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

Nitish R. Bastola, M.S.
Graduate Research Assistant
Department of Civil and Environmental Engineering
University of Nebraska-Lincoln

Muhammad Ahmed, M.S.
Graduate Research Assistant
Department of Civil and Environmental Engineering
University of Nebraska-Lincoln

Mahdieh Khedmati, Ph.D.
Research Engineer
Department of Civil and Environmental Engineering
University of Nebraska-Lincoln

Jamilla Teixeira, Ph.D.
Assistant Professor
Department of Civil and Environmental Engineering
University of Nebraska-Lincoln

Hamzeh F. Haghshenas, Ph.D.
Adjunct Professor
Department of Civil and Environmental Engineering
University of Nebraska-Lincoln

Nebraska Department of Transportation Research
Headquarters Address
1400 Nebraska Parkway
Lincoln, NE 68509
ndot.research@nebraska.gov
(402) 479-4697
https://dot.nebraska.gov/business-center/research/

Nebraska Transportation Center
262 Prem S. Paul Research Center at Whittier School
2200 Vine Street
Lincoln, NE 68583-0851
(402) 472-1932
http://ntc.unl.edu

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Nitish R. Bastola, M.S.
Graduate Research Assistant
Department of Civil and Environmental Engineering
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Muhammad Ahmed, M.S.
Graduate Research Assistant
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Hamzeh F. Haghshenas, Ph.D.
Adjunct Professor
Department of Civil and Environmental Engineering
University of Nebraska-Lincoln

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16. Abstract

The use of reclaimed asphalt pavement (RAP) in combination with recycling agents (RAs) (i.e., rejuvenators or softening agents) has gained significant attention from the pavement industry as a sustainable pavement solution, reducing the carbon footprint of manufactured products through the conservation of energy and reduction on the use of raw materials. Current research has found that RAs can improve RAP recycled asphalt mixture's cracking resistance, while being capable of maintaining their rutting resistance. However, there are some concerns about the effect of RAs on the moisture damage resistance and the long-term performance (aging) of these additives. The current need is to maximize the use of RAP in asphalt mixtures by adopting sustainable sources of RAs, such as Triglycerides and Fatty Acids (TF) based RAs which are mostly derived from vegetable oils. However, Phase I of this project found that TF-based RAs are more prone to oxidative aging, which can hamper the long-term performance of asphalt binders and mixtures. In the current project (Phase II), we focused on adopting the simultaneous utilization of RA and antioxidants to prevent the oxidative aging of RA-modified binders and mixtures. To this end, different binder blends and high-RAP mixtures were developed using five different antioxidants alongside the high-RAP binder modified with one source of TF-based RA. At the binder level, rheological performance tests were conducted focusing on high-temperature rutting, and mid and low-temperature cracking assessments at short- and long-term aging conditions. Additionally, at the mixture level, two antioxidants were selected to develop high-RAP asphalt mixtures modified with TF-based RA, and mechanical performance testing focusing on mid-temperature cracking, rutting, and moisture damage susceptibility were performed. At the binder level, the results revealed that the addition of TF-based RA enhanced the binder's cracking resistance but increased the rutting susceptibility. Antioxidants did not affect the rutting and cracking parameters; however, their effect on resisting long-term aging was antioxidant-type specific. At the mixture level, the selected dosage of TF-based RA could not enhance the mixture cracking resistance significantly. Also, the effects of TF-based binders were not observed at long-term aging conditions. Similar to the binder level results, the use of antioxidants to retards oxidative aging was type-specific, and one antioxidant, Zinc diethyldithiocarbamate (ZnDEC), provided such superior aging-resistant function.

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Chapter 1 Introduction

The use of reclaimed asphalt pavement (RAP) in combination with recycling agents (RAs) has gained significant attention from the pavement industry as a sustainable pavement solution, reducing the carbon footprint of manufactured products through the conservation of energy and reduction on the use of raw materials. A study performed by the National Asphalt Pavement Association (NAPA) in 2019 found asphalt mixtures in the United States are mixed with an average of 21.1% RAP materials [1]. Currently in the state of Nebraska, the use of RAP ranges from 25% to as high as 55% depending on the mixes being used, however, there is further interest towards increasing the amount of RAP in asphalt mixtures [2]. The major reason for the increased use of RAP in the production of recycled asphalt mixtures is the positive effects of RAs reported in many studies [3-5]. The use of properly engineered RAs and mix designs can effectively recover the properties of the aged asphalt binders from RAP materials and provide equivalent, and in some cases better performing, pavements. Therefore, the pavement industry is interested in the use of even higher percentages of RAP (high-RAP mixtures). In most cases, concerns about cracking performance of high-RAP mixtures can be addressed with the help of RAs while being capable of maintaining the rutting resistance of the mixtures [3, 6, 7]. However, some RAs such triglycerides/fatty acids (TF) based RAs obtained from vegetable oils has shown drawbacks regarding their effects on binder, the mixture's moisture resistance, and long-term performance [6, 8-12]. One potential alternative to counterbalance the effects of binder and mixtures modified by RAs is with the combined use of antioxidants on the material's blends [13, 14]. Antioxidants are additives used to modify asphalt binders and provide resistance to long-term age hardening. When antioxidants are introduced to the asphalt binders, they control oxidation (a primary aging mechanism) by trapping or scavenging free radicals, which are mostly responsible for initiating and propagating oxidation [15].

The idea of modifying the properties of aged binders using RAs and providing long-term age resistance through the addition of antioxidants seems to be a viable solution. Based on the test results obtained from a previous NDOT research project on RAs and antioxidants (funded proposal number SPR-P1(20) M116), the combination of these technologies was proved effective and can bring significant pavement life cycle cost savings, and provide longer-lasting and more sustainable roadway pavements. However, the focus of this first phase of research was to investigate if this chemistry combination of RAs and antioxidants would work, so it was tested on only one antioxidant, one unmodified asphalt binder, and a selection of RAs.

To make a definitive conclusion about the applicability of this approach and find the best combinations of these additives, further investigation of different types of antioxidants and asphalt binders including polymer modified binders was necessary. In addition, findings at the asphalt binder level needed to be verified considering the performance of asphalt mixtures, including the evaluation of performance-based parameters suggested in the Balanced Mix Design (BMD) approach [16]. Moisture susceptibility is also important to consider because some additives may be incompatible and cause inadequate adhesion and cohesion.

1.1 Objectives

The main goal of this second phase study is to identify the effects of simultaneous use of TF-based RA and antioxidant additives on the performance of high-RAP binders and mixtures. The specific objectives of this study are as follows:

- Evaluate the effects of different antioxidant dosages on the high-temperature PG grade of the studied high-RAP binder blends modified with TF-based RA.
- Evaluate the rheological performance of high-RAP asphalt binders modified with TF-based RA and selected dosages of different antioxidants based on the high-temperature

rutting parameter, and mid- and low-temperature cracking parameters.

- Evaluate the mechanical performance of high-RAP recycled mixtures modified with the selected antioxidants and RA based on rutting, moisture damage, and mid-temperature cracking performance-based parameters.

1.2 Methodology

To achieve the research goals, five antioxidants and one TF-based RA were selected. Those additives were used to produced high-RAP asphalt binders blends with various additive contents. Dynamic shear rheometer and bending beam rheometer tests were performed to obtain binder blend properties and PG grades, and the results were later used to calculate the high-temperature rutting parameter and mid- and low-temperature cracking parameters to assess the modified high-RAP binder performance. In addition, the mechanical performances of high-RAP mixtures modified with two selected antioxidants and the TF-based RA were assessed based on the results from the Hamburg wheel tracking test (HWTT) and semi-circular bending Illinois Flexibility Index Test (SCB-IFIT). Figure 1.1 shows the experimental plan.

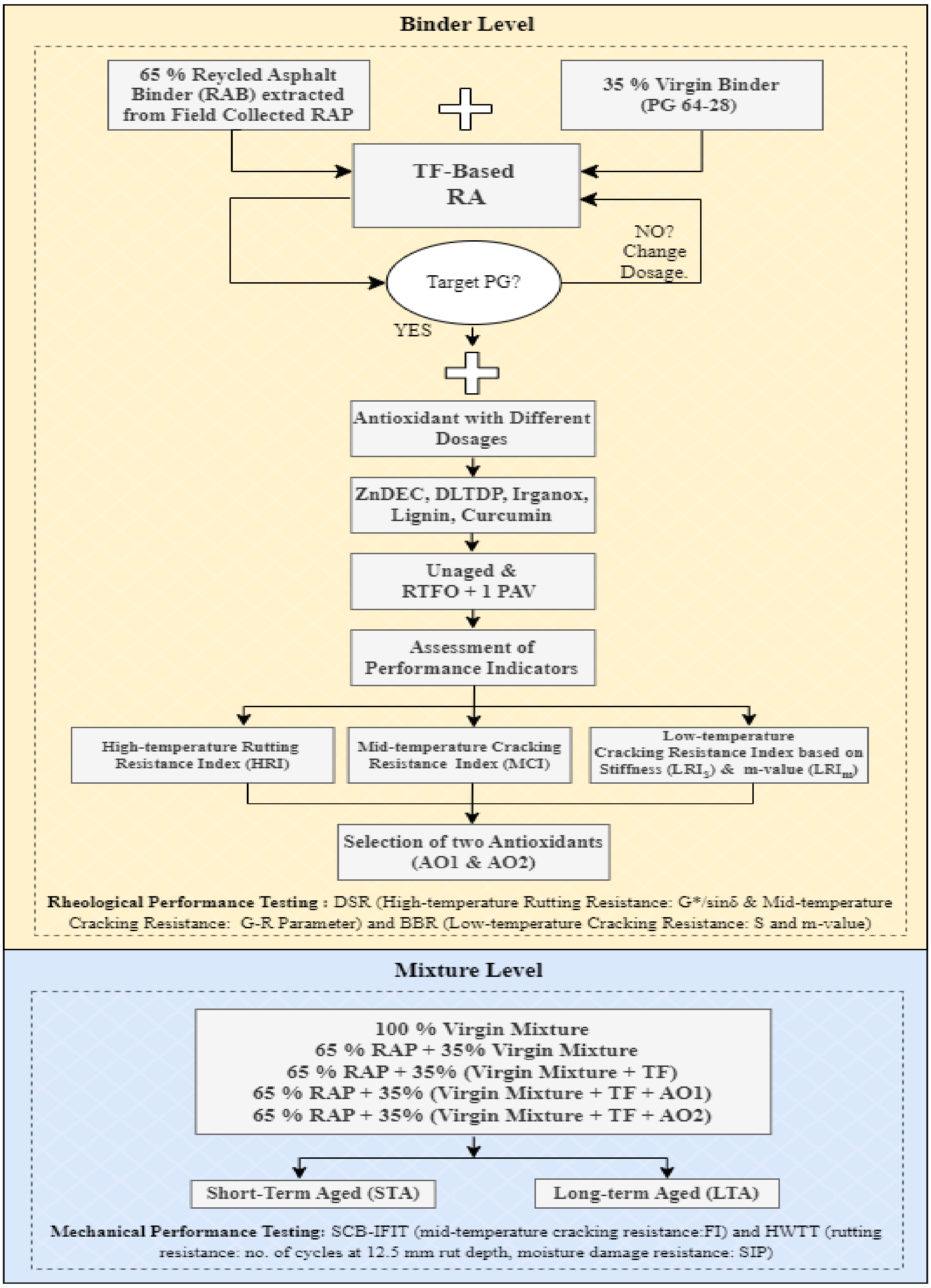


Figure 1.1 Methodology for the research study.

1.3 Organization of the Report

This report was organized in five chapters. The first chapter presents the introduction and the research objectives and methodology. In Chapter 2, a summary of the results obtained in Phase I of this project and additional literature review related to antioxidant assessment methods is presented. Chapter 3 describes the materials and specimen fabrication procedures used. In Chapter 4, the experimental results are presented and discussed showing the effects of the selected RA and antioxidants and additive dosage on the binder's performance grade, and aging indices. In addition, mixture level performance test results are presented and discussed to verify the effects of the selected additives in the STA and LTA performance of high-RAP recycled mixtures. Ultimately, Chapter 5 summarizes the major findings of this project and proposes recommendations for future work.

Chapter 2 Background

The use of RAP has grown tremendously since its use promotes environmental preservation through recycling and reducing raw material use and reducing the overall recycled mixture costs. Despite its environmental and cost benefits, the amount of RAP in asphalt mixture is oftentimes limited due to the asphalt mixture's cracking susceptibility as a result of the aged natured of RAP materials [17, 18]. Therefore, potential solutions that could lead to higher contents of RAP in recycled asphalt mixtures but still maintain a satisfactory overall recycle mixture performance are being sought to promote pavement sustainability. The use of RAs stands out as a potential solution to maximize the use of RAP [19, 20].

The National Center for Asphalt Technology (NCAT) have differentiated the types of RAs to be used in asphalt pavement based on their source, such as paraffinic oils, aromatic extracts, naphthenic oils, triglycerides/fatty acids, and tall oils [21]. In addition to NCAT classification, in recent years, the characterization of RAs based on their chemical properties has been developed. In that context, functional groups associated with each of the recycling agents, as well as saturated-aromatics-resin-asphaltene (SARA) fractions and elemental analysis to understand carbon, hydrogen, nitrogen, oxygen, and sulfur content, are identified. [22]. Several studies have been conducted to verify the ability of RAs to improve asphalt binder and mixture performance [23-28]. Some studies presented negative impacts of RAs based on performance observations, particularly for rutting and moisture susceptibility [5, 6, 19, 25]. Haghshenas et al. [6] reported that with the use of RA from the group of triglycerides/fatty acids and tall oils, a lower moisture damage resistance with a higher possibility of cohesion and adhesion failures was observed by a surface free energy test. Additionally, based on the study conducted by Zhang and Bahia [5] for the mixture level utilizing petroleum and bio-based RA, the rutting and moisture damage resistance of the RAP mixture diminished, and it took a smaller amount of cycles to reach a 12.5 mm rutting depth and the occurrence of the stripping inflection point. A similar observation on reduced rutting and moisture damage resistance was also made by Zhang et al. [19] when seven different RAs were introduced to the RAP mixture. In another study, Haghshenas et al. [29] also reported that the addition of aromatic extract to the RAP mixture could decrease the rutting resistance as evidenced by the flow number testing results. More specifically, in terms of aging susceptibility, triglycerides and fatty acid (TF) based RAs had a higher tendency to age compared to the other RAs. TF-based RAs tend to show positive effects on the binder as well as on the mixture performance initially, but eventually the positive effects of TF-based RAs diminishes [30, 31]. To improve the long-term performance of binders modified with RAs, Haghshenas et al. [13] explored the simultaneous use of RAs with an antioxidant. Different categories of RAs, including paraffinic oil, triglycerides/fatty acids, and tall oils, were simultaneously used with an antioxidant in highly recycled binders. Considering the modifications, several binder level tests were performed at different aging conditions, such as the dynamic shear rheometer test to assess mid-temperature cracking and high-temperature rutting resistances, and the bending beam rheometer test to assess low-temperature cracking resistance. It was found that such a combination of RAs and an antioxidant could enhance the long-term performance of recycled asphalt binder. More importantly, this method also enhanced the long-term performances of RA groups, which had a higher propensity to oxidative aging.

To verify the effects of simultaneous use of RA and antioxidants, Phase I of this project was conducted solely focused on five categories of RAs and one type of antioxidant additive [2]. A summary of the Phase I project is presented in Section 2.1 of this chapter to provide a brief insight into the major results and conclusions obtained, along with the limitations and further needs that led to the consideration and completion of this research project (Phase II). Furthermore, apart from the Superpave parameters used in Phase I, other indices were used to assess the effectiveness of the studied antioxidants, as described in Section 2.2 of this chapter.

2.1 Summary of Phase I Project

For Phase I of this study, five different RAs (Table 2.1) were selected to produce modified binders and asphalt mixtures. Initially, the RAs were subjected to chemical characterization tests such as Fourier Transformation Infrared (FTIR) Spectroscopy, Saturate Aromatic Resin Asphaltene (SARA), and elemental composition. Then, different blends of RA-modified binders combined with one type of antioxidant, Zinc Diethyldithiocarbamate (ZnDEC), were produced, and binder samples were subjected to rheological tests. In the end, selected modified binders were used to produce high-RAP asphalt mixtures to see the effects of those additives on the mixture level. The studied mixtures were subjected to the semi-circular bending (SCB) test and Hamburg wheel tracking tests (HWTT) for cracking resistance, rutting, and moisture damage resistance assessment. The final report from Phase I provides detailed information on the procedures used and a brief summary of the project outcomes from each task is presented in the next sections [2].

Table 2.1 RAs utilized (Phase I).

Category	**Physical state and colour**	**Description**	**Viscosity (60 °C, Pa.s)**
Paraffinic Oils	liquid/colourless	refined used lubricating oils	0.019
Aromatic Extracts	viscose/brown	refined crude oil products	0.120
Naphthenic Oils	viscose/yellow	engineered hydrocarbons	0.102
Triglycerides/ Fatty Acids	liquid/colourless	derived from vegetable oils	0.017
Tall Oils	liquid/reddish Brown	paper industry by-products	0.034

2.1.1 Chemical Characterization of RAs

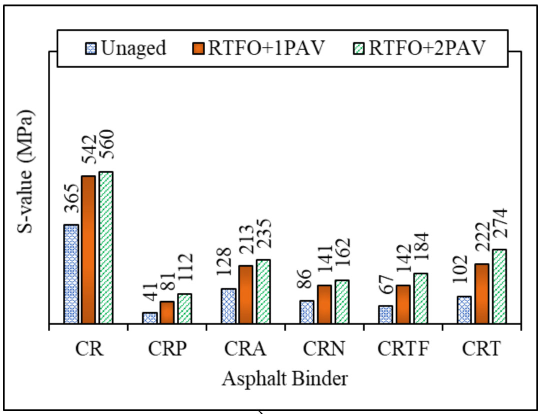
As mentioned before, three chemical tests were performed to characterize the studied RAs such as Fourier Transformation Infrared (FTIR) Spectroscopy, Saturate Aromatic Resin Asphaltene (SARA) Analysis, and Carbon, Hydrogen, Nitrogen, Oxygen, and Sulphur (CHNOS) test for elemental analysis. Based on the FTIR testing results, it was found that the studied RAs presented different functional groups. Among the utilized RAs, aromatic extracts, naphthenic oils, and paraffinic oils had an FTIR spectra similar to unmodified virgin binders. However, tall oils and triglycerides/fatty acid based groups of RAs had peaks around the wavelength of 700, 1100, and 1700 associated with the functional group of alcohol, dialkyl/aryl sulfones, and esters, respectively, that were not found in virgin binder. These functional groups might play an active part in aging and moisture sensitivity if utilized in asphalt binders and mixtures.

