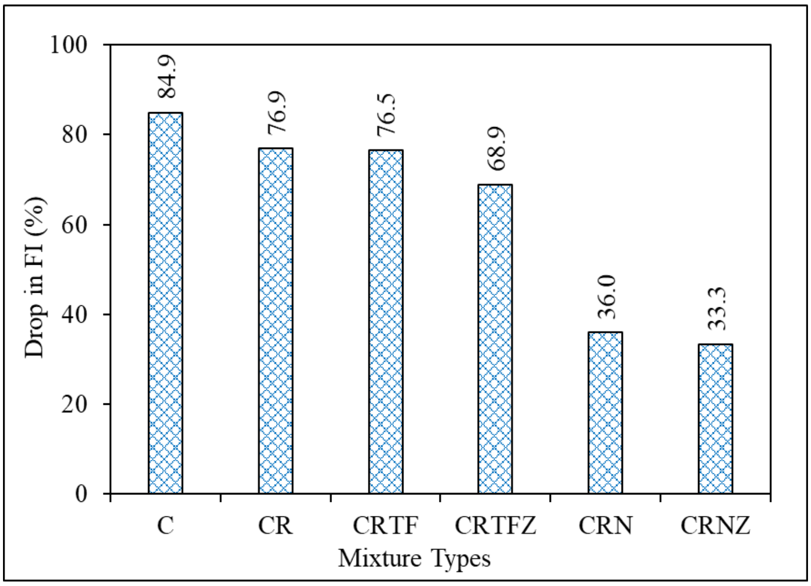


Figure 4.10 Percentage drop in FI of mixtures after LTA.

As shown in Figure 4.10, the ZnDEC-modified specimens experienced a lesser drop in the FI, attributed to the anti-aging effect of the ZnDEC used in this study. Additionally, based on the percentage drop in FI, it can be inferred that the effect of AO was more pronounced in the mixture modified by the RAs, which was more susceptible to aging. In other words, mixtures modified by TF were more susceptible to aging than those modified by N and showed a greater effect of ZnDEC.

4.4.2 High-Temperature Rutting and Moisture Susceptibility: Hamburg Wheel Tracking Tests (HWTT)

The HWTT was employed to evaluate the rutting and moisture damage resistance of the studied asphalt mixtures following the AASHTO T 324 [76] standard procedure. For this purpose, two specimens of each studied mixture were maintained in a water bath at 50°C and subjected to repetitive loading induced by a metallic wheel passing at a rate of 52 passes per minute. As the test progressed, the number of wheel passes and the respective rutting depth were recorded by the transducers attached to the machine. In this study, the number of cycles at a rutting depth of 12.5 mm was utilized as a rutting performance indicator, while the stripping inflection point (SIP) was used as a moisture performance indicator. The SIP was defined as the number of wheel passes obtained at the intersection of the creep slope and the stripping slope, as shown in Figure 4.11. A higher SIP number indicated better moisture damage resistance.

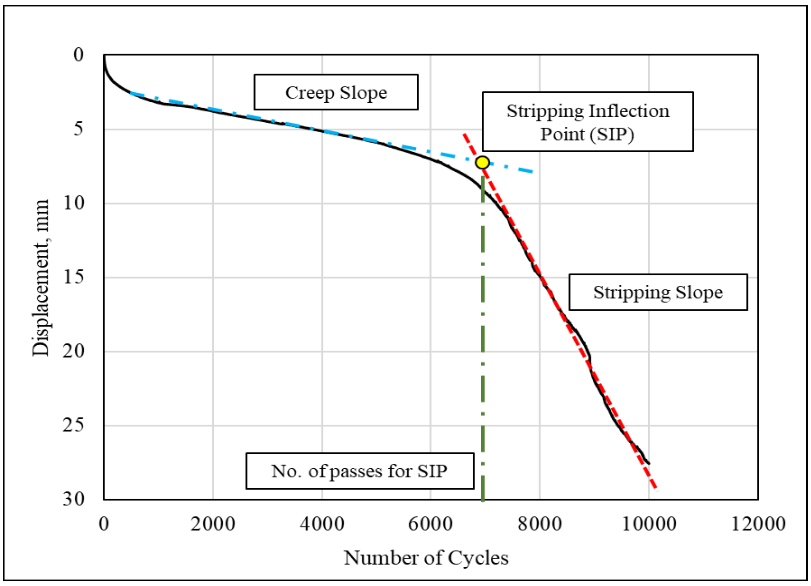


Figure 4.11 Typical HWTT results.

