Effect of Chemical Composition of Bio- and Petroleum-Based Modifiers on Asphalt Binder Rheology

Punit Singhvi 1,*, Javier J. García Mainieri 1, Hasan Ozer 2, Brajendra K. Sharma 3 and Imad L. Al-Qadi 1

1 Illinois Center for Transportation, University of Illinois at Urbana-Champaign, Champaign, IL 61820, USA; jjg5@illinois.edu (J.J.G.M.); alqadi@illinois.edu (I.L.A.-Q.)
2 School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ 85281, USA; hasan.ozer@asu.edu
3 Prairie Research Institute–Illinois Sustainable Technology Center, University of Illinois Urbana-Champaign, Champaign, IL 61820, USA; bksharma@illinois.edu
* Correspondence: singhvi3@illinois.edu

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Featured Application: This study provides guidelines for asphalt binder modifier selection to produce low modulus binders (softer binders) to meet desired quality. The research focuses on reducing expected cracking susceptibility of modified asphalt binders after long-term aging. The study recommends the development of engineered modifiers for specific paving applications.

Abstract: In recent years, increased use of recycled asphalt materials (RAP) has created a need for softer binders to compensate stiffer binder coming from RAP. Economic alternatives, like recycled oils and proprietary bio-based oils, can be potential modifiers that will reduce the dependence on petroleum-based alternatives. However, there is limited information on the long-term rheological performance of binders modified with proprietary modifiers. These modifiers are chemically complex and their interaction with binders further complicates the binder chemistry. Therefore, the objective of this study was to evaluate the impact of modifier chemistry on modified binders’ long-term cracking potential. A base binder of Superpave Performance Grade (PG) 64-22 was used to develop PG 58-28 binder using six different modifiers. An unmodified PG 58-28 was included for a comparative analysis. A few modified binders rheologically outperformed the base binder and others performed similarly. The modifier derived from recycled engine oil showed the worst performance. Chemical analysis indicated that the best performing modified binders had significant amounts of nitrogen in the form of amines. On the other hand, poor performing modified binder had traces of sulfur. Additionally, modifiers with lower average molecular weights appeared to have a positive impact on the performance of aged binders.

Keywords: Asphalt modification; modifier chemistry; long-term aging; asphalt rheology; phase angle; delta T.

1. Introduction

Asphalt concrete (AC) is one of the most commonly used pavement materials in the United States and worldwide. More than 400 million tons of AC are produced in the US annually, which requires 20 million tons of asphalt binder [1]. AC mixture is a heterogeneous composite of asphalt binder, mineral aggregates, and air voids. The performance of AC mixtures is greatly affected by aggregate characteristics, binder chemistry and rheology, mixture volumetrics, and aging. Aging of AC is a continuous process; it is dominated by volatilization and oxidation of asphalt binder in the...
short- and long-term, respectively. Volatilization in binders refers to loss of lighter fractions when exposed to high temperatures and occurs during the production and construction stages. Oxidation in binders is caused by photo-oxidation and thermal oxidation during pavement’s service-life [2]. Aging increases AC brittleness that may result in cracking. Hence, binders with superior aging resistance characteristics may delay AC cracking and increase pavement service life.

Asphalt binder (AB) is an important component for the construction of AC pavements. It is currently produced from the fractional distillation of crude petroleum at refineries. In recent years, the increasing use of harder and aged recycled asphalt materials in pavement applications has significantly increased the need for softer ABs [1]. Logistical limitations and the cost of refineries to produce softer ABs instead of products of higher financial value, result in a shortage of soft straight-run or unmodified AB in the market [3].

To overcome the current demand for softer ABs, traditional petroleum-based “softeners”, like AB flux and aromatic oils are blended with straight-run AB [4]. Blending “softeners” with readily available products, like recycled oils and bio-based oils, provides an opportunity to manufacture required AB economically and reduce the dependence on petroleum-based products.

A variety of proprietary products are available to modify AB to achieve softer grades. They are used with limited knowledge about their long-term performance. Poor durability and/or extended cracking issues have been identified when re-refined engine oil bottoms (ReOB) and waste engine oils (WEO) have been blended in AB [5–9]. On the other hand, use of certain bio-based oils in ABs increases the oxidation potential which makes pavements vulnerable to cracking over the long-term [10]. This limits or restricts the use of these products. However, there are some specialized bio-based softeners that have shown enhanced long-term performance of ABs and reduced cracking potential [11]. Therefore, the potential of bio-based modifiers to produce softer PGs is investigated in this study. A ReOB-based modifier was included in this study for comparison purposes.

Superpave Performance Grading (PG) is a rheology-based system, currently used to trade and specify AB in the United States. The PG system has limitations in identifying long-term performance of modified asphalt binder (MAB). The use of bio-based modifiers can significantly impact AB chemistry and rheology without changing its Superpave grading. The current challenges for the market-entry of MAB are: (i) their complex chemistry, (ii) their uncertain long-term rheological performance, and (iii) the lack of a robust grading system that can discriminate them to ensure long-term performance.

Low-temperature performance of AB is critical to prevent adverse effects of thermal cracking. Use of recycled asphalt pavements (RAP) – obtained from milling of old asphalt layers – and recycled asphalt shingles (RAS) – typically obtained from either tear-off shingles or manufactured waste shingles – has increased in AC pavement and requires adequately-performing binders to avoid premature cracking [12–18]. The $\Delta T_r$ parameter has been used to assess the low-temperature induced cracking performance of AB [19,20]. Low-temperature ductility of AB has been related to pavement cracking performance [21]. Glover et al. [22] developed a rheological parameter based on dynamic shear rheometer (DSR) frequency sweep tests, that strongly correlates to low-temperature ductility; a simplification of this parameter is known as the Glover–Rowe (GR) parameter [23]. Literature provides $\Delta T_r$ and GR parameters as good low-temperature cracking indices [19]. Therefore, frequency sweeps and bending beam rheometer (BBR) tests were considered in this study to obtain them and evaluate asphalt binder’s expected cracking performance.