Similarly, SARA analysis was undertaken to determine the fraction of saturates, aromatics, resins, and asphaltenes. The major role of RAs is to restore the balance between the maltenes (saturates, aromatics, and resin) and the asphaltenes phase in the RAP binder, which changes during the aging process. The studied RAs presented different fractions of SARA components. Aromatic extracts utilized in the study showed a similar maltene composition as in the binder, while the other RAs had some dissimilarities on one of the maltene fractions. For instance, the triglycerides/fatty acids showed only a resin fraction on its maltene composition, while tall oil did not present a saturate fraction. On the other hand, paraffinic and naphthenic oils contained a higher portion of saturates. Additionally, the percentage of carbon, hydrogen, nitrogen, oxygen, and sulfur in each RA was determined and compared with the unmodified virgin binder (PG 64-22). One of the important observations was that triglycerides/fatty acids and tall oil presented a higher percentage of oxygen, while other RAs did not. This difference in the percentage of oxygen might play an important role since it could lead to more oxidative aging effects on the binders.

2.1.2 Rheological Characterization of Binder modified with RAs and Antioxidant

The performance of RA-modified binders based on rheological testing results was investigated to understand the capability of RAs to enhance the performance of aged asphalt binders. For that, a binder blend consisting of 65% laboratory-prepared recycled asphalt binder (RAB) and 35% virgin binder (PG 64-22) was made and named CR. The CR was further mixed with different RAs. The notations CRP, CRA, CRN, CRTF, and CRT were provided, referring to CR modified by paraffinic oils, aromatic extracts, naphthenic oils, triglycerides/fatty acids, and tall oils, respectively. The resulting binder compositions were subjected to short- and long-term aging according to the standards ASTM D2872 and ASTM D6521, respectively. Additionally, the studied binders were subjected to more extreme aging conditions, i.e., 2 PAV and 5 PAV to further assess the long-term aging effects.

After that, different tests were performed to investigate the low- and mid-temperature cracking. The bending beam rheometer (BBR) testing procedure based on ASTM D6648 was utilized to obtain the low-temperature cracking parameters of the studied binders. Mid-temperature cracking was assessed based on the Glover-Rowe (G-R) concept. For that, Dynamic Shear Rheometer (DSR) tests were performed at 45˚C and 10 rad/s. Then, the complex modulus (G*) and phase angle (δ) results were recorded and used to plot the black space diagram, and the G-R parameter was determined, as presented in Figure 2.1 c. It is observed that the addition of RAs to the CR binder increased the phase angle while decreasing the stiffness. Based on G-R parameters, CRA, CRTF, and CRT performed satisfactorily for up to 40 hours of aging (RTFO+2 PAV). Similarly, crack onset time, referred to as the time to initiate cracking, was also found from the same diagram, and the result showed that the binders CRA, CRTF, and CRT passed the RTFO+ 2PAV criteria. In contrast, CR, CRP, and CRN failed in the binders before reaching 40 hours of onset damage, which was not favorable for long-term performances.



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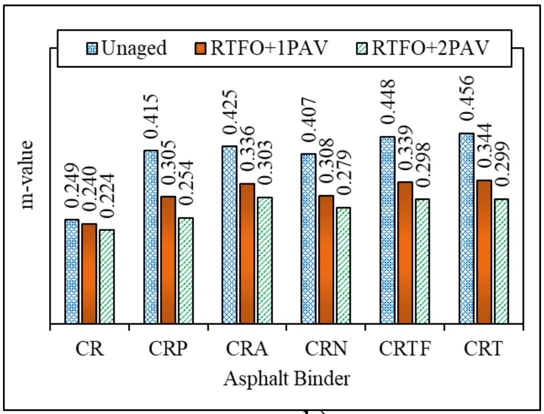

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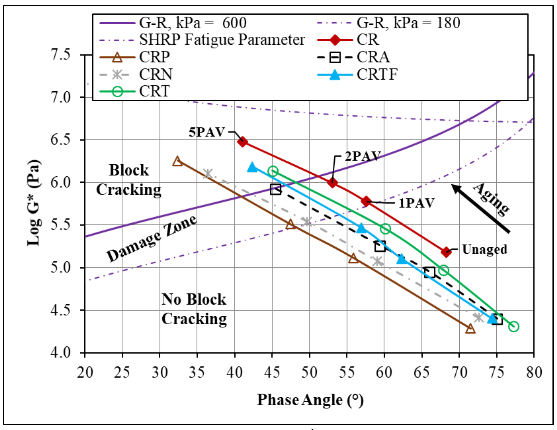


c)

Figure 2.1 a) BBR test results (S-value) at -18 ºC and b) BBR test results (m-value) at -18 ºC, and c) Mid-temperature cracking performance for different binder blends.

To verify the simultaneous effects of RA and antioxidant, some binder blends that had aging susceptibility with the addition of given RAs were further modified with the antioxidant ZnDEC. Binders modified with three groups of RAs (paraffinic oils, triglycerides/fatty acids, and tall oils) were simultaneously treated with ZnDEC and the resulting blends were named CRPZ, CTFZ, and CRTZ. Moreover, CR was also treated with ZnDEC and named CRZ. Then, high-temperature rutting, and mid-temperature and low-temperature cracking were assessed to consider the effects of the additives on the high-temperature PG (Figure 2.2 a), G-R parameter (Figure 2.2 b), and m- and S- values (Figure 2.2 c and d), respectively.

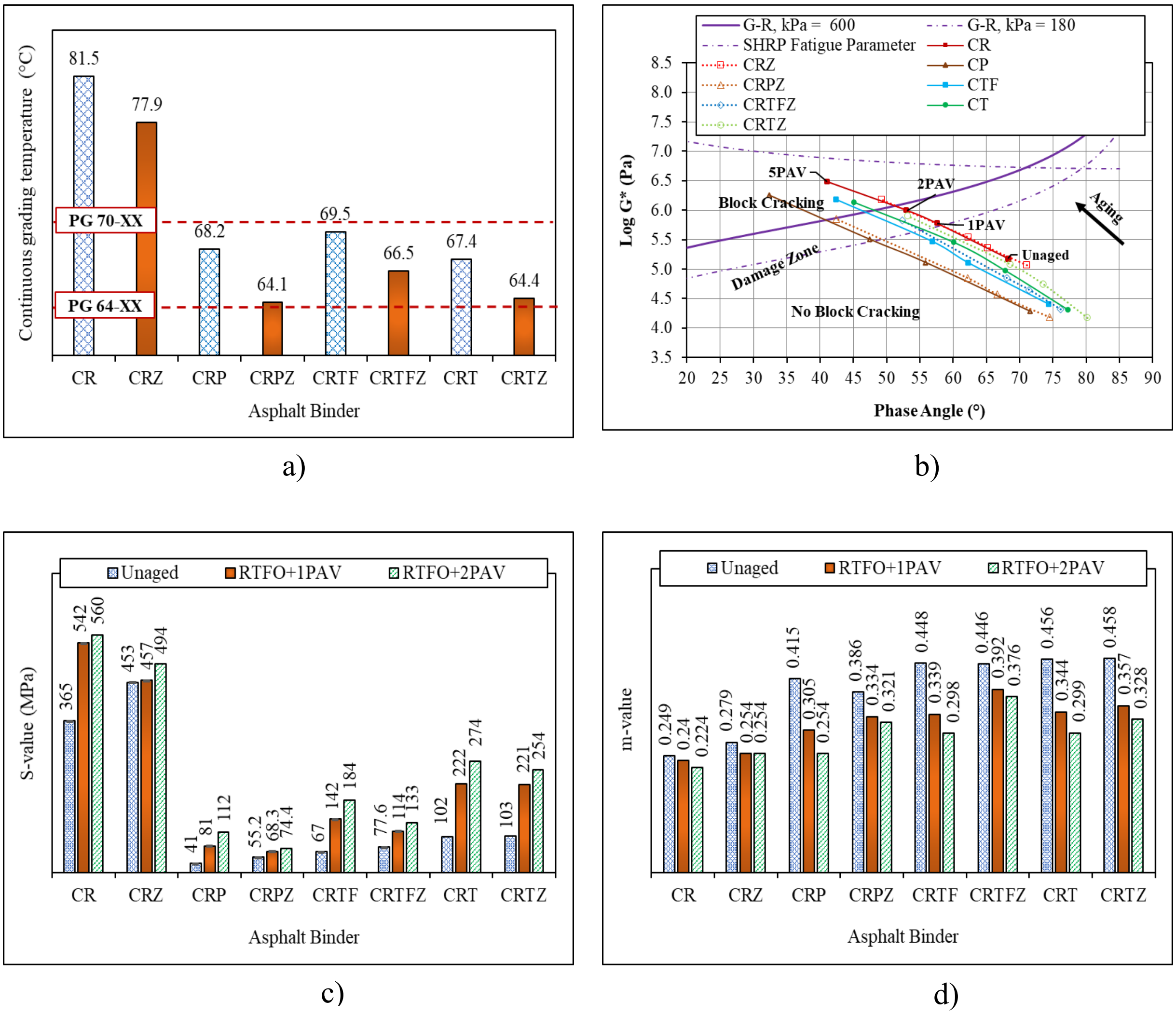


Figure 2.2 a) High-temperature rutting performance, b) Mid-temperature cracking performance, c) BBR test results (S-value) at -18 ºC, and d) BBR test results (m-value) at -18 ºC for different binder blends.

From Figure 2.2, it can be seen that the use of RAs softened the CR considerably, leading to a decrease in the high-temperature PG values. A small softening effect was observed with the addition of ZnDEC. The addition of ZnDEC reduced the mid-temperature cracking susceptibility, as observed in Figure 2.2 b. Regarding the low-temperature performance (Figure 2.2 c and d), the addition of ZnDEC provided a lesser change in the stiffness after aging, followed by an m-value of greater than 0.3 under both RTFO + 1 PAV and 2 PAV aged conditions. Lesser stiffness and higher m-values after aging supported the efficacy of ZnDEC in enhancing long-term performance at low temperatures of -18 ºC.

2.1.3 Mechanical Performances of Asphalt Mixtures Modified with selected RAs and ZnDEC Antioxidant

Phase I of the study also characterized the mechanical performance of the asphalt mixtures using binder blends modified with two selected RAs (naphthenic oil and triglycerides/fatty acids) and the ZnDEC antioxidant. The mixtures were prepared using 65% laboratory-prepared RAP materials and 35% virgin materials, keeping the same combined gradation and binder content in all cases. Further details on the materials were presented in the published report for Phase I of this project [2]. The selection of the two RAs was based on their sources of origin and their aging susceptibility as determined from the binder level of the study. The nomenclature used to distinguish mixtures was maintained as in the binder scale analysis, i.e., C, CR, CRTF, CRTFZ, CRN, and CRNZ, where C is the mixture without any aged materials, and CR represents mixture with 65% RAP. Additionally, CRTF, CRTFZ, CRN, and CRNZ represent the mixture modified with triglycerides/fatty acids, naphthenic oils, and ZnDEC. The studied asphalt mixtures were ultimately tested for cracking, rutting, and moisture damage susceptibility. Cracking performance was assessed based on the analysis of the flexibility index obtained after conducting the Semi-circular Bending-Illinois Flexibility Index Test (SCB-IFIT) test according to the AASHTO T 393 standard. The rutting and moisture damage susceptibility was assessed based on the number of cycles required for the mixture to reach 12.5 mm depth of rutting and the stripping inflection point, respectively, using an HWTT device and following the standard AASHTO T 324.

Based on the average FI results at STA (Figure 2.3 a), it was observed that the utilization of two different sources of RAs resulted in enhanced cracking performance. For

LTA, it was found that in between two RAs used at the mixture level, the long-term performance of the mixture modified with triglycerides/fatty acids was worse than that of naphthenic oil and was confirmed with statistical analysis. Considering this, ZnDEC was utilized simultaneously to understand if an antioxidant could help reduce the aging susceptibility of high-RAP mixtures modified with RAs. It was found that the use of ZnDEC provided some aging resistances in such mixtures. However, the enhancement of the aging resistance varied based on the type of RA used, and the simultaneous use of naphthenic oil and ZnDEC was able to provide a statistically significant enhancement in cracking performance after LTA.

From the HWTT results, it was found that the use of RAs resulted in a softer mixture with lesser rutting resistance (Figure 2.3 b). A similar trend was followed regarding moisture damage resistance (Figure 2.3 c); the mixture with triglycerides/fatty acid based RAs was more susceptible to moisture than the naphthenic oil, likely due to the prevalence of the hydroxyl functional group in such categories of RAs. ZnDEC slightly lowered the rutting and moisture susceptibility of the mixture, considering its insoluble nature. The reduction in the moisture damage resistance was more prominent in the mixture modified with Naphthenic oil, which might be an effect of incompatibility that arose due to the percentage of saturates in those kinds of oils.

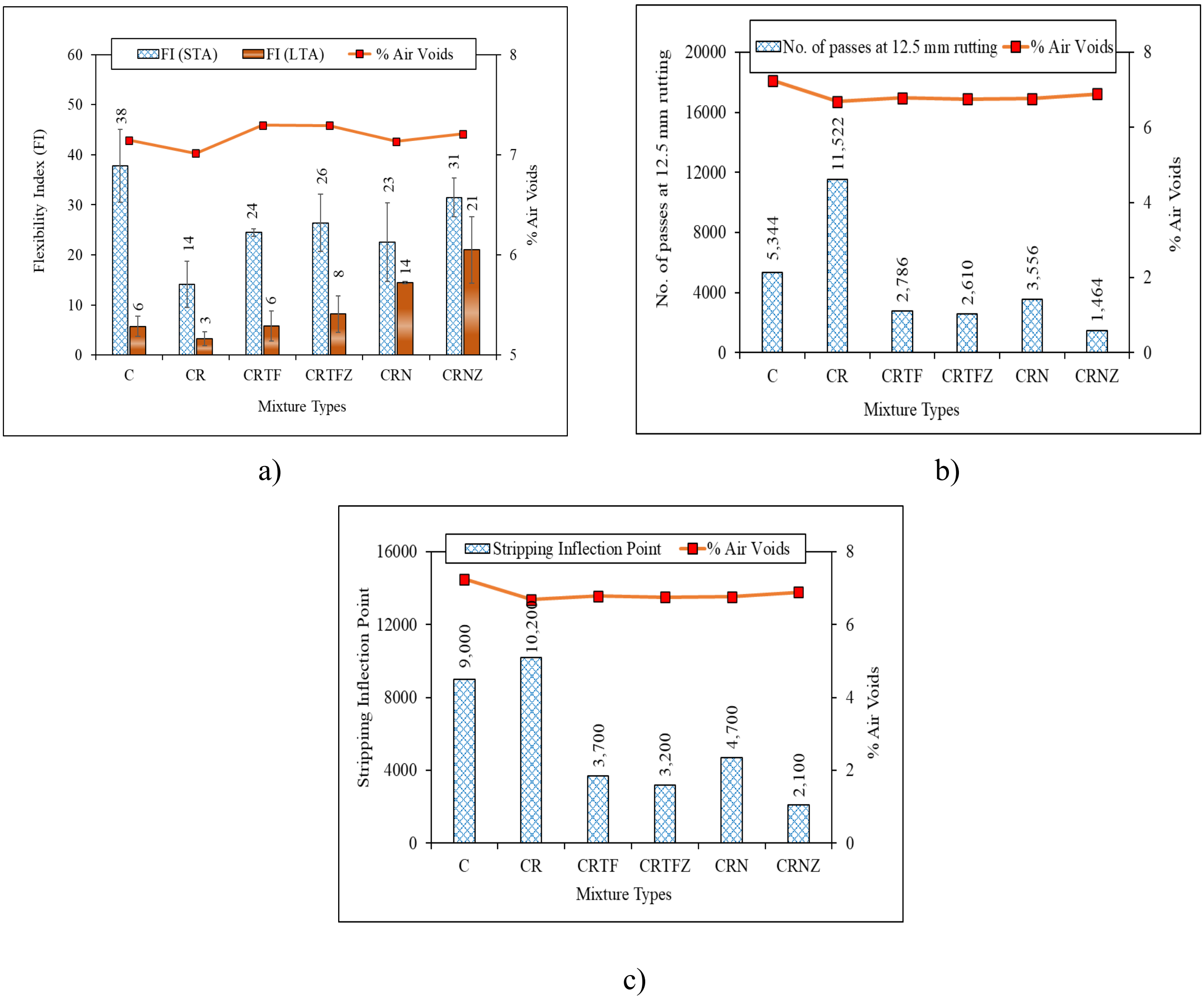


Figure 2.3 a) Cracking resistance, b) rutting resistance, and c) moisture damage resistance.

2.2 Limitations in Phase I of the Project

Based on the outcome of Phase I of this project, it can be concluded that the RA from triglycerides/fatty acids group was more prone to oxidative aging. However, the simultaneous use of RAs and antioxidants at the binder level enhanced the long-term performance, potentially due to the retarding of aging mechanisms with the aid of the antioxidant. Similar effects were also observed in the mixture level. However, regarding the rutting and moisture susceptibility, the utilized additives resulted in soft mixtures making them more susceptible to rutting compared to an unmodified RAP mixture. Moreover, the moisture damage resistance was diminished due to the use of the selected modified binders.