4.4.3 Permanent Deformation (Rutting) Resistance

The rutting test results are shown in Figure 4.12. The CR mixture exhibited relatively higher rut resistance compared to the C mixture, withstanding more than twice the number of cycles to reach a 12.5 mm rut depth. This result was anticipated since RAP materials are stiffer due to the presence of RAP aged binder, resulting in higher resistance to permanent deformation. However, the addition of the studied RAs (N and TF) had a negative effect on the rutting resistance as there were a smaller number of cycles to reach 12.5 mm rut depth compared with the high-RAP control mixture (CR). Moreover, the values obtained for mixtures with additives were even lower than the virgin control mixture (C), without RAP. This effect can be attributed to the softening effect of RAs, which might be desirable to reduce the cracking susceptibility of high-RAP mixtures but can be negative with respect to rutting resistance. It is worth noting that the optimal dosage of the RAs was determined based on the PG approach. This approach aimed to restore the PG of the CR binder, which was composed of laboratory-made RAP binder and virgin materials, towards the PG of the C binder. Therefore, it is still inconclusive whether the aging performed to obtain the laboratory-made RAP mimics the same level of aging as at the binder level or more tests need to be incorporated at the binder scale to account for the resistance to permanent deformation at the binder level.

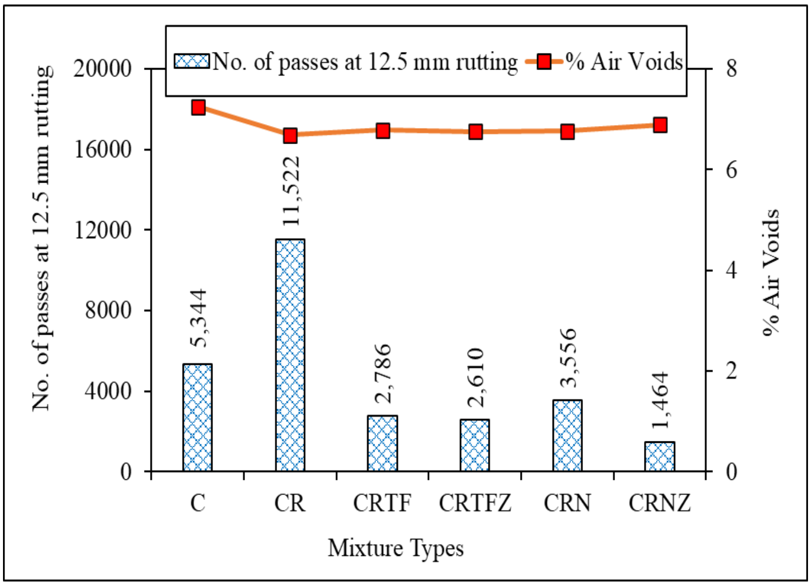


Figure 4.12 Summary of HWTT results of specimens.

4.4.4 Moisture Susceptibility

The SIP values obtained for the studied mixtures are presented in Figure 4.13. The highest moisture damage resistance was attributed to the CR. The aged, stiffened materials in the RAP mixture positively enhanced moisture damage resistance [29, 96]. Moreover, mixture C also had considerable resistance to moisture based on its higher SIP values. However, the results show that the addition of RAs negatively affected the moisture damage resistance of the CR mixture as the SIP of CR decreased from 10,200 to 3,700 for CRTF and 3,950 for CRN. Although there was not a big difference in the moisture damage resistance of CRTF and CRN, a slightly lower moisture damage resistance occurred because of the prevalence of a hydroxyl-related functional group unique to TF used in this study. The addition of ZnDEC did not provide great changes on moisture damage resistance.