Limitations of using Superpave’s $|G’|\sin\delta$ to assess intermediate-temperature cracking susceptibility of asphalt binders are well reported [3,24]. Black space diagrams may provide insights to the rheological properties that drive cracking susceptibility at intermediate temperature.

Asphalt cracking is further aggravated with aging. Field aging depends on geographical location and environmental factors and varies along the pavement depth. The current pressure aging vessel (PAV) aging for 20 hours at 90, 100, or 110 °C and a pressure of 2.1 MPa is not sufficient to represent realistic long-term aging of binders [22,25]. Meanwhile, researchers are investigating 40-hour PAV as an alternate solution [26]. Aging up to 60-hour PAV has also been used to evaluate AB long-term
performance [27]. Laboratory aging conditions of 20-hour, 40-hour, and 60-hour PAV were investigated in this study.

Chemical composition of AB plays an important role in durability of asphalt pavements [28]. Modifiers’ chemical composition can affect AB compatibility and susceptibility to oxidation, changing its rheological properties and long-term performance [3,27,29,30]. Chemical characterization of ABs and MABs was conducted, in many studies, using elemental analysis, gel permeation chromatography (GPC), Fourier-transform infrared spectroscopy (FTIR), and thin-layer chromatography flame ionization detection (TLC-FID). Carbonyl and sulfoxide indices from FTIR have been widely used to track oxidation and evaluate the impacts of long-term aging on binder characteristics [31–35]. Molecular weight tends to increase with aging in binders and has been reported by several authors [30,33,36–38]. Asphalt binders are composed of maltenes and asphaltenes and their interaction with aging drives the mechanical properties of the binder [28,30,38–41].

There is a need for understanding the impact of various modifiers on ABs and their resulting long-term field performance. Simple laboratory protocols with reasonable and consistent predictive capabilities of field performance are essential to optimize modifier selection and dosage. Therefore, the objective of this study was to evaluate modifiers’ chemical characteristics and their impact on MAB’s long-term cracking potential. The fundamental relationship between chemical composition of modifiers and its effect on MAB’s rheological properties was investigated.

2. Materials and Methods

2.1. Materials

Various sources of bio-based products were selected to produce “softer” MABs with equivalent or better long-term performance as the binder obtained from crude oil sources. Softer binders are defined as binders with lower modulus and lower PG. Such binders are commonly used to control cracking in colder climates or neutralize RAP’s relatively stiff binder. PG 58-28 was the target binder grade to be produced using commonly available PG 64-22 as base binder, referred to as S1. The base binder was selected and sampled from a refinery terminal in Illinois, USA. Five bio-based AB modifiers and one ReOB modifier available in the US industry were procured for modification. The names of the modifiers used in this study are kept confidential and are designated as shown in Table 1 from hereon. Table 1 lists the modifier type as provided by the suppliers. MABs were labelled with base AB’s designation and modifier’s designation followed by dosage (% by weight) of modifier in the blend, e.g., S1-A-3.5 represents MAB obtained from the base binder S1 blended with 3.5% (% by weight) of modifier “A”. A softer unmodified binder, PG 58-28 (labelled as S5), was also included in the study as a benchmark for modified binders.

| Modifier | Type 1 |
|----------|--------|
| A        | NA 2   |
| C        | Fatty acid derivative |
| D        | Bio-oil blend |
| E        | Modified vegetable oil |
| G        | Glycol amine |
| K        | ReOB |

1 as reported by suppliers (from US); 2 not provided by the suppliers.

2.2. Asphalt Binder Modification

Modifier blending methodology, binder heating cycles, temperatures applied during splitting process, and storage are discussed in this section. A high shear mixer (Cafarmo BDC1850) with a Heidolph PR31 ringed propeller (33-mm diameter fan) was used for blending. The blending was performed at a steady temperature of 130 ± 10 °C. The temperatures were maintained using a Glas-
Col LLC heating mantle capable of handling 1-L capacity aluminum can. The methodology is illustrated in Figure 1.

Figure 1. Modifier blending approach (a) labelled cans of base binder divided in five sets; (b) 3.8L cans split into 6-1.0L cans; (c) shear mixer for blending and modifier addition; (d) modified binder split into 4-24 mL cans; and (e) 3-24 mL cans from different sets combined to produce materials for all aging conditions.

The following were the steps for modifying binders used for chemical and rheological characterization:

1. PG 64-22 binder was sampled from the refinery terminal in 110-3.8 L cans. They were labelled from 1 to 110 in the order they were collected. The base binder was then grouped in five different sets as shown in Figure 1a.
2. Binder from each set was split to 6 cans of around 500 g each (Figure 1b). Each can was heated to 135 °C for 2 hours to reach a flowing state and was stirred prior to splitting. The split samples were then stored for modification.
3. Before modification, the split base binder (S1) was heated for 30 min in a heating mantle (Figure 1c) to reach 130 ± 10 °C to ensure that material was steadily flowing prior to blending.
4. The modifier was added (weight measured with a 0.01 g readability scale), the propeller was inserted half-way into the depth of the material and was set to 1,000 rpm for 20 min. During blending, the temperature was maintained at 130 ±10 °C and formation of vortices was prevented to avoid air bubbles in the blend.
5. After blending, the MAB was divided into 4-24 mL cans (Figure 1d).
6. Steps 3 to 5 were repeated for the binders from different sets mentioned in Step 1 for obtaining representative samples.
7. Later, 3-24 mL cans from different batches of each MAB were combined to proceed with aging conditioning (Figure 1e).