Overall, the study provided a holistic overview of the use of RAs and antioxidants at both the binder and mixture levels; however, a few limitations existed in Phase I of this study, including the use of only one type of antioxidant in effectively judging the long-term performance of RAP binders and asphalt mixtures simultaneously modified with RA and antioxidants. In addition, the RAP utilized in Phase I of the project was laboratory-aged, which might not represent the true field conditions. Also, in Phase I, a non-polymer binder was utilized. Therefore, in the current Phase (Phase II) of this project, these limitations are being overcome most suitably, with a great focus on the efficacy of different antioxidants on long-term high-RAP binder and mixture performance. Field-collected RAP materials, polymer-modified binders, and diverse groups of antioxidants are utilized with one type of RA. This plan was developed to understand the wider scope of interactions between aged materials, RAs, and antioxidants. For that, several rheological and chemical indices established in the literature were quantified to understand and compare the efficacy of the antioxidants in effectively enhancing the aging resistance of high-RAP binders. Section 2.3 provides a summary of different methods that can be used to obtain those suggested indices.

2.3 Use of Antioxidants and their Types

Antioxidants are added to binders to enhance their durability by preventing or slowing down oxidative processes that can cause aging, hardening, and degradation [32]. Primarily, antioxidants trap and scavenge free radicals, which initiate and propagate oxidation. In addition, there are several other mechanisms for antioxidants to function in asphalt binder, and based on that, five common types of antioxidants are defined.

- Primary Antioxidants (Radical Scavengers): These antioxidants prevent the initiation of oxidation by neutralizing free radicals, which are highly reactive molecules that can cause chain reactions leading to oxidation and include phenolic antioxidants and amines commonly referred to as OH and NH group, respectively. They are highly effective in retarding oxidation by donating hydrogen to free radicals and stabilizing them before they can damage the asphalt binder [33]. Some examples of this category of antioxidants include Vitamin E, furfural, and Irganox-1010 [34]. A few studies found that utilizing primary antioxidants resulted in resistance to thermos-oxidative resistance of asphalt binder with enhanced ductility, penetration, and decreased complex modulus after aging [33] [35].

- Secondary Antioxidants (Peroxide Decomposers): Secondary antioxidants work by decomposing peroxides, which are intermediates in the oxidation process. They work in tandem with primary antioxidants to terminate oxidative chain reactions. Generally, these types of antioxidants are sulfur and phosphorous compounds, and typical examples are phosphite and thioesters, which convert peroxides into stable, non-reactive molecules, preventing further oxidation [33]. One of the common secondary antioxidants being researched in the asphalt industry is ZnDEC. It has been found that ZnDEC could retard the aging procedures as well as improve the low- and mid-temperature cracking resistance of asphalt binder [15, 36].
- UV Stabilizers: Ultraviolet (UV) radiation from the sun can accelerate the oxidation of binders by breaking down the molecular structure. UV stabilizers absorb or reflect UV radiation, preventing it from initiating oxidation processes. These are crucial for materials exposed to sunlight. Common UV stabilizers include hindered amine light stabilizers (HALS) and UV absorbers like benzotriazoles. Considering UV stabilizers, Cong et al. reported that the binder with UV stabilizers had greater photostability, and aging related to UV radiation could be reduced [37].
- Metal Deactivators: Transition metals, such as iron or copper, can catalyze oxidation in binders. Metal deactivators chelate these metal ions, effectively neutralizing their catalytic effects. By binding to these metals, they reduce their ability to accelerate

oxidation, thus enhancing the lifespan of the binder [32].

- Synergists: These substances enhance the effectiveness of primary and secondary antioxidants when used together. Synergists do not act as antioxidants on their own but help increase the efficiency of other antioxidants, often by stabilizing or regenerating them during the oxidation process [38].

Each type of antioxidant serves a different purpose, ensuring that the binder resists degradation caused by environmental factors such as oxygen exposure, UV radiation, and catalytic metals. However, many researchers emphasized that oxidative aging is the most common phenomenon in asphaltic materials [32, 33, 39]. Therefore, this research study focuses on using the two most common types of antioxidants, i.e., primary and secondary, which directly influence the oxidation-related aging of asphaltic materials.

2.4 Indices for Assessing the Effectiveness of Antioxidants

Several indices have been proposed to verify the performance of modified asphalt binders. The most common one is the Superpave rutting parameter, $G^*/\sin\delta$, which relates the complex modulus (G^*) and phase angle (δ) and it is used to evaluate the high-temperature binder performance. Likewise, the stiffness (S-value) and relaxation constant (m-value) parameters obtained from BBR tests are defined to evaluate the low-temperature cracking resistance of binders [40]. The sole use of Superpave parameters in assessing the aged nature of modified asphalt binders, including binders modified with innovative additives such as RAs and antioxidants, might be limited. Therefore, other parameters are proposed in the literature. For instance, Glover et al. [41] suggested a parameter known as the DSR function ($G'/(\eta'/G')$) that could relate the storage modulus (G') and the dynamic viscosity (η') of binders tested at 15°C and 0.005 rad/s to their ductility, and assess the binder mid-temperature cracking susceptibility. The parameters were derived considering the low-temperature ductility of binders is affected by aging. Later on, Glover and collaborators [42] suggested another parameter, the Glover-Rowe (G-R) parameter, which defined the relationship of the complex modulus (|G*|) and phase angle (δ) of asphalt binders at 15°C and a frequency of 0.005 rad/s as $G^*[\cos(\delta)]^2/\sin\delta$. The G-R parameter facilitated the plotting of ductility-based failure planes in the Black Space Diagram, being useful for capturing the aging susceptibility of asphalt binders. Moreover, the role of different types of additives, including antioxidants, in the binder chemical characteristics and their long-term effects is critical to optimize the use of these materials. Therefore, many recent studies delve into the chemical and rheological characterization of asphalt binders [12, 15, 29, 43] and some indices are being used to quantify those effects.

In terms of chemical-based indices, two well-known indices are the carbonyl and sulfoxide aging indices. They are obtained using FTIR spectrometer results, and quantifying the area under a range of specific wave numbers related to those functional groups [44]. Thus, comparisons between aging indices can help to distinguish the effects of different additives and aging conditions on binder aging characteristics [45].

Additionally, rheological indices are also utilized to assess the efficacy of antioxidants. In this case, different indices are developed utilizing the results of primary parameters such as G*/sinδ, S-values and m-value, and G-R parameter under different binder conditions [46]. For instance, Ahmed et al. [47] utilized different aging indices to characterize the effects of different antioxidants on recycled asphalt binders extracted from RAP used in Nebraska modified with RAs. The following indices (Table 2.2) were considered to quantify the long-term effects of antioxidants and RAs under the aging conditions of unaged and RTFO + 1 PAV aged. Utilizing these indices, the efficacy of adding different antioxidants to prevent the oxidative aging of highly recycled binder modified with triglycerides/fatty acid based recycling agents were understood, and these indices provided a clear differentiation of such modifications. The lower value presented by HRI, MCI, and

LCI_S showed the efficacy of utilized antioxidants in enhancing long-term performance, while higher LCI_m results in enhanced efficacies of such modification.

Table 2.2 Suggested rheological indices to assess the efficacy of additives.

Indices	Representation
High-Temperature Rutting Resistance Index (HRI)	$\mathbf{HRI} = \frac{\boldsymbol{G^*}/\mathbf{sin}\delta(\mathbf{RTFO + 1PAV})}{\boldsymbol{G^*}/\mathbf{sin}\delta(\mathbf{Unaged})}$
Mid-temperature cracking Resistance Index (MRI)	$\mathbf{MCI} = \frac{\mathbf{G - R\ (RTFO + 1PAV)}}{\mathbf{G - R\ (Unaged)}}$
Low-Temperature Cracking Resistance Index based on Stiffness (LRI_s)	$\mathbf{LCI_s} = \frac{\mathbf{S - value\ (RTFO + 1PAV)}}{\mathbf{S - value\ (Unaged)}}$
Low-Temperature Cracking Resistance Index based on m-value (LRI_m)	$\mathbf{LCI_m} = \frac{\mathbf{m - value\ (RTFO + 1PAV)}}{\mathbf{m - value\ (Unaged)}}$

Chapter 3 Materials, Studied Blends, and Specimens Preparation

In this chapter, the raw materials used (antioxidants, binders, and aggregates) and the studied binder and mixture blends are presented, along with the sample preparation procedures.

3.1 Materials

3.1.1 Recycling Agent (RA)

Crude corn oil was selected as the RA on this Phase II project. It is a vegetable-based oil categorized as a triglycerides/fatty acid (TF). The major reason for selecting this particular RA is due to its susceptibility to oxidative aging observed in Phase I of the project. Therefore, it was intended herein to assess the effects of antioxidants on reducing oxidative aging of binders and mixtures modified with TF-based RA. The description of the selected RA is presented in Table 3.1. A generic descriptor is used for labeling the RA, in this case, TF.

Table 3.1 RA used in this study.

Category	**ID**	**Physical state and color**	**Description**	**Viscosity Ratio**
Triglycerides/Fatty Acids	TF	liquid/reddish	Crude Corn Oil	0.869

3.1.2 Antioxidants

Five different types of antioxidants were used in the study. These antioxidants included Zinc diethyldithiocarbamate (ZnDEC), Dilauryl thiodipropionate (DLTDP), Pentaerythritol tetrakis (Irganox-1010), Lignin, and Curcumin. Each of these antioxidants falls into the group of either primary or secondary antioxidants or metal chelators, which can be used to retard aging due to oxygen exposure. Primary antioxidants have OH or NH groups that break the chain of oxidation reactions by accepting and donating electrons. In contrast, secondary antioxidants of phosphorous and sulfur compounds can easily form peroxide and hydroperoxide for stabilizing oxidation reactions [48, 49]. The metal chelators perform differently by trapping metallic compounds responsible for forming free radicals that accelerate the asphalt binder's aging. Similarly, the antioxidants utilized in this study were also categorized based on the mechanisms they used as antioxidants. In this case, the antioxidants fell into two groups: peroxide decomposers and hindered phenol, which is mainly due to the availability of different types of free radicals in an antioxidant [50]. Another differentiating factor in these five antioxidants is their sources. Lignin and Curcumin were derived from plants, while the other antioxidants were derived from chemical sources. A summary of the properties of the antioxidants used is presented in Table 3.2.

3.1.3 Recycled Asphalt Pavement (RAP)

Field collected RAP was used in this study. The sample was obtained from a local asphalt plant stockpile near Lincoln, Nebraska. 1.5 tons of RAP were collected and transported to the storage area in the CEE Materials Lab at the University of Nebraska-Lincoln (UNL). To prevent exposure to moisture and further aging, the material was stored in plastic bags at a room temperature of around 23 °C (73 °F). The RAP materials were used as a recycle aggregate to produce high-RAP mixtures. In addition, extracted RAP-binder was used to produce different blends of binders, as detailed in Section 3.1.5.

Table 3.2 Antioxidants utilized in this study.

Antioxidants	ZnDEC	DLTDP	Irganox 1010	Lignin	Curcumin
Scientific Name	Zinc diethyl-dithiocarbamate	Dilauryl thiodipropionate	Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate)	N/A	N/A
State Color	Solid White	Solid White	Solid White	Solid Reddish Brown	Solid Yellow
Density (g/cm^3)	1.47 at 25 °C	0.97 at 25 °C	1.15 at 25 °C	1.40 at 25 °C	0.93 at 15 °C
MP (°C)	172-176	41	110-125	257	183
BP (°C	N/A	580	1005	N/A	N/A
Chemical Formula	$C_{10}H_{20}N_2S_4Zn$	$C_{30}H_{58}O_4S$	$C_{73}H_{108}O_{12}$	$C_{18}H_{13}N_3Na_2O_8S_2$	$C_{21}H_{20}O_6$
Sources	Chemical Products	Chemical Products	Chemical Products	Plant Products	Plant Products
Type	Secondary	Primary	Primary	Primary	Primary/ Metal Chelator
Mechanism	Peroxide Decomposer	Peroxide Decomposer	Hindered Phenol	Hindered Phenol	Hindered Phenol

3.1.4 Aggregates

Limestone and gravel (2A and 3ACR types) virgin aggregates with a nominal maximum aggregate size (NMAS) of 12.5 mm were used in this study. The aggregate blend used to study high-RAP mixtures was made up of 35% virgin aggregates and 65% RAP. Figure 3.1 shows the gradation of the field-collected RAP materials, the virgin materials, and the blend of virgin and RAP materials. The final combined aggregate blend (RAP+Virgin Aggregates) is within the minimum and maximum control points set by the Nebraska Department of Transportation (NDOT) [51].

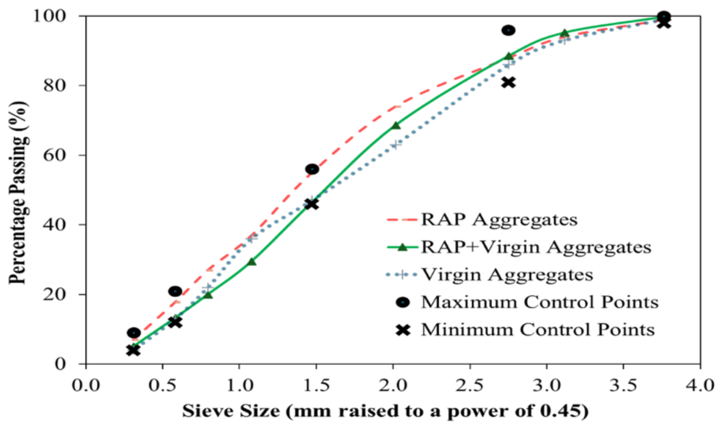
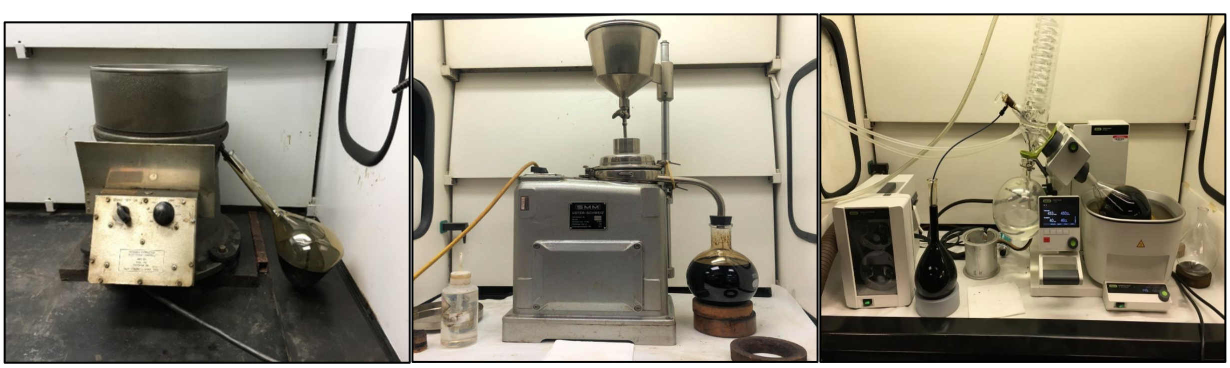


Figure 3.1 Aggregate gradation.

3.1.5 Asphalt Binders

A PG 64-28 binder from Flint Hills was selected as a base binder for this study. The base binder was mixed with RAP extracted binder, hereafter named RAB, to produce the reference binder samples. The RAB was obtained using a three-step procedure based on ASTM D 2172 [52], ASTM D1856 [53], and ASTM D 5404 [54] for centrifuge extraction, microcentrifugation, and rotavapor recovery processes, respectively, and they are illustrated in Figure 3.2. The continuous PG grade of the RAB was determined to be PG 81.8-18.



(a) (b) (c)

Figure 3.2 Binder extraction process from RAP a) Centrifuge extraction, b) Microcentrifuge extraction, and c) Rotavapor recovery.

3.2 Binder Blends and Testing Specimens Preparation

3.2.1 Binder Blends

After the extraction process, a blend of 65% of the RAB and 35% of the virgin binder (PG 64-28) were prepared, named CR. The percentage of RAB was chosen based on the final goal of developing a high-RAP mixture with 65% RAP, as is further explained in Section 3.1.6, and assuming 100% binder availability from RAP. The continuous PG grade of the CR blend was obtained as PG 76.4-24.3. The CR binder was modified with TF, named CRTF, at a dosage of 3.5% of RA. The dosage was determined based on the PG approach to meet the base binder grade of PG 64-28. Finally, the selected antioxidants were added to the CRTF at different dosages to verify the effects of different antioxidants and the dosage on the modified binder characteristics. It is important to mention that the blends were produced using a high-shear mixture, maintaining the shear rate of 2000 rpm and the temperature of 150 °C for one hour during the blending process. Initially, CR and CRTF were prepared, and then different antioxidants were added at different dosages to the CRTF samples. The initial antioxidant dosage for CRTFZ3 was based on the Phase I results of this study. For the other antioxidants, the initial dosages were based on literature review, leading to the blends CRTFD0.25, CRTFI2.5, CRTFL0.05, and CRTFC0.05. Then, adjustments were made arbitrarily to see the effects of antioxidant dosages on the binder rheology. Table 3.3 presents the overall composition of the studied binders (highlighting the blends with initial dosages of antioxidants) and the adopted ID used in the analysis of the results.

Table 3.3 Binder ID and Composition.