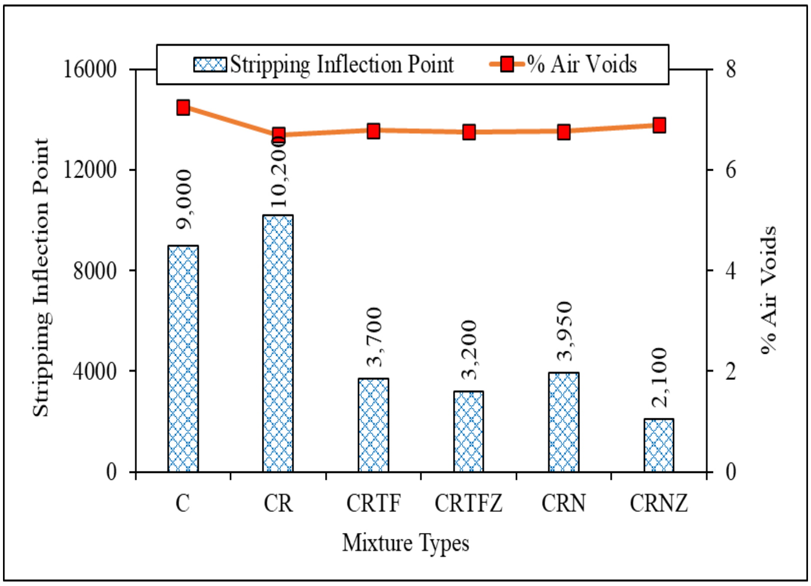


Figure 4.13 SIP of specimens.

4.5 Classification of RAs and Selection System

RAs have been extensively used within the asphalt pavement community, with thorough investigations into their effects on the engineering properties of asphalt binders and mixtures. However, there remains a need to establish a guideline for the classification system and selection of RAs. As a result of our findings, a colorful circle guideline for the classification and selection system of RAs has been developed and is presented in Table 4.12. This table serves as “information only”, providing guidance for the characterization and classification of RAs.

All combinations of binders, additives, aggregates, and mixes must undergo testing and design processes to meet the desired properties and performance standards. Additionally, RAs may exhibit variability based on their source, raw material production, and potential modifications by the manufacturer. Further modifications and enhancements might be necessary to achieve specific design and performance qualities. The typical dosage rates are determined for mixtures containing 50 - 65% RAP. However, these rates may vary depending on the mix design.

Table 4.12 Guideline for Characterization and Classification of RAs.

Types			**Characterization**												**Comments**
			Effectiveness								**Cautionary**		**Advisory**		
			Benefits								Limitations		Potentially Necessary Modifications and Enhancements		
Classification	**Category**	**Description**	**Lowers Low Temperature Grade**	**Lowers High Temperature Grade**	**Effects Rut Resistance**	**Improves Low Temperature Crack Resistance (standard aging)**	**Improves Low Temperature Crack Resistance (extended aging)**	**Improves Mid Temperature Crack Resistance**	**Colloidal Index Improvement**	**Typical Dosage Rates**	**Moisture Damage Susceptibility**	**Degradation from Extended Aging**	**Anti-stripping to Improve Moisture Damage Resistance**	**Antioxidants for ExtendedAging and Oxidation Damage Resistance**	
Class I	Paraffinic Oils	Refined used lubricating oils. This material can also be obtained from the petroleum distillation processes (e.g., Recycled Engine Oil Bottoms).	◖	●	◖	●	○	○	○	10-15%		🔴		🟡	Compatibility testing is recommended
Class II	Aromatic Extracts	Refined crude oil products or solvent extracts from distillates containing polar aromatic oil components.	◖	◖	◖	●	●	●	●	10-20%					
Class III	Naphthenic Oils	Engineered hydrocarbons for asphalt modification, generally moderate aromatic content and a low paraffin (wax) content.	◖	◖	◖	●	○	○	○	12-18%		🔴		🟡	Compatibility testing is recommended
Class IV	Triglycerides and Fatty Acids	Derived from vegetable and plant oils. It contains other chemical elements in addition to triglycerides and fatty acids (e.g., soybean oil, corn oil, cotton seed oil, palm oil).	●	●	◖	●	◖	●	●	3-10%	🔴	🔴	🟡	🟡	Formulations need to provide moisture damage resistance
Class V	Tall Oils	Paper industry byproducts. Also produced to make emulsifiers and fatty acids. It can vary on type of wood that is pulped in the Kraft process.	◖	●	◖	●	◖	●	●	6-10%	🔴	🔴	🟡	🟡	Formulations need to provide moisture damage resistance