Aging conditions used in the study were: Unaged (UA), Rolling Thin-Film Oven (RTFO) in accordance with American Association of State Highway and Transportation Officials (AASHTO) specification T240-13, 20-hour Pressure Aging Vessel (PAV) including vacuum degassing and in accordance with AASHTO specification T28-12, 2PAV and 3PAV. 2PAV and 3PAV conditions were obtained by running continuous 40-hour and 60-hour PAV cycles, respectively. Once samples reached their required aging conditions, they were stored in small 30 mL cans until tested to avoid multiple heating cycles. To avoid changes in chemical and rheological properties, cans once heated for testing were not re-used. Same treatment was given to the unmodified base binder S1 and unmodified reference binder S5.
2.3. Modifier Chemistry Experimental Program

2.3.1. Elemental Analysis

Elemental analyses of modifiers were conducted in an Exeter Analytical (Chelmsford, MA, USA) CE-440 elemental analyzer. The proportions of carbon, hydrogen, nitrogen, and sulfur (CHNS) elements in the material’s composition were expressed in percent. The proportion of oxygen (O) was obtained by subtracting CHNS percentage from 100.

2.3.2. Chemical Functional Groups

Thermo Nicolet Nexus 670 FTIR spectrometer was used to detect the chemical functional groups present in modifiers in the range of wavenumbers 600-4,000 cm\(^{-1}\). Data was collected at a resolution of 4 cm\(^{-1}\) with number of scans set to 128. Three replicates were tested for each modifier. The method was based on attenuated total reflection (ATR).

2.3.3. Molecular Weight Analysis

The molecular weight analysis was conducted using GPC. The system consists of a Waters 2695 separation module connected to two Styragel HR1 SEC columns (7.8 mm × 300 mm) in series followed by a Waters 2414 RI detector and a computer with Empower Pro and data acquisition software. Samples of 3% w/w were prepared in tetrahydrofuran (THF), a carrier solvent with a flow rate of 1.0 mL/min and an injection volume of 20 μL; they were filtered using a 0.45 μm millipore polytetrafluoroethylene (PTFE) syringe filter to remove suspended particulates. To detect analytes, a constant flow of fresh eluent was supplied to the column via a pump.

The resulting chromatographic data was processed for number-average molecular weight (\(M_n\)), weight-average molecular weight (\(M_w\)), and polydispersity index (PDI) using Equations (1)–(3), respectively. The molecular weights were calculated based on the component molecular weights (\(M_i\)) determined from the retention time calibration curve and signal intensities (\(N_i\)).

\[
M_n = \frac{\sum M_i N_i}{\sum N_i} \quad (1)
\]

\[
M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} \quad (2)
\]

\[
PDI = \frac{M_w}{M_n} \quad (3)
\]

The retention time calibration curve was developed by fitting log-scale molecular weights to their retention time for standard material with known molecular weights using a 3-degree polynomial. The fitted curve was then used to measure the molecular weights of unknown modifiers using the chromatographic data. The distributions with shorter retention times correspond to larger molecular size whereas longer retention times represent smaller sizes. The molecular weights are reported in Daltons.

2.3.4. Binder Fractionation

Two percent (weight by volume) solutions of the modifiers were prepared in dichloromethane and filtered through a 0.45 μm millipore PTFE syringe filter to remove insoluble suspended particles from the solution. The suspended particles are referred to as residue from hereon. The sample solution (1 μL) was spotted on chromrods coated with a thin film of silica gel, using a microsyringe. The separation of bitumen into four generic fractions: saturates, aromatics, resins, and asphaltenes (SARA) was performed in a three-stage development process using n-heptane, toluene, and THF. The chromrods were dried for 10 min and humidified in NaNO\(_2\) for 10 min between each development. The chromrods were scanned with an Iatroscan MK-5 analyzer (Iatron Laboratories Inc., Tokyo,
Japan) with a flame ionization detection (FID), which provided chromatograms with peaks for SARA composition.

One of the used modifiers (G) was insoluble in dichloromethane. However, the modifier dissolved in water, acetone and methanol and hence the sample was prepared in methanol for performing the test.

2.4. Binder Rheology Experimental Program

Rheological characterization of binders included determining Superpave performance grade, $\Delta T_c$, and frequency sweep test parameters using a dynamic shear rheometer (DSR). Two replicates were tested for each rheological test and an average value was reported. AASHTO-intra-laboratory precision limits were obeyed. Specifically, in the case of frequency sweeps, the coefficient of variation was limited to 7% on any complex modulus measurement. All DSR measurements were performed in a Kinexus KNX2712 equipment with an active hood for temperature control while the BBR measurements were performed on a Cannon instrument.

The modifier dosage was selected to achieve similar PG for all modified binders in this study. Superpave system of grading is the current method of selecting binders in the US. Even though the binders tested for this study (except the base binder and one of the modified binders) would be assigned the same grading by this system, their chemistry could affect their rheological characteristics and susceptibility to oxidation; hence, it may affect their long-term performance. Given that the same base binder (S1) was used, the differences reported in the study’s experimental program were caused by the modifiers.

2.4.1. Superpave Performance Grading (PG)

All the binders used in the study were tested for Superpave PG. The tests were performed in accordance with AASHTO specifications: T315-19 (DSR) and T313-19 (BBR). Continuous PGs (true grades) were also determined.