Binder ID	Binder Composition
C	PG 64-28
CR	35% PG 64-28+ 65% RAB
CRTF	31.50% PG 64-28+ 65% RAB + 3.5% TF
CRTFZ3	28.5% PG 64-28+ 65% RAB + 3.5% TF + 3% ZnDEC
CRTFZ6	25.5% PG 64-28+ 65% RAB + 3.5% TF + 6% ZnDEC
CRTFD0.25	31.25% PG 64-28+ 65% RAB + 3.5% TF + 0.25% DLTDP
CRTFD1	30.5% PG 64-28+ 65% RAB + 3.5% TF + 1% DLTDP
CRTFI2.5	29% PG 64-28 + 65% RAB + 3.5% TF + 2.5% Irganox 1010
CRTFI0.1	31.40% PG 64-28 + 65% RAB +3.5% TF + 0.1% Irganox 1010
CRTFL0.05	31.45% PG 64-28 + 65% RAB +3.5% TF + 0.05% Lignin
CRTFL0.1	31.4% PG 64-28 + 65% RAB +3.5% TF + 0.1% Lignin
CRTFC0.05	31.45% PG 64-28 + 65% RAB +3.5% TF + 0.05% Curcumin
CRTFC0.1	31.4% PG 64-28 + 65% RAB +33.5% TF + 0.1% Curcumin

3.2.2 Binder Testing Specimens Preparation

Different binder specimens were produced for PG grading, and low-temperature cracking, mid-temperature cracking, and high-temperature rutting tests. These tests were performed utilizing DSR and BBR specimens under virgin (non-aged), short-term aging (STA) and long-term aging (LTA) conditions. The binder STA condition was performed using a thin-film oven (RTFO) test, as defined on ASTM-D2872 [55]. Hence, a pressure aging vessel (PAV), following the ASTM-D6521 standard [56], was utilized for LTA. The standard LTA (RTFO + 1PAV) was followed for aging the binder. The PAV temperature was 100 °C under a pressure of 2.1 MPa during the aging process. After that, the necessary specimens were fabricated for running each of the tests discussed earlier.

3.3 Mixtures Blends and Testing Sample Preparation

3.3.1 Mixture Blends

A control mixture, named C, was obtained by mixing 100% virgin materials, i.e., base binder PG 64-28 and virgin aggregates. Then, the high-RAP mixture was obtained by mixing 65% RAP with 35% virgin materials. The high-RAP mixtures were designed to meet the NDOT criteria for Superpave Recycled (SPR) [51]. SPR is one of the most common types of recycled asphalt mixtures used in Nebraska. Although the current NDOT specification allows the use of 55% RAP in SPR mixtures, this research was aimed and performed considering the future goal of NDOT in increasing the RAP content to 65%.

The RAP binder content was determined to be 4.75%. Therefore, base binder PG 64-28 was added to obtain the overall high-RAP mixture binder content of 5.2%, assuming 100% RAP binder availability. This mixture was named CR. The volumetric parameters of the two control mixtures (C and CR) and the NDOT guidelines for SPR mixtures are presented in Table 3.4.

Table 3.4 Volumetric parameters of the control mixtures.

Properties	**NDOT SPR Requirements**	**Amount**	
		C	**CR**
Binder Content (%)	>5 %	5.2	5.2
Dust to Binder Ratio	0.7-1.7	1.0	1.0
Design Air Voids (%)	3 ± 1%	3	3
No. of Gyrations	65	65	65
Voids in Mineral Aggregate (%)	N/A	13	13
Voids Filled with Asphalt (%)	N/A	79	78

Apart from two control mixtures, three modified mixtures were prepared based on the use of TF and antioxidants. It is to be highlighted that only two antioxidants were selected based on the analysis of binder-level testing results, as presented in Chapter 4. Table 3.5 shows the studied mixtures, with respective IDs,

Table 3.5 Mixture ID and Composition.

Mixture ID	**Mixture Composition**	**Proportion for 1000 grams of mixture**				
		Base Binder	**Aggregates**	**RAP**	**RA**	**Antioxidant**
C	Base Binder + Aggregates	52.0	948.0	-	-	-
CR	35 % C + 65% RAP	21.1	331.8	650.0	-	-
CRTF	CR+ TF	19.3	331.8	650.0	1.8	-
CRTFZ3	CRTF + ZnDEC	17.7	331.8	650.0	1.8	1.6
CRTFD0.25	CRTF +DLTDP	19.2	331.8	650.0	1.8	0.1

Note: Deficit binder in RAP to reach 5.2% binder content was adjusted using the base binder.

All mixtures were subjected to short- and long-term aging conditions. The short-term aging (STA) was performed by heating the loose mixture at 135 °C for four hours, in accordance with AASHTO R 30. For long-term aging (LTA), the procedure in the National Cooperative Highway Research Program (NCHRP) Report 09-54 [57] was followed. In this procedure, the mixture was conditioned at 95 °C for three days and then used to prepare the specimen for cracking tests. This simulates the long-term cracking performance of the asphalt mixture after eight years of field aging under 20 mm below the pavement surface, considering the climatic conditions in Nebraska (Figure 3.3).

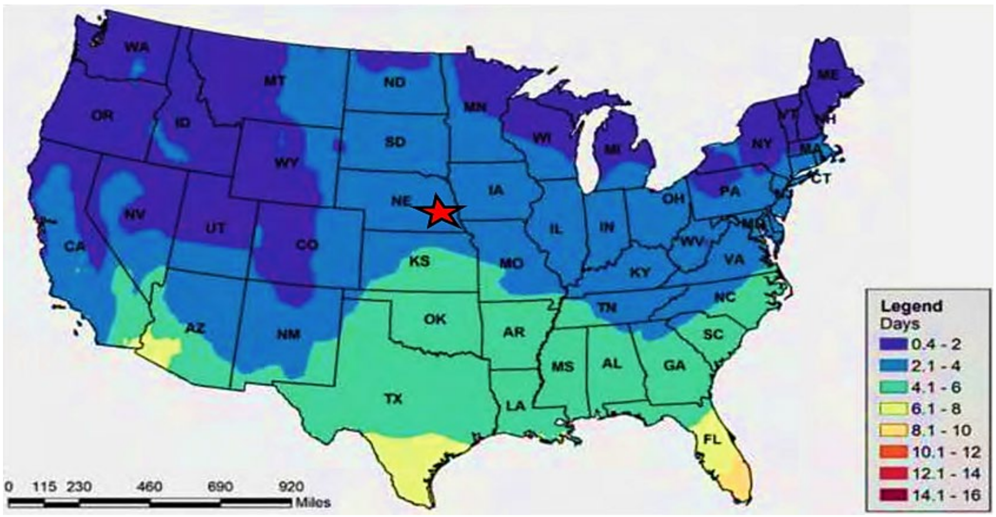


Figure 3.3 Long-term aging duration to simulate years under 20 mm depth [57].

3.3.2 Mixture Testing Specimens Preparation

This study investigates the cracking, rutting, and moisture susceptibility of compacted asphalt mixtures modified with a TF and two antioxidants. Cracking performance is assessed utilizing the Semi-circular Bending-Illinois Flexibility Index Test (SCB-IFIT), while the Hamburg Wheel Tracking (HWT) test was performed to investigate performance related to rutting and moisture susceptibility. Several specimens were fabricated to initiate these tests, and the process related to the specimen fabrication is presented below.

3.3.2.1 Semi-circular Bending-Illinois Flexibility Index Test (SCB-IFIT) Specimen

The SCB-IFIT test was performed to evaluate the cracking performance of asphalt mixtures modified with the use of an RA and different antioxidants. For this test, asphalt mixtures were compacted using the Superpave gyratory compactor (SGC) and a SGC specimen with a height of 170 mm and diameter of 150 mm with 7 ± 0.5% air voids was initially prepared. The SGC specimen was sliced 10 mm from the top and bottom to eliminate the non-uniform air voids in these regions, and the remaining portion of the specimen was cut into thirds, each with a thickness of 50 mm, which was further sliced into a semicircular shape. The sliced semicircular specimen was given a notch of 15±1 mm in length and 2 mm width. For each studied mixture, six specimens were used for testing, and average results and standard deviations are presented. Figure 3.4 show the SGC sample, the reduced 50 mm specimens, and the final SCB specimen positioned in the 3-point bending device.

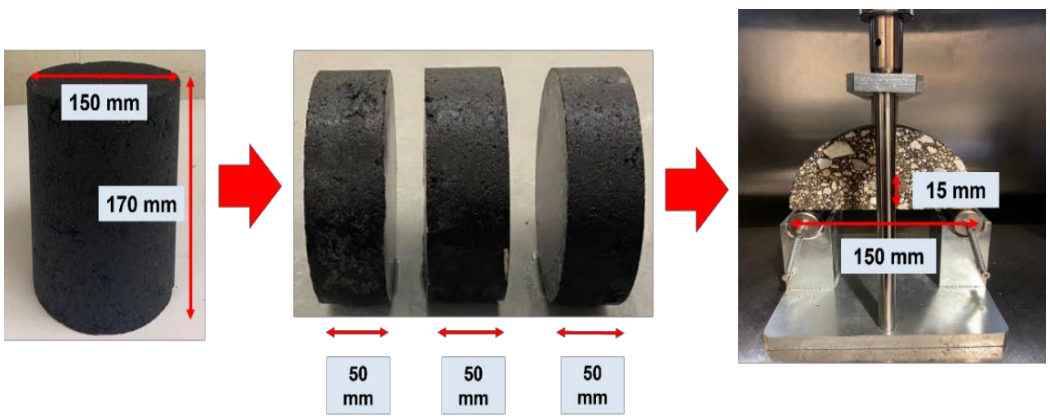


Figure 3.4 SGC specimen, reduced samples, and the SCB sample positioned in the supporting apparatus.

3.3.2.2 Hamburg Wheel-Tracking Test (HWTT) Specimen

The HWTT was used in this study to evaluate the rutting and moisture susceptibility of different asphalt mixtures. HWTT specimens with a diameter of 150 mm and a height of 62 mm were compacted in the SGC, with a target air void level of 7± 0.5%. The specimens were trimmed based on the AASHTO T324 procedure [58] and a pair was fitted in a mold before testing. Two sets of HWTT paired specimens were used for the testing of each mixture. Figure

3.5 shows the samples placed inside the HWTT mold before testing, the HWTT device, and the HWTT samples after testing.

(a) (b) (c)

Figure 3.5 HWT test specimens: (a) before testing, (b) inside the HWT device, and (b) after testing.

Chapter 4 Laboratory Tests, Analysis of Results and Discussion

This chapter outlines the laboratory tests conducted for this study, along with their results and discussion. Rheological tests using a DSR and BBR were performed to determine the appropriate dosage of antioxidants and recycling agents (RA). Rheological characterization was then carried out for unaged and RTFO + 1 PAV-aged binders, focusing on high-temperature rutting, mid-temperature cracking, and low-temperature cracking. Aging indices were established for each binder and additive combination. Finally, mixture-level testing was conducted based on the binder test outcomes. Specifically, the SCB-IFIT was used to evaluate the cracking resistance of asphalt mixtures under STA and LTA conditions, while the HWTT assessed rutting and moisture damage resistance.

4.1 Rheological Performance Testing and Characterization of Asphalt Binders

4.1.1 Dosages of RA, Antioxidants, and Performance Grading (PG)

Performance Grading (PG) of asphalt binders is determined by evaluating the binder's ability to resist distress at both high and low service temperatures. For high-temperature PG (HPG), the DSR is used to measure the binder's resistance to rutting, following ASTM D7175 [42]. The test calculates the complex shear modulus (G^*) and phase angle (δ), with the binder passing if it meets the rutting parameter ($G^*/\sin\delta \geq 1.00$ kPa for unaged binders and ≥ 2.20 kPa for RTFO-aged binders). The highest temperature at which the binder meets each rutting parameter is recorded, and the lowest of these temperatures is reported as the HPG. For low-temperature PG (LPG), the BBR is used to evaluate the binder's resistance to thermal cracking per ASTM D6648 [43]. This test measures the binder's stiffness (S-value $\leq$ 300 MPa) and relaxation (m-value $\geq$ 0.300) at specific low temperatures (-12°C and -24°C in this study). The temperature at which each parameter (S-value and m-value) meets the criteria is recorded, and the lowest temperature (in absolute value) is reported as the LPG. The continuous PG results, averaged from two replicates, are presented in Table 4.1.

Table 4.1 High and low-end performance grading of binders.

Binder ID	**High-Temperature continuous PG (°C)**	**Low-Temperature continuous PG (°C)**
C	68.0	-31.1
CR	76.4	-24.3
CRTF	68.4	-31.2
CRTFZ3	68.4	-33.6
CRTFZ6	66.8	-31.7
CRTFD0.25	67.7	-30.8
CRTFD1	66.1	-32.3
CRTFI0.1	68.2	-31.0
CRTFI2.5	67.8	-29.6
CRTFL0.05	68.5	-32.1
CRTFL0.1	67.4	-30.2
CRTFC0.05	68.8	-29.8
CRTFC0.1	68.7	-29.3

The optimal dosage of TF was established at 3.5% of the total binder weight, in alignment with the PG approach targeting the PG of the C binder. At this dosage, each of the utilized antioxidants was added at two different percentages, and the corresponding PG results are reported in Table 4.1. The PG results indicated that, dependent on the dosage, the addition of antioxidants could soften the binder, which is undesirable. Therefore, it is essential to carefully determine the appropriate dosages of antioxidants to minimize this softening effect. It was observed that the addition of 3% ZnDEC, 0.25% DLDTP, 0.1% Irganox 1010, 0.05% lignin, and 0.1% curcumin on the CR modified binders could meet the high-temperature PG of the virgin binder C. Consequently, these specific dosages (3% ZnDEC, 0.25% DLDTP, 2.5% Irganox 1010, 0.05% lignin, and 0.1% curcumin) were selected for further characterization of rutting and cracking performance.

4.1.2 High-Temperature Rutting Performance

The rutting resistance parameter (G*/sin δ) was calculated for both unaged and RTFO + 1 PAV-aged binders, allowing for a comparison across various aging scenarios, as well as the use of TF and antioxidants. The results are presented in Figure 4.1.

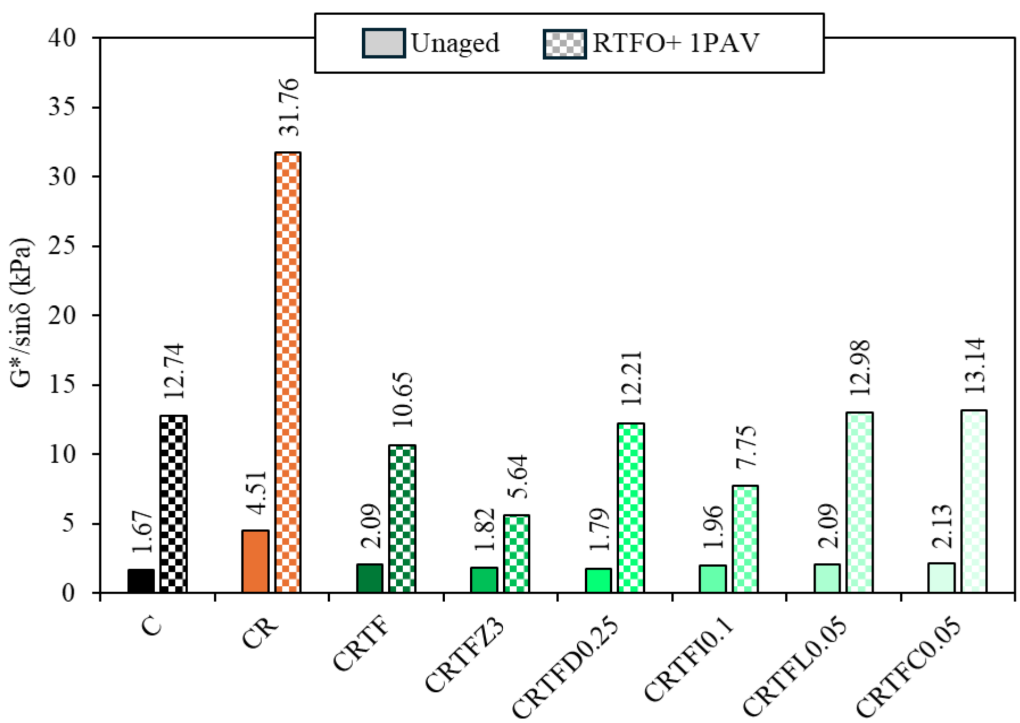


Figure 4.1 Rutting parameter of asphalt binders at 64 °C.

As it can be seen, under unaged conditions the C binder presented the lowest rutting parameter, demonstrating a higher susceptibility to rutting. In contrast, blending 65% recycled asphalt binder (RAB) with 35% C in the CR formulation resulted in the highest rutting resistance. This can be explained by the aged (stiff) nature of the RAB, leading to an increase in the rutting parameter. However, the addition of TF led to a decrease in rutting parameters towards C, signifying the influence of recycling agent in CR. Under unaged conditions, the addition of antioxidants had different effects depending on the antioxidant type. The rutting parameter for CRTFZ3, CRTFD0.25, and CRTFI0.1 was slightly reduced, which could be due to the ability of the antioxidant to reduce the STA effects. When considering the RTFO + 1 PAV aging conditions, the $G^*/\sin\delta$ of the CR binder increased. C binder presented a higher increment in the rutting parameter than the CRTF binder, which could be attributed to the presence of more virgin binder on C (100%) in comparison with CRTF and, therefore, more material susceptible to oxidative aging. In cases where antioxidants were utilized, two antioxidants (ZnDEC and Irganox 1010) provided lower rutting resistance compared to the CRTF binder after RTFO + 1 PAV aging, which can indicate their capability to reduce aging long-term, retarding the stiffness gain due to oxidative effects.