○ Negligible Impact ◖ Moderate Impact ● Large Impact 🔴 Cautionary 🟡 Advisory

Chapter 5 Conclusions and Future Work

5.1 Conclusions

This study investigated the effect of various RAs and one AO (ZnDEC) on the performance of asphalt binders and mixtures. The chemical and physical characteristics of RAs were characterized through FT-IR, SARA, CHNOS, and SFE analysis. Also, the chemical and rheological properties of asphalt binders modified by different types of RAs and one AO were evaluated in various aging conditions, and the possible correlation between the chemical characteristics of the RAs and the rheological properties of the binders was explored. Furthermore, mechanical testing was conducted to evaluate the effects of RAs and AO on the moisture susceptibility as well as cracking and rutting resistance of the asphalt mixtures. The following conclusions can be drawn based on the results and findings:

- The FT-IR analysis revealed that the spectra of aromatic extract, naphthenic, and paraffinic oils were similar to the unmodified virgin binder. However, tall oil and triglycerides/fatty acids RAs showed strong peaks in the region of 1740 cm^{-1} and contained hydrogen bonds.
- The CHNOS analysis showed that triglycerides/fatty acids and tall oil contained high oxygen content, while the oxygen content of aromatic extract, naphthenic, and paraffinic oils had oxygen levels within the range of unmodified virgin binders.
- In the SARA fractions analysis, the aromatic extract was found to contain all three fractions that exist in the maltene phase of a binder. However, compatibility concerns were raised for paraffinic and naphthenic oils due to their high saturate content, typically the lowest in an asphalt binder’s SARA fractions.

- RAs were found to soften aged asphalt binder, but their impact on binder durability varied by source. Triglycerides/fatty acids and tall oil were less effective in maintaining long-term low-temperature cracking resistance compared to aromatic extract, particularly after extended aging (RTFO+2PAV). Furthermore, triglycerides/fatty acids and tall oil increased the likelihood of cohesion and adhesion failure in the CR binder, unlike other RAs. Binders modified with paraffinic and naphthenic oils showed poor long-term performance. A strong correlation was identified between the CI and chemo-rheological properties of the modified binder. The flexural creep stiffness (S-value), high PG temperature, Log complex modulus (G*), and Log Glover-Rowe (G-R) parameter were inversely related to CI while the phase angle and relaxation constant (m-value) were directly related to CI.
- The combined application of ZnDEC with RAs effectively retarded oxidation, improving low- and mid-temperature cracking resistance of asphalt binders.
- The cracking resistance of the high-RAP mixture (CR), estimated by FI, was improved by introducing RAs, and the addition of ZnDEC to RA-modified mixtures resulted in more crack resistance specimens while retarding oxidative aging to some extent.
- The rutting resistance of specimens modified with RAs was lower than that of the virgin specimen (C), which was further intensified by adding ZnDEC as an AO.
- Moisture damage resistance in CR specimens, as estimated by SIP, decreased by the addition of RAs and AO; however, the extent of the effect of ZnDEC on RA-modified mixtures was material-dependent. The addition of ZnDEC to CRTF reduced the moisture damage resistance of the mix negligibly, while for CRN, the effect was considerably higher.

5.2 Future Work

This study focused on the laboratory performance testing of asphalt binder and mixtures containing a high percentage of RAP materials with RAs and one AO, showing a positive effect of these additives. The benefits of using an AO with a group of RAs have been clearly established. Future studies are recommended to examine the efficacy of different AOs combined with RAs. A key recommendation is the implementation of a balanced mix design (BMD) approach, considering the dosages of RAs and AOs. Additionally, employing varied aging and weathering procedures that simulate environmental conditions could offer a more comprehensive understanding of the resistance of AO-enhanced RAs against diverse aging mechanisms and moisture damage. Thermal and molecular analyses could also provide valuable insights into the working mechanism and interaction between RAs, AOs, and binders. The degree of aging in these mixtures may differ from that experienced in the field; therefore, using field-collected RAP materials could be a more effective approach in future studies.