2.4.2. $\Delta T_c$ Parameter

BBR measurements for PAV-aged samples were obtained for PG. Additionally, BBR measurements were recorded for all samples at 2PAV-aged and 3PAV-aged conditions in accordance with AASHTO T313-19 specification.

$\Delta T_c$ was computed using the following Equation (4):

$$\Delta T_c = PG_{Stiffness} - PG_{m-value}$$

where $PG_{Stiffness}$ and $PG_{m-value}$ are the temperatures at which samples pass PG criteria for stiffness and slope of stiffness curve (relaxation), respectively. $PG_{m-value}$ at all aging conditions and $PG_{Stiffness}$ value at PAV condition (except for K-modified binder) were interpolated as stated in [20]. $PG_{Stiffness}$ value at 2PAV and 3PAV conditions, and K-modified binder at all aging conditions, were extrapolated using the same equation.

2.4.3. Frequency Sweep Test

Frequency sweeps were performed after short conditioning (10 cycles of 0.1% strain at 15 °C and a frequency of 0.5–0.61 rad/s). Complex shear modulus ($G^*$) and phase angle ($\delta$) were obtained at all frequencies for all samples at UA, RTFO, PAV, 2PAV, and 3PAV. Data was measured in isotherms of 15 °C, 25 °C and 35 °C. An additional 5 °C isotherm was included for UA and RTFO-aged samples to ensure crossover (when phase angle $\delta$ is 45 degrees) data were measured. Eighteen data points were collected per isotherm in the frequency range from 1.00 rad/s to 62.83 rad/s at constant shear strain of 1.6% for UA, 1.2% for RTFO and PAV-aged samples, and 1.0% for 2PAV and 3PAV samples.

These strains were selected to ensure measurements within linear viscoelastic range (LVER) of the samples. Harmonic distortion between strain excitations and stress responses was lower than 1% for all measurements. In addition, measured torque was in the operational range of equipment for all
sweeps performed. Additionally, a built-in sequence to verify whether measurements for each sample were taken in the LVER was incorporated before the isotherms.

Data from different isotherms were then manually shifted to match G* at 15 °C (reference temperature) to create master curves. Polynomial fitting was performed to obtain the presented black space diagrams.

Glover–Rowe Parameter (GR)

GR parameter was computed using Equation (5):

\[ GR = \frac{G^* (\cos \delta)^2}{\sin \delta} \]  

(5)

G* and δ are the complex shear modulus and phase angle at 15 °C and 0.005 rad/s. G* and δ at 15 °C and 0.005 rad/s were obtained from measured data. In some cases, the data were extrapolated using polynomial fits from master curves and black space diagrams.

3. Results

This section presents the results from chemical compositional testing of the modifiers and rheological testing of the modified and base binders.

3.1. Chemical Characterization of Modifiers

3.1.1. Elemental Analysis

The results from elemental analysis are presented in Table 2. Modifiers A, D, and E show similar elemental composition of carbon, hydrogen, nitrogen and oxygen with additional sulfur in E (0.33%). Modifier K has slightly higher carbon (79.7%) and hydrogen (12.7%) content but is lower in oxygen (5.7%) compared to A, D, and E. Modifier K also has higher sulfur (0.98%) content than E. Modifier C has relatively higher nitrogen (3.5%) and oxygen (14.9%) and is low on Carbon (70.1%) in comparison to A, D, E, and K. Modifier G possesses very different composition compared to all other modifiers. Its elemental oxygen (33.1%) and nitrogen (9.0%) contents are the highest while the carbon (47.9%) is the lowest compared to other modifiers.

| Sample | C (%) | H (%) | N (%) | O (%) | S (%) |
|--------|-------|-------|-------|-------|-------|
| A      | 77.3  | 11.9  | 0.4   | 10.4  | 0.001 |
| C      | 70.1  | 11.5  | 3.5   | 14.9  | 0.004 |
| D      | 76.1  | 11.8  | 0.8   | 11.3  | 0.03  |
| E      | 77.1  | 11.5  | 0.6   | 9.9   | 0.33  |
| G      | 47.9  | 10.0  | 9.0   | 33.1  | 0.00  |
| K      | 79.7  | 12.7  | 0.9   | 5.7   | 0.98  |

3.1.2. Fourier Transform Infrared Spectroscopy (FTIR)

Figure 2a shows the full FTIR spectra for all modifiers, from which chemical functional groups present in the modifiers can be identified. The majority of the absorbance peaks were observed in wavenumbers ranging from 1,000 to 1,800 cm\(^{-1}\) (Figure 2b) and 2,700 to 3,200 cm\(^{-1}\) (Figure 2c).
Figure 2. FTIR spectra for modifiers from (a) 600-4,000 cm\(^{-1}\); (b) 1,000-1,800 cm\(^{-1}\); and (c) 2,700-3,200 cm\(^{-1}\).