The primary focus of using antioxidants was to evaluate their efficacy in enhancing aging resistance. Therefore, the high-temperature rutting index (HRI) was employed to assess the effectiveness of the antioxidants in relation to the long-term performance of the binder. The HRI at 64 °C was calculated using Equation 4.1, and the results for each binder are presented in Figure 4.2.

$$HRI = \frac{G^*/sin\delta(RTFO + 1\ PAV)}{G^*/sin\delta(unaged)} \qquad \text{Equation 4-1}$$

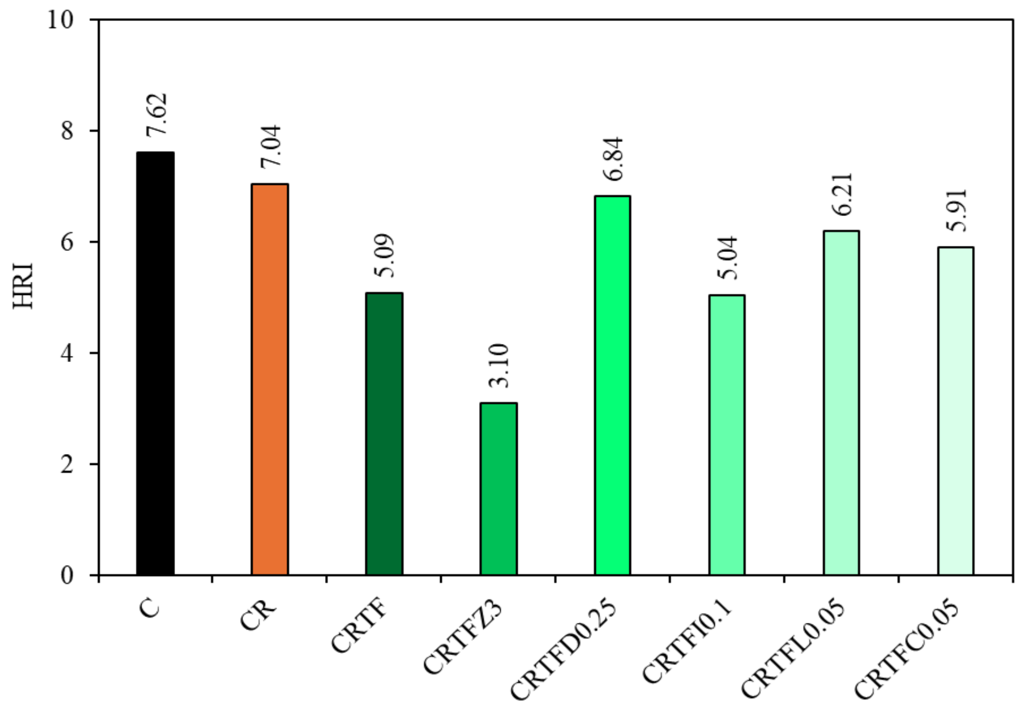


Figure 4.2 HRI results of asphalt binders at 64 °C.

Based on Figure 4.2, the HRI assessment of the C binder revealed a value of 7.62, which exceeds those of the other binders examined in this study. This result indicates that the control binder was more susceptible to aging than the other studied binders. The elevated HRI value of the control binder may be attributed to its composition, as it consists of 100% virgin binder, which tends to age more readily. However, blending the control binder with 65% RAB resulted in a noticeable decrease in the HRI to 7.04. This reduction can be attributed to the fact that RAB, having already undergone field-induced aging, exhibits less sensitivity to aging effects compared to the C binder.

Moreover, with the addition of TF, the HRI was further reduced. Different antioxidant types exhibited varying behaviors regarding aging resistance. ZnDEC outperformed all other antioxidants, achieving an HRI of 3.10. Its effectiveness in reducing aging in TF-modified binders has been supported by recent studies [13, 36, 59]. The superior performance of ZnDEC is likely due to its role as a peroxide decomposer, which reduces free radical formation and slows down the oxidation process.

Irganox 1010 provided an HRI value of 5.04, indicating a slight reduction in the aging susceptibility of CRTF. Its lower efficacy compared to ZnDEC may stem from its tendency to physically adsorb to the binder rather than chemically react, limiting its effectiveness against aging [60]. DLTDP did not demonstrate effectiveness as an antioxidant in the TF-modified binders despite being derived from chemical sources like ZnDEC and Irganox 1010. The formation of free radicals during aging hindered DLTDP's functionality, resulting in the poorest performance among the antioxidants tested [61].

Additionally, the plant-based antioxidants lignin and curcumin did not yield significant improvements in CRTF aging resistance, with HRI values of 6.21 and 5.91, respectively. This indicates their ineffectiveness in mitigating oxidative aging. Several studies have reported similar findings regarding the limited long-term performance enhancement of asphaltic materials by these plant-based antioxidants [62-64]. These studies highlighted that the interaction between these antioxidants and binders was primarily physical blending rather than a chemical reaction, which contributed to the lack of anti-aging effects. Overall, these findings emphasize the critical role of targeted antioxidant modifications in enhancing binder durability.

4.1.3 Mid-Temperature Cracking Performance

The mid-temperature cracking resistance of asphalt binders was evaluated using the Glover-Rowe (G-R) concept. The G-R parameters ($\frac{G^*(cos\delta)^2}{sin\delta}$) were measured for unaged and RTFO+1 PAV-aged binders at 45 °C and 10 rad/s, utilizing an 8-mm diameter geometry with a 2-mm testing gap on a Dynamic Shear Rheometer (DSR). Figure 4.3 presents the G-R parameters for each binder under both unaged and RTFO+ 1 PAV-aged conditions.

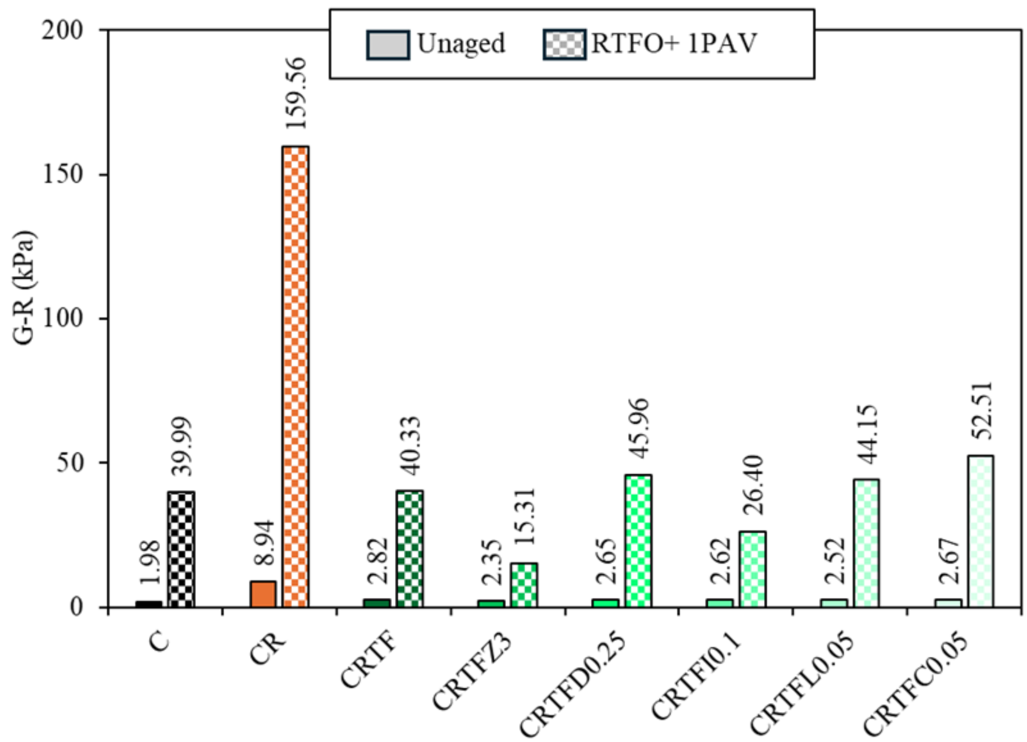


Figure 4.3 G-R Parameter for different binders at 45 °C.

It can be noticed that all binders met the G-R parameter criterion of ≤ 180 kPa [65]. Notably, the C binder exhibited the lowest G-R parameter value under unaged and RTFO + 1 PAV-aged conditions, indicating good resistance to mid-temperature cracking. In contrast, the G-

R parameter for the CR binder was significantly higher than those of the other binders in both unaged and aged conditions, signifying a greater susceptibility to mid-temperature cracking. The addition of TF to the CR binder softened the material, resulting in a lower G-R parameter value and enhanced resistance to mid-temperature cracking for the CR binder containing 65% RAB. This improvement was consistent across both unaged and RTFO + 1 PAV-aged conditions. Furthermore, under unaged conditions, different antioxidants provided mid-temperature cracking resistance comparable to that of the CRTF binder. However, after long-term RTFO + 1 PAV aging, the impact of the antioxidants became more pronounced. ZnDEC and Irganox 1010 yielded lower G-R parameter values than the CRTF binder, thereby enhancing mid-temperature cracking resistance. Conversely, the other three antioxidants were found to reduce cracking resistance, as indicated by their higher G-R parameter values.

To further assess the efficacy of each antioxidant in resisting oxidative aging of the binders under the unaged and RTFO + 1 PAV aged conditions, the Mid-Temperature Cracking Index (MCI) was calculated as shown in Equation 4.2, and MCI values of each of the binder blends are presented in Figure 4.4.

$$\boldsymbol{MCI = \frac{G - R(RTFO + 1\ PAV)}{G - R(unaged)}} \qquad \text{Equation 4-2}$$

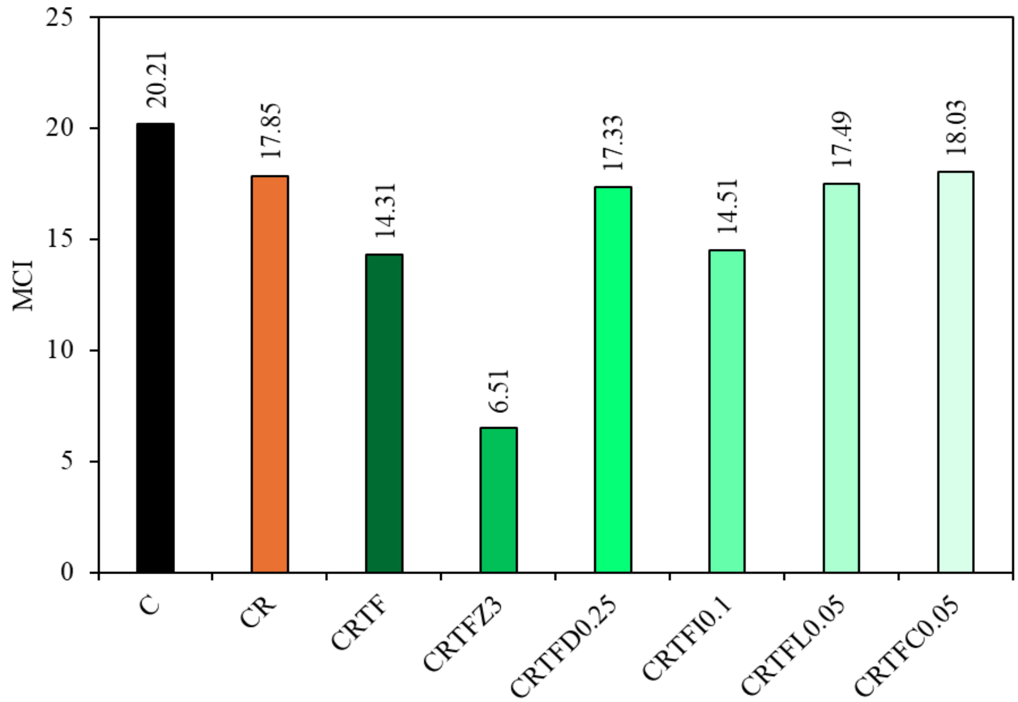
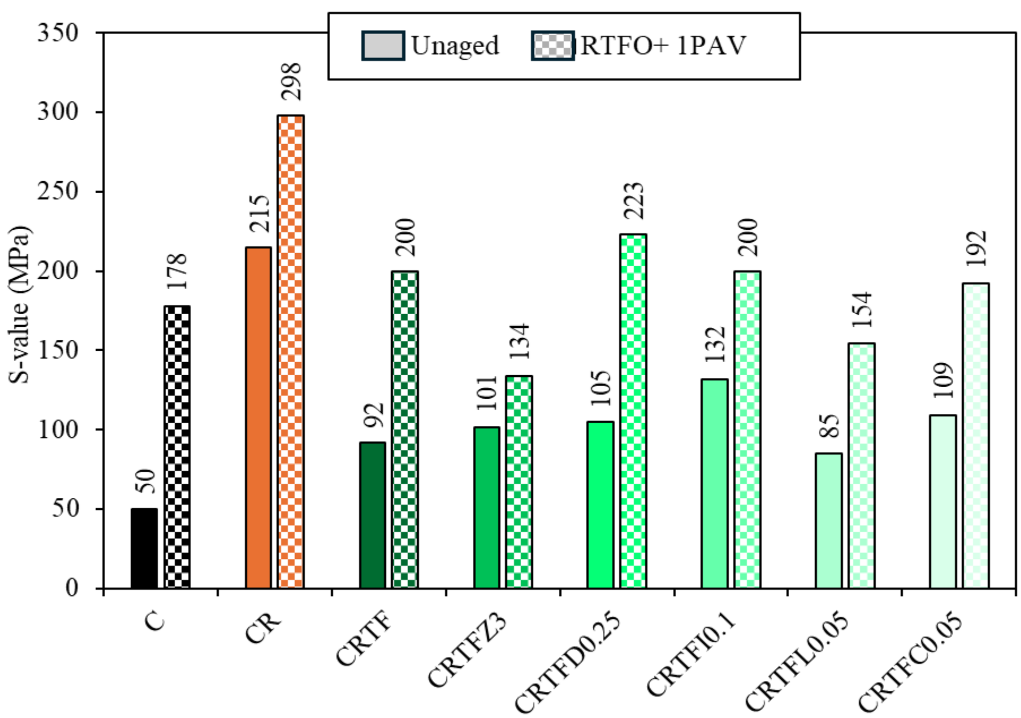


Figure 4.4 MCI results of asphalt binders at 45 °C.

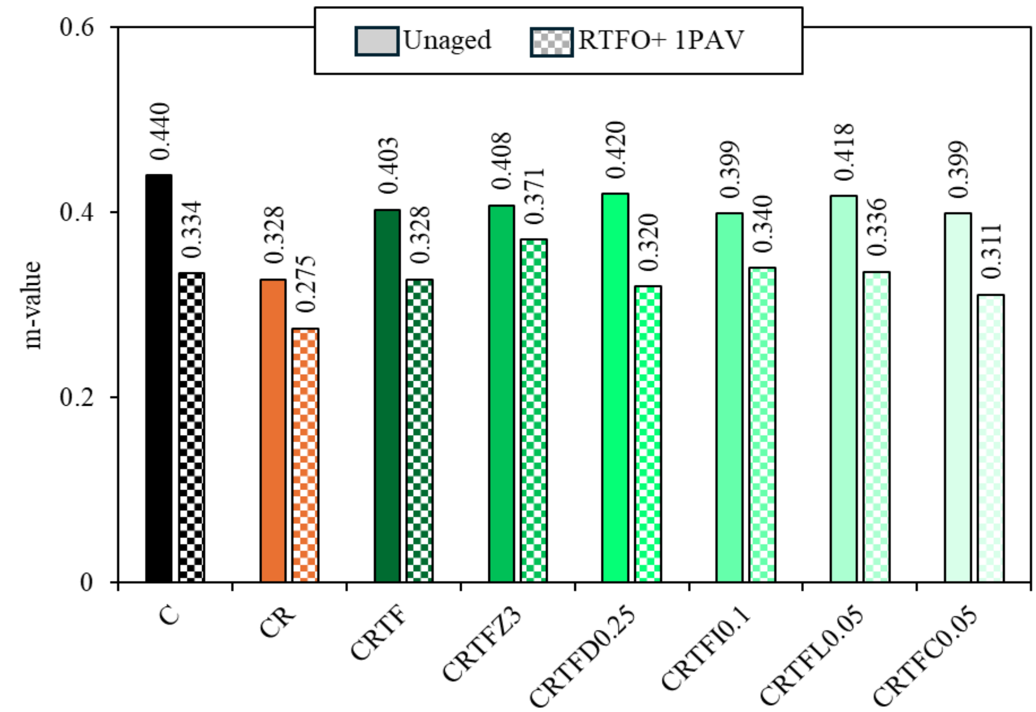
A similar trend to HRI is observed in each of the cases. The C binder exhibited the highest aging susceptibility according to the MCI, while the CR binder displayed a lower MCI. As mentioned before, this result can be attributed to CR binder composition, which consists of 65% RAB and 35% virgin binder. The RAB has already experienced field aging, making it less sensitive to further aging processes. Moreover, the use of RA-modified binder slightly lowered the MCI value. More importantly, using ZnDEC as an antioxidant further reduced the aging susceptibility of CRTF at mid-temperature. However, the other antioxidants, including Irganox 1010, which had a slightly better-aging resistance based on HRI, proved ineffective in preventing RA-modified binder oxidative aging at mid-temperature. This result emphasized that four antioxidants, including DLTDP, Irganox 1010, Lignin, and Curcumin, were not aging resistant at mid-temperature.

4.1.4 Low-Temperature Cracking Performances

The low-temperature cracking resistance of asphalt binders was evaluated at -28 °C following ASTM D6649 [43] using a BBR device. The stiffness, referred to as the S-value, and the relaxation constant, known as the m-value, were determined for the binders under both unaged and RTFO + 1 PAV aged conditions. The results are presented in Figure 4.5 a and b.



(a)



(b)

Figure 4.5 BBR test results at -28 °C a) S-value and b) m-value.

As shown in Figure 4.5 a, the C binder exhibited the lowest S-value in both unaged and RTFO + 1 PAV aged conditions. However, when considering the rate of change after aging, the C binder had a 256% increase, the highest among all tested binders, indicating its significant susceptibility to aging. In contrast, the CR binder displayed the highest stiffness but had the lowest increase in S-value (38%) after RTFO + 1 PAV aging, emphasizing its lower tendency to age. However, with the addition of TF, the increment rate of the S-value rose to 117%, indicating that the CR binder became more susceptible to aging. This heightened susceptibility of the TF-based RA is evident in this performance metric, particularly under the selected RTFO + 1 PAV aging cycle [9].