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Appendix A Feasibility Study on Using Different UTMs

A comparison between the use of two different types of UTM, namely the newly purchased 30 kN and the one available in the UNL materials lab with a 25 kN capacity, is provided in this section. This task was performed to verify the functioning of the UTMs and to validate if both the UTMs provided similar results. In addition, this will provide an opportunity to use two UTMs simultaneously in NDOT-funded projects in the future.

To this end, all the mixtures outlined in Table 3.5 were used to prepare the SCB test specimen for verification purposes. The naming details of the mixture types are also presented. However, concerning the use of two UTMs, the nomenclature of UTM25 was followed for the old UTM, and UTM30 was followed for the new UTM. Eventually, cracking performance testing was carried out for all the specimens in both the UTMs, considering the AASHTO T 393 protocol at 25°C with a loading rate of 50 mm/min. FI was used as a parameter to characterize the cracking performances of different asphalt mixtures with the use of two different UTMs. The FI values for each of the mixtures concerning the use of UTM25 and UTM30 are presented in Figure A.1 under the STA and LTA conditions. It can be observed that with the use of both types of UTMs, the FI values were similar in each of the cases of the mixtures at all aging conditions. This suggests both UTMs provided similar results based on cracking performance testing.

Moreover, to further validate the results from both UTMs were statistically similar, Tukey's HSD test was performed at a 95% confidence level, and grouping was provided for each mixture. The test was performed independently between the mixtures at two different aging conditions after confirming that the p-value obtained after the ANOVA test was less than the α-level (i.e., 0.05). The results of the ANOVA analysis are presented in Table A.1 and Table A.2, where a lower p-value than the α-level was observed.

Table A.1 ANOVA analysis: single factor for the FI values at STA Condition for Both UTMs.

Source of Variation	Sums of Squares (SS)	Degree of Freedom (df)	Mean Squares (MS)	F	P-value	F crit
Between Groups	1993.39	11	181.22	19.17	2.84E-09	2.22
Within Groups	226.93	24	9.46			
Total	2220.32	35				

Table A.2 ANOVA analysis: single factor for the FI values at LTA Condition for Both UTMs.

Source of Variation	Sums of Squares (SS)	Degree of Freedom (df)	Mean Squares (MS)	F	P-value	F crit
Between Groups	1524.28	11	138.57	41.05	7.52E-13	2.22
Within Groups	81.02	24	3.38			
Total	1605.29	35				

Consequently, Tukey’s HSD analyses were performed using two UTMs and six mixtures considering both aging conditions, and the summary of the test results is presented in Table A.3 and Table A.4. It was observed that the mean FI value for each mixture obtained from both the UTMs shares at least one similar grouping, signifying the results obtained from the UTMs were similar. Similar observations were made for both types of mixtures under STA and LTA conditions. This validates that utilizing two different UTMs with the same mixtures provided similar results, and both UTMs can be utilized simultaneously for research activities.