Following are the observations from the FTIR spectra shown in Figure 2:

- All modifiers show characteristic peaks in the range of 2,800-3,000 cm\(^{-1}\) and 1,300-1,460 cm\(^{-1}\) which correspond to C-H stretching and C-H bending, respectively (Figure 2a).
- Peaks at 2,850, 2,920, 2,955, and 3,008 cm\(^{-1}\) correspond to C-H stretching and are observed in modifiers A, C, D, E, and K (Figure 2c). These peaks are absent in G. Instead, a distinct broad peak at 2,860 cm\(^{-1}\) in G was observed (Figure 2c). This peak is representative of N-H stretching specific to amine salt.
- The common peak at 1,460 cm\(^{-1}\) in all the modifiers shows the presence of C-H bending for alkanes (Figure 2b). It is the most common functional group present in hydrocarbons.
- Series of peaks were observed from 1,000-1,300 cm\(^{-1}\) in all modifiers (Figure 2a). This may reflect the presence of either alkoxy (-C-O-), phenyl (=C-O=), or C-N stretching.
- Peaks for modifiers A, C, D, and E at 1,165 cm\(^{-1}\) show the presence of a common functional group which can be either of alkoxy (-C-O-), phenyl (=C-O=), or C-N (Figure 2b). Because a negligible amount of nitrogen was observed in these modifiers, the probability of alkoxy (-C-O-) or phenyl (=C-O-) groups presence is higher.
- An accentuated peak at 1,120 cm\(^{-1}\) for G and a smaller peak around 1,050 cm\(^{-1}\) for C might correspond to C-N stretching (Figure 2b). This is characteristic of amine stretching (1,000-1,250 cm\(^{-1}\)).
• Smaller peaks at 1,350 and 1,375 cm\(^{-1}\) for modifier K correspond to stretching of sulfoxide (\(-\text{S}=\text{O}\)) group (Figure 2b).

• Strong peaks of carbonyl (\(-\text{C}=\text{O}\)) stretching were observed in modifiers A, C, D, and E between 1,650-1,800 cm\(^{-1}\). The peaks are close to wavenumber 1,742 cm\(^{-1}\) which may reflect the presence of aldehydes, ketones, esters, or carboxylic groups (\(-\text{C}=\text{O}\)). However, a very small peak for modifier G was also observed closer to wavenumber 1,650 cm\(^{-1}\) which is characteristic of amides (\(-\text{NC}=\text{O}\)) (Figure 2b). There is no peak for modifier K in this region.

• Modifier G and C have a single broad peak in range of 3,100-3,500 cm\(^{-1}\) (Figure 2a). This peak is usually due to the stretching in alcohols (O-H) or secondary amines (\(-\text{R}\text{R}'\text{N-H}\)). Based on elemental analysis, G and C have higher nitrogen content compared to other modifiers. Therefore, presence of secondary amines is highly likely in these modifiers.

• The spectral analysis results of modifiers confirm the type as provided by the suppliers (Table 1). No information on modifier A’s composition was provided; however, the FTIR results suggest that modifier A has characteristics similar to the bio-oil blend (modifier D).

3.1.3. Gel Permeation Chromatography

The average molecular weights (\(M_\text{n}\) and \(M_\text{w}\)) for modifiers A, C, D, and E ranged from 3,700 to 4,700, and for G it is around 2,500 with polydispersity index (PDI) in a range of 1.03-1.13 as shown in Table 3. Interestingly, modifier K has a high \(M_\text{n}\) of 8,933 and significantly higher \(M_\text{w}\) of 48,784 which is the reason for high PDI of 5.46. The plot showing retention times (Figure 3) suggests that even though modifiers A, C, D, and E have similar range of molecular weights, \(M_\text{n}\) and \(M_\text{w}\) (Table 3), their molecular size distribution varies. Following are the observations from GPC analysis as per Figure 3:

• The molecular weight distribution in modifier A and D showed two peaks at similar retention times but with different intensities. The larger peak occurred at lower retention times than the smaller peak, which indicates presence of two different sized molecules with higher proportion of larger size particles.

• Modifier C has a similar two peak distribution to A and D. However, the two peaks occur at longer retention times, indicating that the respective weights are smaller than A and D.

• Modifiers E and G have one sharp peak indicating the presence of single weight molecule. However, the peaks occur at different retention times which represent different particles.

• Modifier G has the largest retention time suggesting lower average molecular weight.

• Modifier K has the largest molecular weights among the modifiers. The molecular size distribution is wider compared to all other modifiers with two peaks. The wider distribution indicates a wide range of molecular size present in modifier K, resulting in a high PDI.

| Modifier | Number-Average Molecular Weight (\(M_\text{n}\)) | Weight Average Molecular Weight (\(M_\text{w}\)) | Polydispersity Index (PDI) |
|----------|---------------------------------------------|---------------------------------------------|----------------------------|
| A        | 4,450                                       | 4,616                                       | 1.04                       |
| C        | 3,709                                       | 3,971                                       | 1.07                       |
| D        | 4,345                                       | 4,909                                       | 1.13                       |
| E        | 4,684                                       | 4,805                                       | 1.03                       |
| G        | 2,349                                       | 2,596                                       | 1.11                       |
| K        | 8,933                                       | 48,784                                      | 5.46                       |

Table 3. Number-average molecular weight, weight-average molecular weight, and polydispersity index of modifiers.
3.1.4. Thin Layer Chromatography Flame Ionization Detection (TLC-FID)

Table 4 shows the SARA composition and the unfiltered residue for different modifiers. Following are the observations from SARA analysis:

- Modifiers A, C, D, and E are primarily composed of resins.
- Modifiers A and D consist of some aromatics (A=19.7% and D=10.5%), limited asphaltenes (A=4.6% and D=7.5%), and some saturates (A=8.3% and D=1.1%).
- Modifiers C and E show limited or no presence of aromatics and saturates. They are primarily composed of resins (C=70.1% and E=83.4%) and asphaltenes (C=23.2% and E=13%).
- Modifier K has a significant proportion of saturates (59.3%) and exceptionally high residue content (26%) compared to other modifiers.