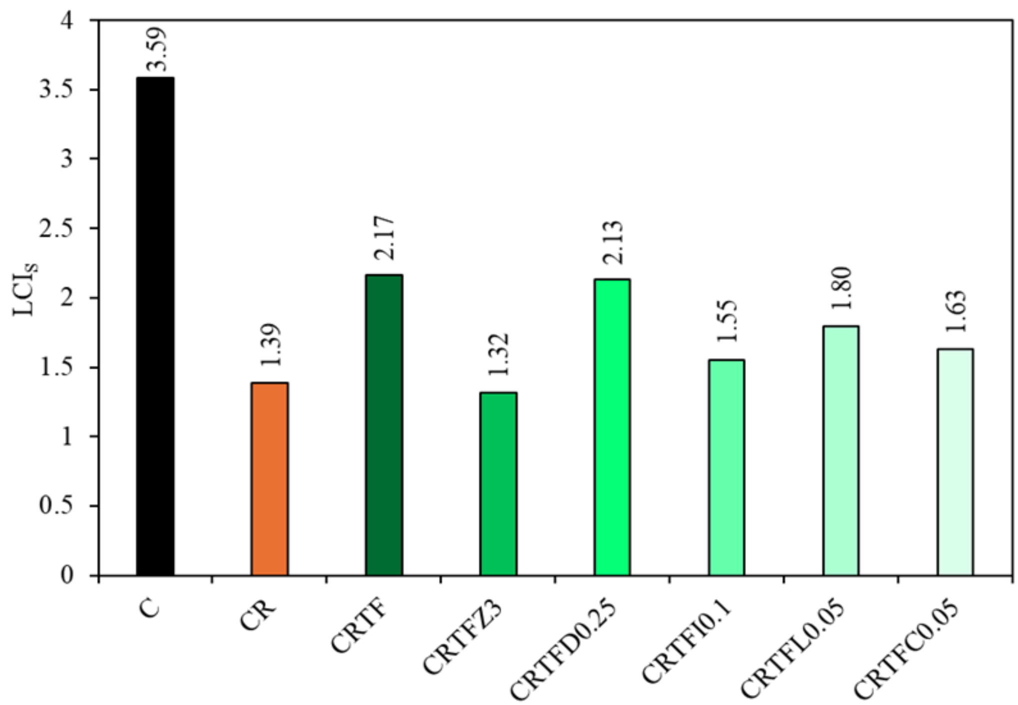
Furthermore, the four antioxidants—ZnDEC, Irganox 1010, Curcumin, and Lignin—demonstrated effectiveness in enhancing long-term performance, as indicated by the lower or similar S-values of these antioxidant-modified binders compared to CRTF after RTFO + 1 PAV aging. Additionally, the rate of increase in the S-value was significantly lower for the antioxidant-modified binders compared to CRTF, highlighting their enhanced efficacy as antioxidants based on the S-value.

Furthermore, the low-temperature performance measured as the m-value (Figure 4.5) indicated that the C binder had the highest m-value under unaged conditions, reflecting its superior resistance to low-temperature cracking. In contrast, the stiffer CR binder exhibited the lowest m-value, indicating the poorest performance among all the binders under unaged conditions. However, the addition of TF to the CR binder improved the m-value by 23%. Notably, the m-value for all antioxidant-modified binders was enhanced under unaged conditions, likely due to the softening effects of these antioxidants. After long-term aging, the m-value of the C binder decreased, experiencing the most significant drop of 24%. Although the CR binder showed a lower rate of decrease in m-value compared to the C binder, the addition of TF slightly increased the CR binder's aging susceptibility (16% versus 19%). It was found that the drop in m-value was lower for CRTFZ3 and CRTFI0.1 compared to CRTF, indicating that ZnDEC and Irganox 1010 effectively slowed down the aging process. In contrast, the other three antioxidants resulted in a greater decrease in m-value than CRTF itself, suggesting they were less effective in preserving the aging resistance of the binder.

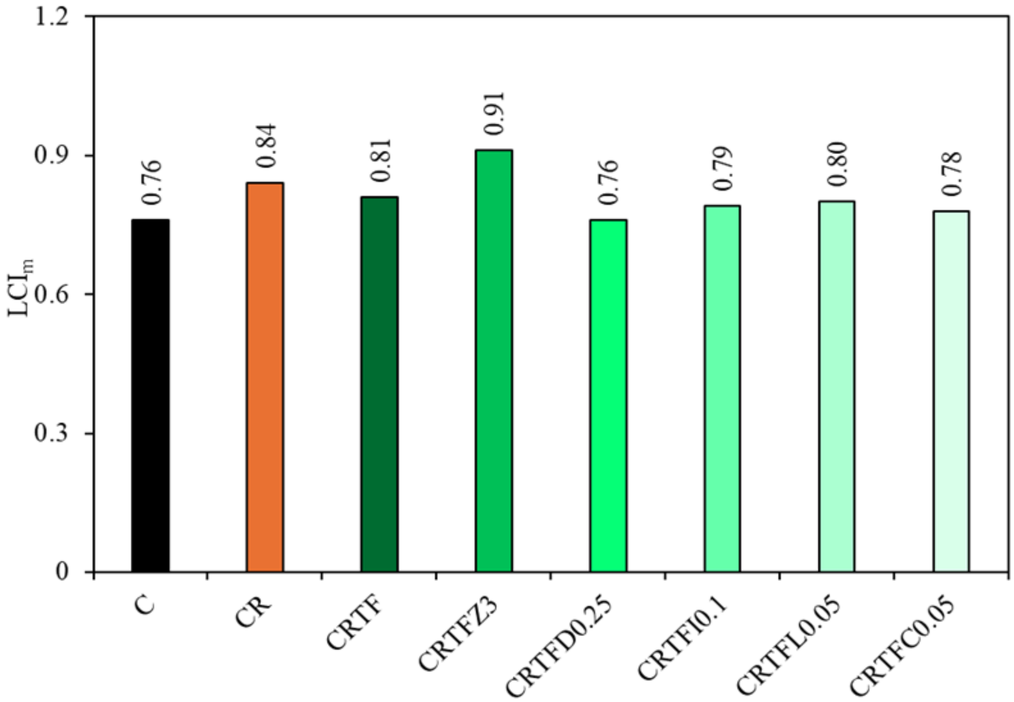
To further assess and quantify the effectiveness of each antioxidant in resisting oxidative aging of the binder modified with TF at low temperatures, we utilized two different indices: the low-temperature cracking indices based on S-value and m-value (LCI_S and LCI_m), as defined in Equations 4.3 and 4.4. Additionally, Figure 4.6 a and b present a comparison of these two indices for the various binders. It is to be noted that lower LCI_S and higher LCI_m are favorable for an antioxidant to be effective.

$$LCI_S = \frac{S - value(RTFO + 1\ PAV)}{S - value(unaged)} \quad \text{Equation 4-3}$$

$$LCI_m = \frac{m - value(RTFO + 1\ PAV)}{m - value(unaged)} \quad \text{Equation 4-4}$$



(a)



(b)

Figure 4.6 LCI results of asphalt binders at 28 °C a) LCI_S and b) LCI_m.

As shown in Figure 4.6 a, the aging index LCI_s is highest for the C binder, while in terms of LCI_m the same binder obtained the lowest value, indicating its greater susceptibility to aging. In contrast, the CR binder demonstrated better aging resistance, as reflected in its LCI_s and LCI_m value when compared to the C binder. However, the aging resistance of the CR binder declined with the incorporation of TF, showing that TF adversely affects long-term performance. The addition of all five antioxidants resulted in improved aging resistance when considering the stiffness-based parameter, LCIS. The binder modified with antioxidants exhibited lower LCIS values than the CRTF binder, indicating enhanced aging resistance. However, regarding the LCI_m, only ZnDEC effectively improved the long-term performance of the CRTF binder. The other antioxidants—DLTDP, Irganox 1010, Lignin, and Curcumin—did not enhance aging resistance based on LCI_m, particularly in low-temperature performance characterization. This suggests that each antioxidant possesses unique properties that must be thoroughly understood to optimize performance in asphalt binders. Such variability in antioxidant effectiveness has been widely documented in the literature [45, 51].

4.1.5 Summary of Antioxidant Effects on High-RAP Binders with RAs

In summary, the binder testing results focused on high-temperature rutting, mid-temperature cracking, and low-temperature cracking characterizations, utilizing a 65% RAP binder, TF-based RA, five different antioxidants, and a virgin binder. The findings indicate that the effectiveness of antioxidants in preventing oxidative aging of TF is specific to the type of antioxidant used. Among the various aging indices analyzed, two antioxidants—ZnDEC and Irganox 1010—enhanced the long-term performance of the TF-modified binders. In contrast, the other three antioxidants (DLTDP, Lignin, and Curcumin) generally proved ineffective. Notably, ZnDEC emerged as the most effective antioxidant, while DLTDP was identified as the least effective based on the results of the indices ranking presented in Table 4.2.

Table 4.2 Ranking of Antioxidant Modified Binders.

Rank	**HRI**	**MCI**	**LCI_s**	**LCI_m**
1	CRTFZ	CRTFZ	CRTFZ	CRTFZ
2	CRTFI	CRTFI	CRTFI	CRTFL
3	CRTFC	CRTFD	CRTFC	CRTFI
4	CRTFL	CRTFL	CRTFL	CRTFC
5	CRTFD	CRTFC	CRTFD	CRTFD

These findings underscore the necessity of thoroughly evaluating the impact of antioxidants on different binder formulations and carefully considering their suitability for specific applications in asphalt pavement construction and recycling practices. Additionally, to accurately mimic field conditions, it is crucial to understand the effect of antioxidants on mixture-level performance, particularly when using TF-based RA and RAP. Therefore, the best and worst-performing antioxidants (ZnDEC and DLTDP) identified in the binder level used mixture level analysis. Subsequently, mechanical performance characterizations of both modified and unmodified asphalt mixtures were conducted, assessing mid-temperature cracking resistance, rutting performance, and moisture damage resistance.

4.2 Mechanical Performance Testing and Characterization of Asphalt Concrete

4.2.1 Mid-Temperature Cracking Performance of Asphalt Mixtures

SCB-IFIT, in accordance with AASHTO T 393 [66] testing protocol, was followed for mid-temperature cracking performance evaluation. SCB test specimens were placed inside the environmental chamber of a Universal Testing Machine (UTM) maintained at 25° C for two hours. Then, each sample was placed and tested in the loading frame of a three-point bending configuration. Monotonic loading was applied to the specimen at a 50 mm/min rate until failure. Displacement and corresponding reaction force, as shown in Figure 4.7, were recorded during testing and were used further in cracking performance analysis. The load (P) *vs.* load-line displacement (u) curve obtained from the SCB testing process was used to infer about the cracking performance of specimens. For that, several parameters were obtained with the output results.

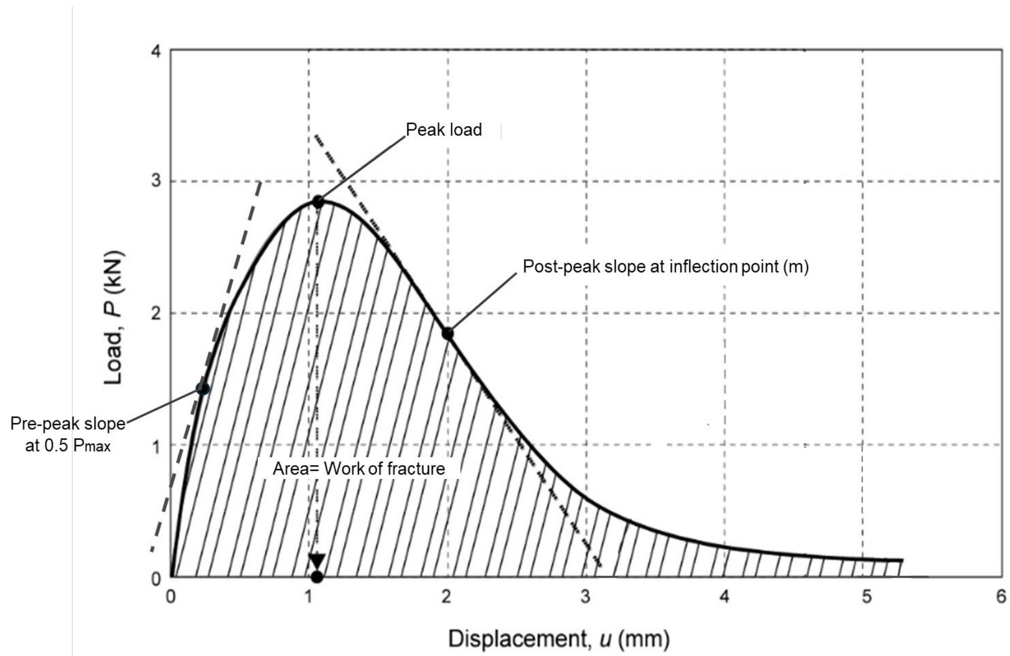


Figure 4.7 Load *vs.* displacement curve and output parameters.

⇒ Peak load: the maximum load supported by the specimen.

⇒ Pre-peak slope: a measure of the material initial stiffness (no damage) obtained dividing the load P at one-half of the Pmax by its correspondent displacement in the first part of the load-displacement curve.

⇒ Fracture Energy, *Gf*: The fracture energy Gf is calculated by dividing the work of fracture (the area under the load–displacement curve) by the ligament area (the product of the ligament length and the thickness of the specimen) of the SCB specimen prior to testing.

Eventually, the flexibility index (FI) was adopted as a parameter to evaluate the cracking performance of the mixes, as presented in Equation 4-5.

$$FI = A \frac{G_f}{|m|} \qquad \text{Equation 4-5}$$

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

Figure 4.8 represents the load and displacement relationship for each of the types of mixtures utilized in this study under STA and LTA conditions. Table 4.3 shows the main parameters used to evaluate the effects of additives on the high-RAP mixture cracking performance.

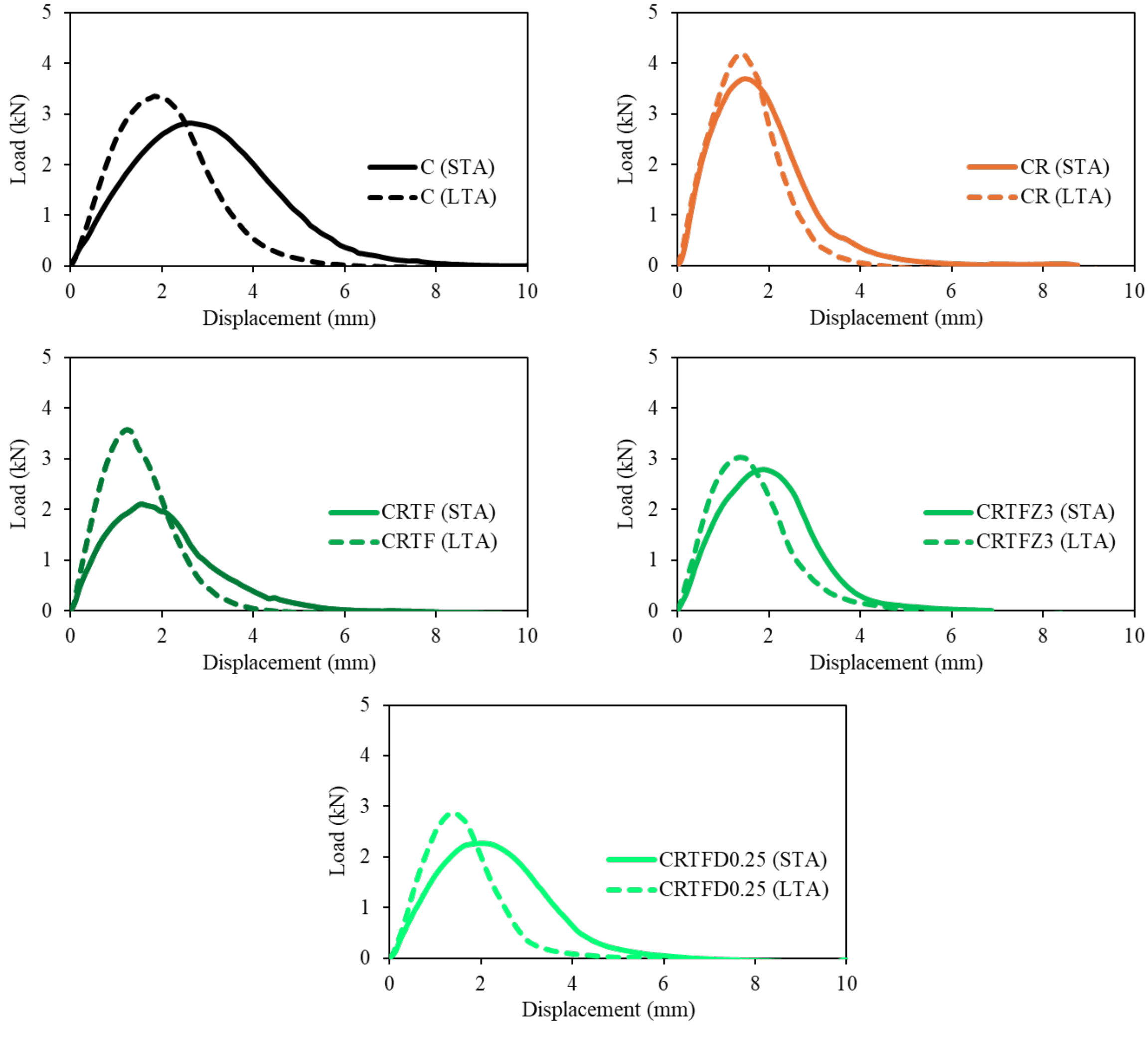


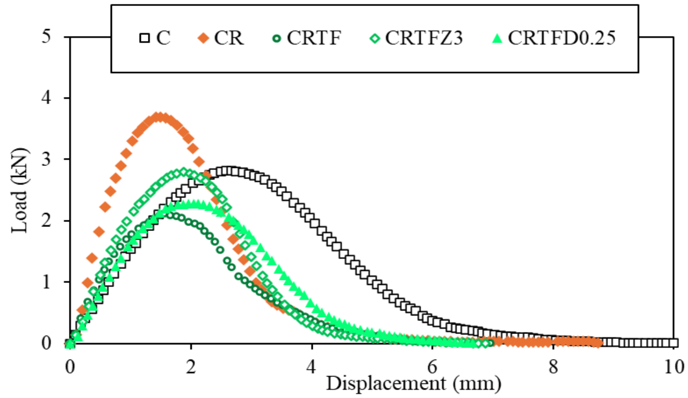
Figure 4.8 Load and displacement relationship for each mixture.