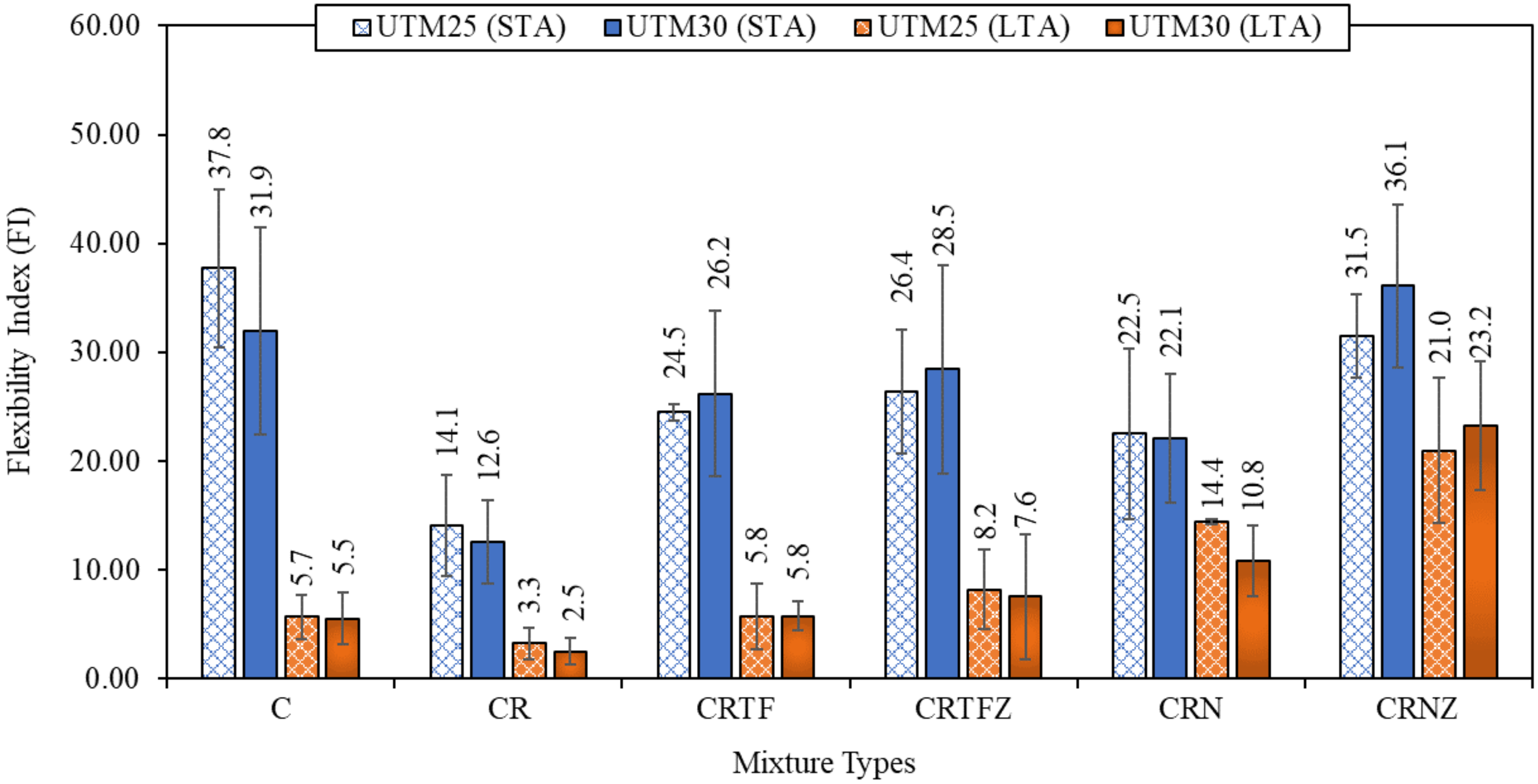

Figure A.1 FI Values for all the mixtures at STA and LTA conditions using two UTMs.

Table A.3 Summary of Tukey's HSD test results (α=0.05) for FI values at STA Condition.

	STA Condition			
Mixture Types	**Mean FI Values**		**Tukey’s HSD Grouping**	
	UTM 25	**UTM 30**	**UTM 25**	**UTM 30**
C	37.8	31.9	A	A, B, C
CR	14.1	12.6	F, G	G
CRTF	24.5	26.2	C, D, E	C, D, E
CRTFZ	26.4	28.5	C, D, E	B, C, D, E
CRN	22.5	22.1	D, E, F	E, F
CRNZ	31.5	36.1	A, B, C, D	A, B

Table A.4 Summary of Tukey's HSD test results (α=0.05) for FI values at LTA Condition.

	LTA Condition			
Mixture Types	**Mean FI Values**		**Tukey’s HSD Grouping**	
	UTM 25	**UTM 30**	**UTM 25**	**UTM 30**
C	5.7	5.5	D, E	D, E
CR	3.3	2.5	D, E	E
CRTF	5.8	5.8	D, E	D, E
CRTFZ	8.2	7.6	C, D	C, D, E
CRN	14.4	10.8	B	B, C
CRNZ	21	23.2	A	A