Modifier G possesses unique characteristics which are different from other modifiers. It is a water-soluble modifier and did not dissolve in the solvent used for other modifiers. Modifier G is also toluene insoluble which suggests there is no presence of asphaltic materials. Hence, the SARA approach seems inappropriate to characterize the chemical composition of modifier G. Furthermore, solubility of G in water can have moisture durability issues in AC designed from this modified binder which is not in the scope of this study. Therefore, AC properties to evaluate the effect of moisture should be investigated.

Table 4. Percentage composition of saturates, aromatics, resins, asphaltenes and residue for modifiers.

| Sample ID | Saturates (%) | Aromatics (%) | Resins (%) | Asphaltenes (%) | Residue (%) | Total (%) |
|-----------|---------------|---------------|------------|-----------------|-------------|-----------|
| A         | 8.3           | 19.7          | 62.5       | 4.6             | 4.9         | 100.0     |
| C         | 0.0           | 0.0           | 70.1       | 23.3            | 6.6         | 100.0     |
| D         | 1.2           | 10.5          | 78.5       | 7.5             | 2.3         | 100.0     |
| E         | 0.0           | 0.1           | 83.4       | 13.0            | 3.5         | 100.0     |
| K         | 59.3          | 0.4           | 10.3       | 4.0             | 26.0        | 100.0     |

Note: Results for modifier G cannot be determined using TLC-FID.
3.2. Rheological Characterization of Modified Binders

3.2.1. Superpave Grading

Base binder, S1 (PG 64-22), was modified to PG 58-28 using modifiers provided in Table 5. All the modifiers were able to convert the base binder to the acceptable limits of PG 58-28 except modifier K (ReOB). Figure 4a shows the continuous PG for base binder, unmodified PG 58-28 (S5), and modified binders. The selection of modifier dosage was based on (i) achieving similar high temperature true grades (0.6 °C standard deviation) and (ii) obtaining similar true-grade results to S5’s (±1.2 °C).

Table 5. Continuous and Superpave Performance Grade (PG) of base binder, unmodified binder and modified binders.

| Binder ID | High PG | Low PG | Continuous PG | Superpave PG |
|-----------|---------|--------|---------------|--------------|
| S1        | 66.4    | -23.7  | 66.4-23.7     | 64-22        |
| S5        | 61.1    | -29.5  | 61.1-29.5     | 58-28        |
| S1-A-3.5  | 61.6    | -30.0  | 61.6-30.0     | 58-28        |
| S1-C-3.1  | 61.4    | -30.1  | 61.4-30.1     | 58-28        |
| S1-D-3.1  | 62.1    | -28.3  | 62.1-28.3     | 58-28        |
| S1-E-3.1  | 62.3    | -30.7  | 62.3-30.7     | 58-28        |
| S1-G-6.5  | 60.8    | -28.5  | 60.8-28.5     | 58-28        |
| S1-K-10   | 59.4    | -27.3  | 59.4-27.3     | 58-22        |

For modifier K, none of the dosages from 6% to 12% were able to produce a PG 58-28 binder. It was observed that increase in the addition of modifier K had a softening effect on high and intermediate temperature grades (Figure 4b and c). In case of low temperature PG, the stiffness was reduced with increasing modifier dosage whereas m-value was not affected (as shown in Figure 4d). Moreover, the low temperature PG for K was controlled by the m-value which failed to meet required criteria. The 10% dosage for K was chosen to obtain the continuous PG closest to PG 58-28.
3.2.2. Delta Tc ($\Delta T_c$)

$\Delta T_c$ for PAV, 2PAV, and 3PAV conditions was computed for all binders (Figure 5). The modification to S1 increased the $\Delta T_c$ values, at all aging conditions, for all modified binders except when modifier K (ReOB) was used. A higher, or less negative, $\Delta T_c$ can be related to better resistance to low-temperature cracking. Departments of Transportation in Maryland, Kansas, Pennsylvania, New York, New Jersey, Delaware, and Vermont restrict $\Delta T_c$ to be greater than $-5^\circ$C after 40-hour PAV conditioning while some other states use a limit for $\Delta T_c$ after 20-hour PAV [20].

On comparing unmodified binder S5 to G and C modified binders, the later ones showed similar $\Delta T_c$ in PAV aging condition. However, with prolonged aging (2PAV and 3PAV), G-modified binder outperformed S5, followed by C-modified binder. MABs with modifiers A, D, E, and K had lower $\Delta T_c$ than S5. It is widely accepted that the presence of ReOB increases low-temperature cracking susceptibility of AB [5–9], which is also observed in this study. K-modified binder has the lowest $\Delta T_c$ at all aging conditions.

It is important to note that with aging, the effect on $\Delta T_c$ values are predominantly driven by the m-value criterion. In all cases, $\Delta T_c$ becomes more negative with aging, indicating more pronounced loss of relaxation (reduction of m-value) than stiffening of the material. Stiffnesses were not as greatly affected by aging.

The $\Delta T_c$ parameter suggests that modified binders may have similar long-term cracking resistance with the unmodified S5. On the other hand, K-modified binder (ReOB) has the lowest $\Delta T_c$, which is well beyond the acceptable thresholds suggested in the literature [20].

3.2.3. Frequency Sweep Test

In this section, complex modulus master curves, black space diagrams, and rheological parameter, GR, are presented for, RTFO, PAV, 2PAV, and 3PAV aging conditions.
Complex Shear Modulus Master Curves

Complex modulus master curves were determined at a reference temperature of 15 °C. Figure 6a–d show the progression of complex modulus at different aging conditions, for limited low reduced-frequency range. This range was selected to represent low-temperature (non-load associated) cracking conditions. Following are the observations from Figure 6.