Table 4.3 SCB-IFIT parameters obtained for each studied mixture at STA and LTA conditions.

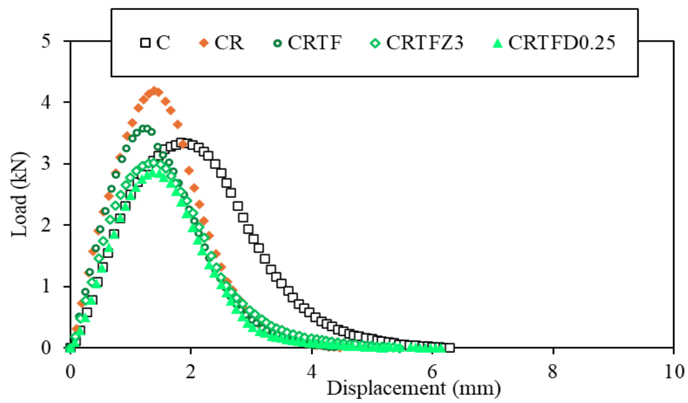
Mixture	Pre-peak Slope at 0.5 Pmax	SD	Peak Load (kN)	SD	Fracture Energy (J/m^2)	SD	FI	SD
				STA Condition				
C	1.47	0.32	2.81	0.32	3278.33	526.00	32.50	0.70
CR	3.84	0.10	3.72	0.20	2477.50	275.00	11.80	0.90
CRTF	2.35	0.29	2.49	0.26	1712.00	266.00	13.20	2.20
CRTFZ3	2.09	0.30	2.79	0.32	2271.17	124.00	10.40	3.00
CRTFD0.25	1.53	0.15	2.33	0.30	2227.17	289.00	15.70	3.30
				LTA Condition				
C	2.96	0.54	3.46	0.13	2923.83	243.00	11.80	2.10
CR	4.12	0.94	4.23	0.60	2395.33	250.00	5.40	1.67
CRTF	3.64	0.73	3.64	0.30	2073.00	322.00	7.30	2.12
CRTFZ3	3.58	0.52	3.07	0.26	1973.33	225.00	7.90	2.05
CRTFD0.25	2.99	0.06	2.94	0.06	1737.50	117.00	6.40	2.90

Note: SD = Standard Deviation

It can be observed that at LTA, all the mixtures, except for CR, presented a higher peak load before failure as well as a steeper pre-peak slope (representing initial stiffness prior to cracking) and post-peak slope compared to their behavior at STA, which is expected due to the brittle behavior of aged materials. These results emphasized the effect of aging on asphaltic materials. The CRTF shows the greatest susceptibility to aging, when comparing its results at STA and LTA conditions. It is clear that TF had a softening effect when comparing the curves of CRTF with CR mixtures. When antioxidants were added, CRTF mixtures presented a slighter change in the peak load and initial stiffness at LTA in comparison with their behavior at STA, which indiates potential antioxidant effects on the mixtures. A more comprehensive comparison between all the mixtures is provided in Figure 4.9 where each mixture with and without the use of RA and antioxidants are compared to each other.



(a)



(b)

Figure 4.9 Load and displacement relationships for all mixtures a) STA b) LTA conditions.

At the STA, there is an evident softening effect of TF-based RA. A drastic reduction in peak load is observed along with a decrease in the initial stiffness. As seen on both STA and LTA conditions, the initial slope of CR is much steeper than the C mixture, indicating a higher initial stiffness for the high-RAP recycled mixture. The presence of antioxidants also reduced the initial stiffness and peak load compared with the CR mixture, potentially due to the softening effect of the additives. However, the post-peak behavior of the C mixture exhibits a much more ductile behavior than the CR mixtures, indicating the mixture has a better ability to dissipate energy through deformation before final failure.

At LTA, the softening effect of the TF was not observed on CR mixtures, as the mixtures presented similar initial stiffness. It a slight increase in the peak load and a decrease in initial stiffness after LTA was observed for mixtures using antioxidants in comparison with mixtures without antioxidants (CR and CRTF). These results could reflect the effect of antioxidants leading to better long-term performance. Furthermore, there was not much change in the shape of the curve on the post-peak behavior, which means that there was no gain in the material's ductility. To further verify the effects of additives on a high-RAP mixture, the FI was obtained and presented in Figure 4.10.

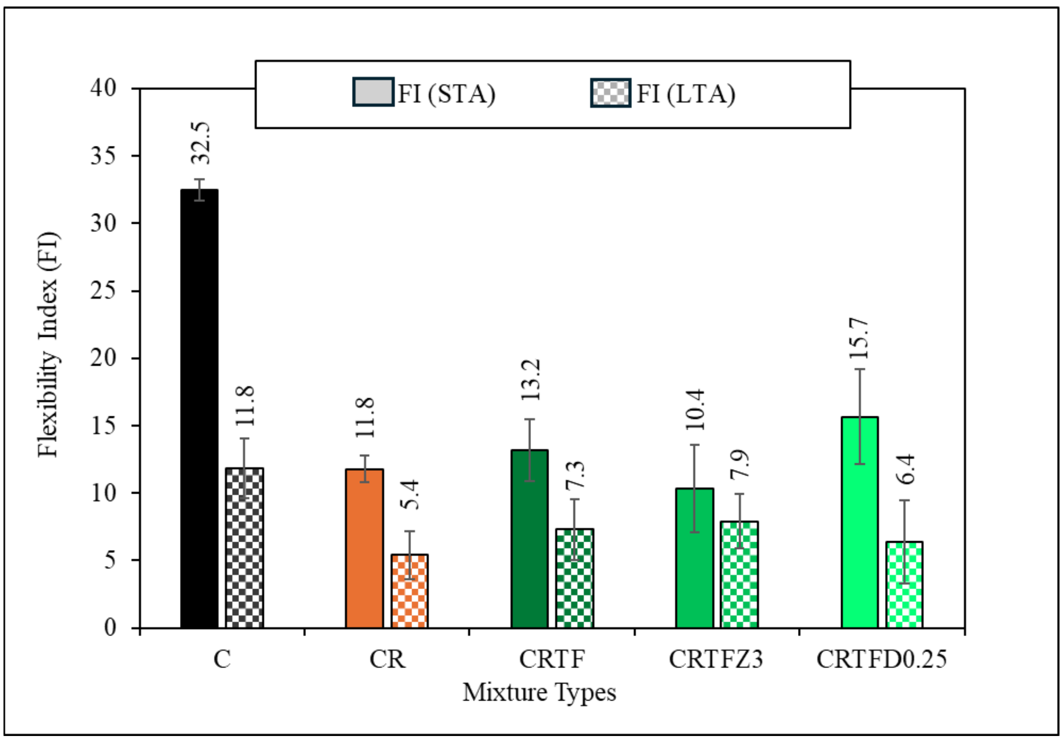


Figure 4.10 Flexibility index values for samples after STA and after LTA.

As expected, it is observed that the CR mixture had a lower FI than the C mixture, indicating its higher susceptibility to cracking. Similar results are attributed to the performance after long-term aging conditions: for the C mixture, the FI value dropped from 32.5 to 11.8, and for the CR mixture, the FI value dropped from 11.8 to 5.4. The prevalence of highly aged materials in the CR mixture resulted in a lesser drop in FI from STA to LTA compared to that of the virgin mixture.

With respect to the effect of adding TF to CR mixtures, CRTF presented a slight increase in the average value of FI in comparison with CR. It is important to mention that at the binder level, the addition of TF had a significant effect in the cracking resistance (according to the G-R parameter). Generally, the phenomena of dispersibility and diffusivity, as described by Carpenter and Wolosick [67], can be used to understand the working mechanism of RA, including TF-based RAs in softening the RAP materials. Based on this phenomenon, the RA forms a lower viscosity layer over the aged asphalt binder and begins to penetrate it. As the RA penetrates, equilibrium is eventually reached, resulting in the soft nature of aged binders and mixtures. The softening effects of RA could be verified based on the changes observed in the pre-peak slope (initial stiffness) and peak loads, but not at the same level of change as observed in the binder phase. Questions remain regarding the level of dispersibility and diffusivity of RA on the mixture scale in comparison with the binder scale. Moreover, the use of RAP could have led to some variability on the gradation. Furthermore, the interactions of aggregates and binder plays an important role in the adhesive fracture, especially at the post-peak behavior, where there is severe damage due to crack evolution. The effects of aggregate gradation and interactions of aggregate and binder can greatly affect the FI values [68, 69] . Those effects are not considered in the binder scale tests or for the dosage of RA. Therefore, a correlation between binder results considering the G-R parameter and mixture results considering FI might not be ideal.

Considering the small differences observed with the addition of TF and antioxidants to CR mixtures, the significance of using each of the additives in the high-RAP asphalt mixture is yet to be justified. For that purpose, Tukey's Honestly Significance Difference (HSD) test was followed at a confidence level of 95%, and grouping was provided for each mixture. Tukey's HSD test was adopted after confirming that the p-value obtained after the Analysis of Variance (ANOVA) test was less than 0.05 as such values of p resemble there exists at least one significant difference between the groups utilized. Tukey's HSD was performed on the combined set of STA and LTA data. The result of that analysis is presented in Table 4.4. Five distinct groups (A, B, C, D, and E) were identified in this case.

Table 4.4 Summary of Tukey's HSD test results (α=0.05) for FI considering STA and LTA conditions together

Mixture Types	**FI (STA)**	**FI (LTA)**
	Grouping	
C	A	C
CR	C	E
CRTF	B, C	D, E
CRTFZ3	**C, D**	**D**
CRTFD0.25	B	E

It can be observed that the studied mixtures had different groupings at STA and LTA conditions, showing the significant effect of LTA on FI values. Also, even though small changes were observed, it was possible to identify different groupings in the statistical analysis. The mixture C had a different grouping under STA conditions than the other mixtures. After LTA, it shared the group with most of the recycled mixture in their STA condition. CR and CRTF share the same groups under STA and LTA conditions, which raises questions on the efficacy of TF to enhance cracking resistance according to the FI parameter. Also, CRTF shared different grouping at STA and LTA conditions, which also shows that the TF might degrade at LTA, leading to more significant changes on FI values. On the contrary, mixture CRTFZ3 shared the same grouping before and after LTA, signifying that the anti-aging effect provided by ZnDEC for these mixtures was significant. This result was not observed for the CRTFD0.25. The results of these analyses showed that at the given dosages, the effectiveness of TF-based RA in enhancing the performance of high-RAP mixtures might be limited to STA conditions. Furthermore, the effect of antioxidants on preventing oxidative aging is type-specific; therefore, careful consideration must be taken while selecting an antioxidant.

4.2.2 Rutting and Moisture Damage Resistance of Asphalt Mixtures

AASHTO T 324 [58] protocol was utilized to assess the rutting and moisture damage resistance of the mixtures utilized in this study. Tests were performed at 50°C with the application of wheel loading of 52 passes/min inside the water. The resulting deformation was recorded by the transducers attached to the machine. For this test, 20,000 passes were provided as the stopping criterion to record the full-depth rutting. The resulted rut depth with respect to the number of cycles is presented in Figure 4.11. From those test outputs, the number of cycles at 12.5 mm rut depth was used to assess the rutting susceptibility of the asphalt mixtures, and the stripping inflection point (SIP) was used to estimate the moisture susceptibility of asphalt mixtures. Figure 4.12 shows the HWTT parameters for five types of mixtures.

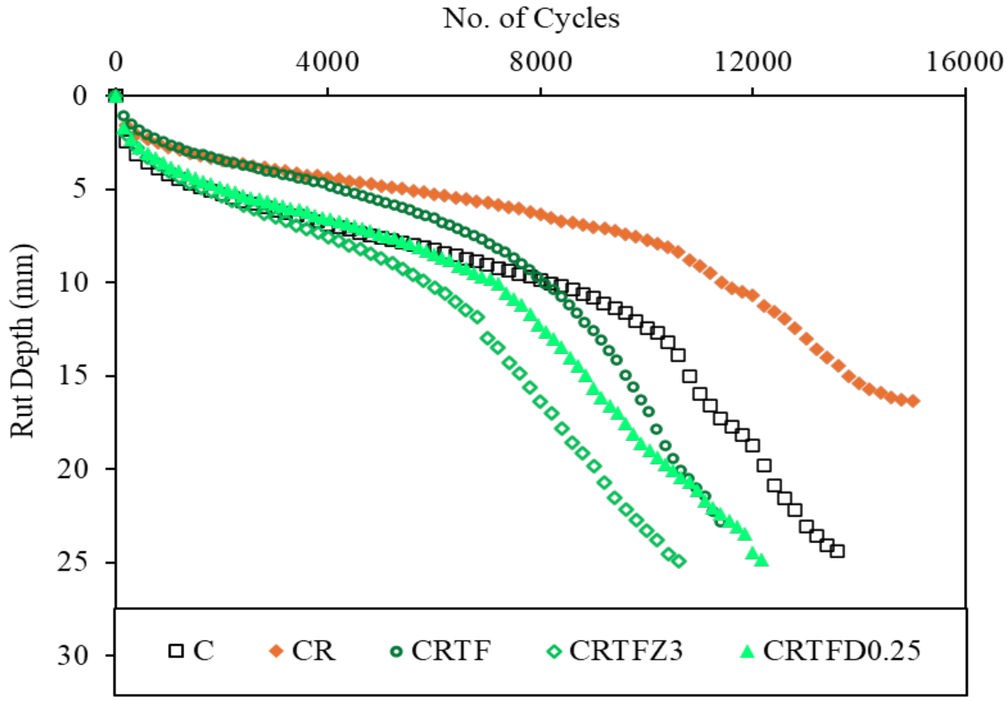


Figure 4.11 Rut depth versus no. of cycles for all mixtures.

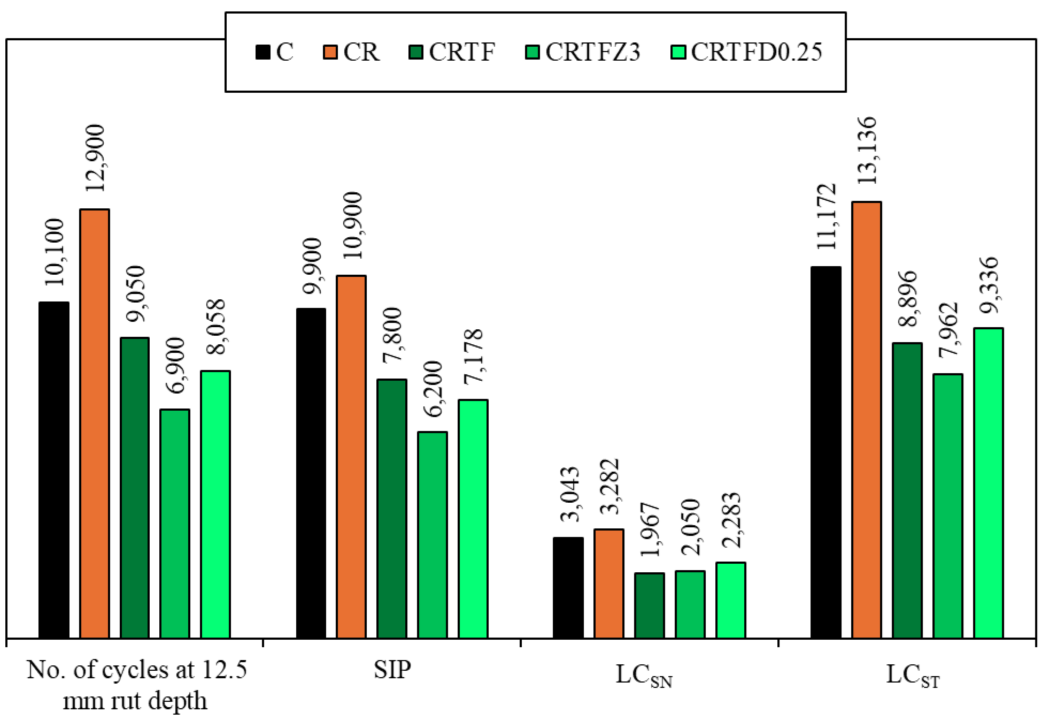


Figure 4.12 HWTT results.

It is observed that the CR mixture had a relatively higher number of cycles at the RD of 12.5 mm. It is common knowledge that higher content of RAP results in higher rutting resistance [8, 70]. A higher stripping inflection point was also observed for the CR mixture, which can be correlated to one of the important findings by Al-Qadi et al. [71], stating that the moisture exposure of RAP in the environment lessens moisture damage. Even though the C mixture presented a significantly higher FI under STA in comparison with the other mixtures, the HWTT results showed that this mixture underwent more cycles to reach the 12.5 mm rutting depth than modified recycled mixtures (CRTF, CRTFZ3, CRTFD0.25). The C mixture also had relatively higher SIP, signifying a higher resistance to moisture.

However, it is important to mention that there is a combined effect of rutting and stripping during the HWTT. To separate the viscoplastic deformation due to the load application and stripping, additional parameters were obtained based on Yin et al. [72]. The authors introduced a parameter named stripping number (LC_{SN}), which represents the maximum number of loading cycles resisted by the mixture before adhesive failure occurs between the binder and the aggregates. For that reason, any deformation until the LC_{SN} can be primarily correlated with viscoplastic deformation. The additional number of cycles (LC_{ST}) to reach the typical rut-depth failure criteria of 12.5 mm combines the effects of stripping and viscoplastic deformation. It can be seen that the mixtures with the addition of TF-based RA presented the lowest LC_{SN} values, indicating that an earlier adhesive failure occurred for these mixtures. The relatively lesser resistance to moisture damage might be due to the prevalence of a hydroxyl functional group in TF-based RA [73, 74]. The prevalence of the hydroxyl functional group results in mixtures that are more susceptible to moisture. The mixes with ZnDEC obtained lower SIP, LC_{SN}, and LC_{ST} values. Those results can be related to the insolubility of ZnDEC in asphalt binder, due to which sufficient coatings were not obtained between ZnDEC particles and binder [47]. Insoluble ZnDEC might degrade the adhesion and bonding between aggregates and binder, making the mixture more susceptible to moisture. On the other hand, the DLTDP-modified mixture (CRTFD0.25) showed a comparable moisture damage resistance to CRTF, implying that the use of DLTDP does not hamper the moisture damage resistance of CRTF.

Chapter 5 Concluding Remarks and Future Works

The research outcomes of Phase I of this study clearly outlined that the TF-based RAs were more prone to oxidative aging than the other groups of RAs. However, simultaneous utilization of antioxidants prevented such oxidative aging and enhanced the long-term performance of the TF-based RA-modified asphalt binders and mixtures. Therefore, in the continuity of Phase I of this project, this phase further explores the wider aspects of using antioxidants with TF-based RA. To this end, five different antioxidants were utilized alongside the high RAP binder modified with TF-based RA, and rheological performance tests were conducted. Additionally, based on the outcomes of the binder testing results, two antioxidants were used simultaneously with the high RAP mixture modified with TF-based RA, and mechanical performance testing was performed to understand the effect of such additives at the mixture level. The important results obtained from the test result analysis are presented below.

- Based on the PG grading approach, a dosage of 3.5% TF-based RA was able to restore the PG grade of high-RAP binder blends to the level of targeted virgin binder. The addition of antioxidants also provided a softening effect to the recycled binder, and hence, special precautions should be taken on the dosage selection to retain the targeted PG.
- Rheological testing results focusing on high-temperature rutting, mid-temperature, and low-temperature cracking performances showed that TF-based RA enhanced the cracking resistances of the studied high-RAP binder blends at mid and low temperatures. However, rutting resistance was lowered due to the softening effect of RA. Antioxidants did not have a considerable effect on these performances. Moreover, the effect of antioxidants in enhancing long-term performance was type and case specific. Using ZnDEC as an antioxidant provided superior long-term performance, followed by Irganox 1010; however, DLTDP and other

antioxidants proved ineffective in enhancing the long-term performance of TF-based RA-modified high RAP binder.

- The softening effect of TF-based RA in the mixture level was also observed, especially considering the pre-peak behavior of the mixtures under SCB tests and under STA conditions; however, such a softening effect was not prominent after LTA. Additionally, FI used as the parameter to assess the cracking resistance of mixtures did not show a statistically significant enhancement of cracking resistance towards the virgin mixture with the use of TF-based RA at a given dosage. The effects of antioxidants were evident when comparing STA and LTA results. Using ZnDEC as an antioxidant in asphalt mixtures resulted in similar performances in both STA and LTA conditions, demonstrating the efficacy of the additive to oxidative aging.
- The HWTT results revealed that the use of TF-based RA might lead to premature moisture damage, which further compromised the overall rutting resistance of the mixture under the HWTT conditions.

Overall, the effect of RA and antioxidants was greatly observed at the binder level. However, the effects of those materials at the given dosages in the mixture level tests were not significant. It some softening was observed at the STA, but the LTA effect of TF-based RA is questionable at the mixture scale. The degree of blending at the mixture level test, the gradation variability induced by field collected RAP materials, and the interactions of TF-modified binders and aggregates at mixture scale need further investigation.

Future Works

The conclusions drawn from this study are the results evidenced by the laboratory testing of the asphalt binders and mixtures. The main questions remaining arise from the efficacy of those materials at the mixture scale tests. The RA dosage based on binder PG approach might not be enough to capture other mechanisms that affects mixture performance. The aging conditions, RAP variability, and degree of blending in the mixture level needs further investigation to optimize the use of rejuvenator agents and antioxidants, and lead to improved performance of high-RAP mixtures under STA and LTA conditions.

References

1. Brett A. Williams, J. Richard Willis, and J. Shacat, *Asphalt Pavement Industry Survey on Recycled Materials and Warm-Mix Asphalt Usage: 2019.* 2019.

2. Bastola, N.R., et al., *Effect of Antioxidant Additives and Recycling Agents on Performance of Asphalt Binders and Mixtures - Phase I.* 2024, Nebraska Department of Transportation.

3. Tran, N., et al., *Effect of a Recycling Agent on the Performance of High-RAP and High-RAS Mixtures: Field and Lab Experiments.* Journal of Materials in Civil Engineering, 2017. **29**(1).

4. Moniri, A., et al., *Laboratory study of the effect of oil-based recycling agents on high RAP asphalt mixtures.* International Journal of Pavement Engineering, 2019. **22**(11): p. 1423-1434.

5. Zhang, Y. and H.U. Bahia, *Effects of recycling agents (RAs) on rutting resistance and moisture susceptibility of mixtures with high RAP/RAS content.* Construction and Building Materials, 2021. **270**.

6. Haghshenas, H.F., et al., *Effect of Recycling Agents on the Resistance of Asphalt Binders to Cracking and Moisture Damage.* Journal of Materials in Civil Engineering, 2021. **33**(10).

7. Haghshenas, H.F., et al., *Relationship between colloidal index and chemo-rheological properties of asphalt binders modified by various recycling agents.* Construction and Building Materials, 2022. **318**.

8. Mivehchi, M., H. Wen, and L. Cantrell, *Systematic evaluation of effects of recycled materials and mix design parameters on the rutting and cracking performance of asphalt mixes.* Journal of Cleaner Production, 2022. **330**.

9. Bastola, N.R., H.F. Haghshenas, and M. Khedmati, *Research on High-RAP Mixtures with Rejuvenator-Field Implementation*. 2021, Nebraska Department of Transportation.

10. Ziari, H., et al., *The effect of rejuvenators on the aging resistance of recycled asphalt mixtures.* Construction and Building Materials, 2019. **224**: p. 89-98.

11. Lu, D.X., M. Saleh, and N.H.T. Nguyen, *Effect of rejuvenator and mixing methods on behaviour of warm mix asphalt containing high RAP content.* Construction and Building Materials, 2019. **197**: p. 792-802.

12. Ahmad, M., M. Khedmati, and H. Haghshenas Fatmehsari, *Using Crude Vegetable-Based Oils and Antioxidants to Improve the Performance of Asphalt Binders.* Transportation Research Record: Journal of the Transportation Research Board, 2023.

13. Haghshenas, H.F., et al., *Increasing the efficacy of recycling agents with simultaneous addition of zinc diethyldithiocarbamate as an antioxidant.* Construction and Building Materials, 2021. **271**.

14. Fatmehsari, H.H. and R. Rea, *Use of Antioxidants and Recycling Agents for Improving Long-Term Performance of Asphaltic Materials* 2021, NuTech Ventures Inc: US.

15. Haghshenas, H.F., R. Rea, and D.F. Haghshenas, *Aging resistance of asphalt binders through the use of zinc diethyldithiocarbamate.* Petroleum Science and Technology, 2019. **37**(22): p. 2275-2282.

16. *Glossary of Terms for Balanced Design of Asphalt Mixtures*, in *Transportation Research Circular*. 2022.

17. Hidalgo, A.E., et al., *The Influence of Reclaimed Asphalt Pavement on the Mechanical Performance of Bituminous Mixtures. An Analysis at the Mortar Scale.* Sustainability, 2020. **12**(20).

18. Zaumanis, M., et al., *Influence of six rejuvenators on the performance properties of Reclaimed Asphalt Pavement (RAP) binder and 100% recycled asphalt mixtures.* Construction and Building Materials, 2014. **71**: p. 538-550.

19. Zhang, R., et al., *Comprehensive Laboratory Evaluation of Recycling Agent Treated Plant-Produced Asphalt Mixtures.* Transportation Research Record: Journal of the Transportation Research Board, 2022. **2676**(9): p. 620-634.

20. Martin, A.E., et al., *Evaluating the Effects of Recycling Agents on Asphalt Mixtures with High RAS and RAP Binder Ratios*. 2019.

21. NCAT, *Researchers Explore Multiple Uses of Rejuvenators*. 2014, National Center for Asphalt Technology, Auburn, AL.

22. Haghshenas, H.F., et al., *Chemical Characterization of Recycling Agents.* Journal of Materials in Civil Engineering, 2020. **32**(5).

23. Al-Saffar, Z.H., et al., *A review on Rejuvenating Materials Used with Reclaimed Hot Mix Asphal.* Canadian Journal of Civil Engineering, 2021.

24. Arámbula-Mercado, E., et al., *Evaluation of recycling agent dosage selection and incorporation methods for asphalt mixtures with high RAP and RAS contents.* Construction and Building Materials, 2018. **158**: p. 432-442.

25. Haghshenas, H., Gabriel Nsengiyumva, Yong-Rak Kim, and a.S.A. Kommidi Santosh, *Research on High-RAP Asphalt Mixtures with Rejuvenators - Phase II*. 2019.

26. Martin, A.E., et al., *The effects of recycling agents on asphalt mixtures with high RAS and RAP binder ratios.* 2015.

27. Nazzal, M.D., et al., *Multi-scale evaluation of the effect of rejuvenators on the performance of high RAP content mixtures.* Construction and Building Materials, 2015. **101**: p. 50-56.

28. Shen, J., S. Amirkhanian, and B. Tang, *Effects of rejuvenator on performance-based properties of rejuvenated asphalt binder and mixtures.* Construction and Building Materials, 2007. **21**(5): p. 958-964.

29. Haghshenas, H.F., et al., *Research on High-RAP Asphalt Mixtures with Rejuvenators - Phase II*. 2020.

30. Ahmad, M., M. Khedmati, and H. Haghshenas Fatmehsari, *Using Crude Vegetable-Based Oils and Antioxidants to Improve the Performance of Asphalt Binders.* Transportation Research Record: Journal of the Transportation Research Board, 2023. **2677**(10): p. 592-604.

31. Bastola, N.R., et al., *Investigating the Field Performance of High- Recycled Asphalt Pavement Mixtures with Bio-oil Recycling Agent.* Transportation Research Record: Journal of the Transportation Research Board, 2024.

32. Sirin, O., et al., *State of the Art Study on Aging of Asphalt Mixtures and Use of Antioxidant Additives.* Advances in Civil Engineering, 2018. **2018**(1).

33. Apeagyei, A.K., *Laboratory evaluation of antioxidants for asphalt binders.* Construction and Building Materials, 2011. **25**(1): p. 47-53.

34. Zhang, Y., et al., *Effects of antioxidants on chemical and rheological properties of asphalt binders from different crude oil sources.* Construction and Building Materials, 2024. **449**.

35. Wu, W., et al., *Investigation on Thermo-Oxidative Aging Properties of Asphalt Binder with Hindered Phenolic Antioxidant.* Journal of Testing and Evaluation, 2018. **46**(2): p. 624-630.

36. Adwani, D., et al., *Interpreting the effectiveness of antioxidants to increase the resilience of asphalt binders: A global interlaboratory study.* Construction and Building Materials, 2023. **366**.

37. Cong, P., et al., *Physical and rheological properties of asphalt binders containing various antiaging agents.* Fuel, 2012. **97**: p. 678-684.

38. Xu, S., et al., *Investigation of Aging Resistance of Organic Layered Double Hydroxide/Antioxidant Composite-Modified Asphalt.* ACS Sustainable Chemistry & Engineering, 2022. **11**(1): p. 267-277.

39. Tauste, R., et al., *Understanding the bitumen ageing phenomenon: A review.* Construction and Building Materials, 2018. **192**: p. 593-609.

40. Li, X., L. Shan, and Y. Tan, *Analysis of different indices for high- and low-temperature properties of asphalt binder.* Construction and Building Materials, 2015. **83**: p. 70-76.

41. Glover, C.J., Davison, R.R., Domke, C.H., Ruan, Y., Juristyarini, P., Knorr, D.B. and Jung, S.H., *Development of a new method for assessing asphalt binder durability with field validation*. 2005, Texas Department of Transportation.

42. Rowe, G.M., *Evaluation of the Relationship between Asphalt Binder Properties and Non-Load Related Cracking* Journal of the Association of Asphalt Paving Technologists, 2011. **80**.

43. Haghshenas, H., et al., *Research on High-RAP Asphalt Mixtures with Rejuvenators and WMA Additives.* Nebraska Department of Transportation (NDOT), SPR-P1(15) M016, 2016.

44. Nsengiyumva, G., et al., *Mechanical-Chemical Characterization of the Effects of Type, Dosage, and Treatment Methods of Rejuvenators in Aged Bituminous Materials.* Transportation Research Record: Journal of the Transportation Research Board, 2020. **2674**(3): p. 126-138.

45. Cong, P., B. Chen, and H. Zhao, *Coupling effects of wasted cooking oil and antioxidant on aging of asphalt binders.* International Journal of Pavement Research and Technology, 2019. **13**(1): p. 64-74.

46. Wang, S., W. Huang, and A. Kang, *Evaluation of Aging Characteristics of High-Viscosity Asphalt: Rheological Properties, Rutting Resistance, Temperature Sensitivity, Homogeneity, and Chemical Composition.* Journal of Materials in Civil Engineering, 2021. **33**(7).

47. Ahmed, M., M. Khedmati, and H.F. Haghshenas, *Using Crude Vegetable-Based Oils and Antioxidants to Improve the Performance of Asphalt Binders.* Transportation Research Record: Journal of the Transportation Research Board, 2023.

48. Apeagyei, A.K., W.G. Buttlar, and B.J. Dempsey, *Investigation of Cracking Behavior of Antioxidant-Modified Asphalt Mixtures (With Discussion).* Journal of the Association of Asphalt Paving Technologists, 2008. **77**.

49. Martin, K.G., *Laboratory evaluation of antioxidants for bitumen.* 1968.

50. Flieger, J., et al., *Antioxidants: Classification, Natural Sources, Activity/Capacity Measurements, and Usefulness for the Synthesis of Nanoparticles.* Materials (Basel), 2021. **14**(15).

51. NDOT, *Superpave Asphaltic Concrete*. 2016, Nebraska Department of Transportation.

52. ASTM, *ASTM D2172-Standard Test Methods for Quantitative Extraction of Asphalt Binder from Asphalt Mixtures*. 2018.

53. D1856, A., *Standard Test Method for Recovery of Asphalt from Solution by Abson Method*. 2021.

54. ASTM, *ASTM D5404-Standard Practice for Recovery of Asphalt Binder from Solution Using the Rotary Evaporator*. 2021.

55. ASTM, *ASTM D2872-Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt Binder (Rolling Thin-Film Oven Test)*. 2022.

56. ASTM, *ASTM D6521-Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)*. 2022.

57. Kim, Y.R., et al., *Long-Term Aging of Asphalt Mixtures for Performance Testing and Prediction: Phase III Results*. 2021.

58. *AASHTO T 324-17: Standard Method of Test for Hamburg Wheel-Track Testing of Compacted Hot Mix Asphalt (HMA)*. 2017.

59. Haghshenas, H.F., R. Rea, and D.F. Haghshenas, *Aging resistance of asphalt binders through the use of zinc diethyldithiocarbamate.* Petroleum Science and Technology, 2019: p. 1-8.

60. An, X., et al., *Effects of Commercial Antioxidants on Aging Resistances of Asphalt Binders.* Advances in Materials Science and Engineering, 2022. **2022**: p. 1-16.

61. Karahadian, C.a.L., R.C., *Evaluation of the mechanism of dilauryl thiodipropionate antioxidant activity.* Journal of the American Oil Chemists' Society, 1988.

62. Yu, J., et al., *Experimental study of soda lignin powder as an asphalt modifier for a sustainable pavement material.* Construction and Building Materials, 2021. **298**.

63. Hu, D., et al., *Performance and mechanism of lignin and quercetin as bio-based anti-aging agents for asphalt binder: A combined experimental and ab initio study.* Journal of Molecular Liquids, 2022. **359**.

64. Abe, A.A., et al., *Spicy Bitumen: Curcumin Effects on the Rheological and Adhesion Properties of Asphalt.* Materials (Basel), 2021. **14**(7).

65. Newcomb, D.E., et al., *Test Methods to Quantify Cracking Resistance of Asphalt Binders and Mixtures*. 2021, Minnesota Department of Transportation.

66. *AASHTO T 393: Standard Method of Test for Determining the Fracture Potential of Asphalt Mixtures Using the Illinois Flexibility Index Test (I-FIT)* 2022.

67. Carpenter, S.H. and J.R. Wolosick, *Modifier Influence in the Characterization of Hot Mix Recyled Material.* Transportation Research Record, 1980. **777**.

68. Rivera-Pérez, J.J. and I.L. Al-Qadi, *Impact of Asphalt Concrete Properties on the Illinois Flexibility Index Cracking and Hamburg Wheel Tracking Test Rutting Potential.* Journal of Transportation Engineering, Part B: Pavements, 2023. **149**(4).

69. Sreedhar, S. and E. Coleri, *Effects of Binder Content, Density, Gradation, and Polymer Modification on Cracking and Rutting Resistance of Asphalt Mixtures Used in Oregon.* Journal of Materials in Civil Engineering, 2018. **30**(11).

70. Imaninasab, R., L. Loria-Salazar, and A. Carter, *Integrated performance evaluation of asphalt mixtures with very high reclaimed asphalt pavement (RAP) content.* Construction and Building Materials, 2022. **347**.

71. Al-Qadi, I.L., et al., *Impact of High RAP Contents on Structural and Performance Properties of Asphalt Mixtures*. 2012, Illinois Department of Transportation.

72. Yin, F., et al., *Novel Method for Moisture Susceptibility and Rutting Evaluation Using Hamburg Wheel Tracking Test.* Transportation Research Record: Journal of the Transportation Research Board, 2014. **2446**(1): p. 1-7.

73. Yousefi, A.A., et al., *Performance of warm asphalt mixtures containing reclaimed asphalt pavement, an anti-stripping agent, and recycling agents: A study using a balanced mix design approach.* Construction and Building Materials, 2023. **363**.

74. Haghshenas, H., et al., *Effect of Softening Additives on the Moisture Susceptibility of Recycled Bituminous Materials Using Chemical-Mechanical-Imaging Methods.* Journal of Materials in Civil Engineering, 2018. **30**(9): p. 04018207-1 - 04018207-10.