1. In Figure 6a, after RTFO aging, modified binders are difficult to differentiate based on their shear modulus values. All the binders have similar master curves representing similar stiffnesses.
2. As the aging progressed to PAV condition, modified binder containing K separates from the rest of the binders at the lower frequency range (Figure 6b) representing a stiffer behavior. Other binders (A, C, D, E, G, and S5) show similar behavior.
3. Upon further aging (2PAV), modified binder containing G slightly separates from the rest of the binders towards lower moduli (Figure 6c), showing a softer behavior. K is again the stiffest and separates from the rest (A, C, D, E, and S5) in this condition.
4. At 3PAV, modified binders containing G and K have clear distinction in moduli, G being the softest and K being the stiffest. All other binders have similar variation in the complex shear modulus as shown in Figure 6d.

Black Space Diagram

Black space diagrams were plotted for RTFO, PAV, 2PAV, and 3PAV aging conditions. A black space diagram shows the variation of complex shear modulus (G*) with phase angle (δ). A reference
temperature of 15 °C was used to obtain these curves. A higher δ at a fixed temperature and G* represents a material more prone to flow in a viscous manner and a lower δ represents a more elastic behavior [42]. Materials with higher δ are less likely to crack in a brittle way. In other words, a lower δ indicates that more energy would be stored, and faster accumulation of stress would be observed during repeated deformation [3]. A good correlation has been demonstrated between isothermal phase angle (especially at 50 °C) and test-pavement cracking severity [43]. Phase angle (at G* = 8967 kPa) has been found to be more repeatable measurement than G* and capable of identifying phase-incompatible asphalt binders [3].

Figure 7a–d show complete black space diagrams for specific aging conditions, whereas the inset figure highlights the effect on δ for G* ranging from 10 MPa to 11 MPa. The motivation for the selection of this G* range was the intermediate-temperature PG criteria [3]. However, a different range of G* selection does not affect the trends in δ and could represent other loading conditions in the field. Some observations from the black space diagrams are the following:

1. For the selected range of G* at RTFO (Inset Figure 7a) aged condition, K-modified binder has the lowest δ with clear distinction compared to other binders. The remaining binders have higher δ values than K-modified binder and are close to each other. C-modified binder has highest δ.

2. As the aging progresses to PAV aging, the separation in δ can be distinguished clearly. K-modified binder is separated from rest of the binders with lower δ (Inset Figure 7b), while G-modified binder has the highest δ followed by C, S5, E, D, and A respectively (close to each other).

3. Upon further aging (2PAV and 3PAV), the trends for highest and lowest δ are again similar to that of PAV aging. However, the separation in δ became more evident (Inset Figure 7c and d). At 3PAV, K-modified binder has the lowest δ followed by E, D, S5, C, and G. The δ values for G-modified binder suggest a greater viscous component in the complex shear modulus, indicating a flowing behavior, thus possibly lower cracking susceptibility.
**Figure 7.** Black space diagrams at reference temperature of 15 °C for aging conditions (a) RTFO; (b) PAV; (c) 2PAV; and (d) 3PAV.

Glover–Rowe (GR) Parameter

GR values are indicated in the black space diagrams, shown in Figure 8, for all aging conditions. Modified binders containing A, D, and E show similar characteristics to unmodified binder (S5) at all aging conditions (Figure 8a). Differently, in case of modifier C, higher resistance to low-temperature cracking was observed.

A GR of 180 kPa is a criterion for damage onset for non-load-associated low-temperature cracking (shown in the red-dotted line in Figure 8), while 450 kPa is indicative for severe cracking (shown in the red-solid line in Figure 8) [23]. As per these thresholds, damage onset initiates around 2PAV while severe damage takes place at around 3PAV condition for S5 and binders containing modifiers A, D, and E.

In Figure 8b, for G-modified binder the evolution of GR parameter suggests higher resistance to aging compared to S5. The GR value for 3PAV of G is similar to that of 2PAV for S5. In contrast, GR for K-modified binder increases at a much faster rate than S5, suggesting potential early damage. The GR values of PAV and 2PAV for K are similar to 2PAV and 3PAV of S5, respectively. Figure 8a,b show that G-modified binder does not reach onset of severe cracking criterion after 3PAV while K-modified binder surpasses the criterion after 2PAV.

**Figure 8.** Black space diagrams showing G* vs phase angle (δ) at reference temperature of 15 °C and reduced frequency of 0.005 rad/s for all aging conditions for (a) modifiers A, C, D, and E compared to unmodified binder S5; and (b) modifiers G and K compared to unmodified binder S5.
4. Discussion

4.1. Summary of Modifier Chemistry

The Elemental analysis showed that modifiers G and C had higher nitrogen content (9% and 3.5%, respectively), while E and K had some sulfur (0.33% and 0.98%, respectively) compared to other modifiers. Modifier G has significantly low carbon (47.9%) and high oxygen (33.1%) content.

FTIR spectra further validated the presence of nitrogen in modifiers C and G with peaks in the ranges of 1,000-1,250 cm\(^{-1}\) and 3,100-3,500 cm\(^{-1}\) which are characteristic of C-N stretching and N-H stretching (from secondary amines), respectively. A distinct peak at 2,860 cm\(^{-1}\) and a small peak at 1,650 cm\(^{-1}\) further validate the presence of nitrogen, as these peaks are representative of amine salt and amides, respectively. Modifiers A, C, D, and E show the presence of carbonyl functionality, which was observed from the carbonyl peaks at 1,742 cm\(^{-1}\).

Molecular weight analysis showed that modifiers A, C, D, and E have average molecular weights in a similar range, modifier G has the lowest weight and K has the highest. In addition, modifier K possesses significantly high PDI indicating a wide variation of molecular species presence. Modifiers, however, have different molecular size distributions, with some modifiers having multiple peaks (A, C, D, and K) and hence, are composed of distinct molecules. On the other hand, others (E and G) had single peak which means they are composed of single molecular size.

Modifier G has a distinct chemical composition compared to other modifiers. It is significantly high on nitrogen and oxygen and relatively low on carbon compared to others. The presence of nitrogen was validated by the FTIR spectra. Peaks corresponding to amine salt and primary and secondary amines were observed. It was found that the molecular weight of G was the lowest single peak distribution. Additionally, modifier C showed relatively higher content of elemental nitrogen in the form of secondary amines which was verified by the FTIR spectrum.

SARA analysis of G was inconclusive and additional characterization with a different method is required to evaluate the chemical characteristics of modifier G. Moreover, its solubility in water requires additional investigation of the AC’s susceptibility to moisture. Modifiers C and E are largely composed of resins and asphaltenes with limited or no saturates and aromatics. While A and D have some aromatics and asphaltenes along with a majority of resins. Modifier K has large amount of insoluble residue with high saturate content and limited resins with traces of aromatics.

Furthermore, modifier A shows similar chemical functional groups, molecular weight and molecular weight distribution to modifier D, which indicates that modifier A may belong to bio-oil category.

4.2. Summary of Modified Asphalt Binder Rheology

Modifiers’ dosages were selected to meet PG 58-28 with true grades close to each other for all MABs to ensure reasonable comparison of rheological properties, except for binder modified with K (ReOB). It was observed that increasing the dosage of K increased high PG, decreased intermediate PG, and decreased low PG stiffness. However, there was no improvement in the relaxation properties of the modified binder with increasing amount of modifier K in the blend. Therefore, dosage for modifier K resulting in a continuous PG closest to PG 58-28 was selected for further investigation. The selected dosage varied from one modifier to the other. This might be one of the reasons for the observed differences in rheology. For instance, increasing the dosage of modifier C can result in a similar performance as that of AB modified with modifier G; but would result in a different Superpave continuous-PG. The focus of the study was to compare binders with similar Superpave characteristics. Dosage variation/optimization is not within the scope of this study, but appears to be a promising research path.

\(\Delta T_\text{c}\) was determined to evaluate the low temperature cracking susceptibility of modified binders for PAV, 2PAV, and 3PAV aging conditions. Relatively high \(\Delta T_\text{c}\) indicates better relaxation properties at low temperatures, which results in better resistance to cracking. Modification of S1 improved the \(\Delta T_\text{c}\) for all MABs except K. Significant improvements were observed when modifiers G and C were used, which even showed better relaxation properties than unmodified binder (S5). G-modified
binder has the highest $\Delta T_c$ for 2PAV and 3PAV conditions, followed by binder modified with C. Differently, K-modified binder has the lowest $\Delta T_c$ values in all aging conditions. MABs containing A, D, and E have $\Delta T_c$ values close to S5 only after 2PAV and 3PAV aging conditions.

Complex shear modulus master curves show that modulus consistently increased for all aged binders. K-modified binder showed distinctly stiff behavior at PAV that was also observed in 2PAV and 3PAV conditions. Other MABs stiffness trends shifted with aging conditions. At UA condition, G-modified binder was the stiffest and after 2PAV and 3PAV, it was the softest binder; which is desired. However, mechanisms of change in modulus for G-modified binder after aging need to be investigated. Modifier G, as discussed before, has distinctive characteristics and needs to be explored with additional testing. Aging after 2PAV and 3PAV, other modifiers have master curves closer to unmodified binder (S5).

The black space diagram was used to evaluate the impact of aging on phase angle (δ). The δ for selected range of $G^*$ shows similar trends after PAV, 2PAV and 3PAV aging. The differences in δ of MABs become more distinct with aging but are always noticeable, which makes δ at a certain $G^*$ a useful parameter to distinguish MABs. Note that this might not be the case when polymers are in the blend [44]. As mentioned earlier, a higher δ at a certain $G^*$ indicates that the material is less prone to cracking in a brittle way at service conditions. Again, MAB containing G has the highest phase angles, followed by C, S5, E, D, and A, while K has the lowest. In addition, the evolution of GR parameter also suggests that G-modified binder is the most resistant to aging while K is the least.

Based on rheological testing, G-modified binder is least susceptible to cracking followed by C-modified binder whereas K-modified binder is the most susceptible. MABs modified with A, D and E show similar rheological characteristics to S5.

4.3. Relationship between Modifier Chemistry and Binder Rheology

Modifier’s chemical make-up contributed significantly to the long-term rheological response of MABs. Nitrogen-based compounds are known for their antioxidant properties [45]. The presence of higher nitrogen content was validated with elemental analyses and FTIR spectra and its impact was observed in the change of frequency sweep measurements as aging progressed. Modifier C, containing 3.5% nitrogen, shows similar or better crack resisting properties than the unmodified product (S5) at PAV, 2PAV, and 3PAV conditions. Superior rheological properties of G-modified binder can be attributed to the presence of high nitrogen content (9.0% in modifier G), which is composed of nitrogen-based compounds like amines. This validates the impact of antioxidants on resisting binder aging, and hence, reducing cracking susceptibility.

On the other hand, sulfur presence in modifiers (0.33%) and K (0.98%) is accompanied by lower expected performance based on the reported rheological parameters. Excessive sulfur content (>4%) in binders can cause increased oxidation due to the formation of additional sulfoxides causing embrittlement in binders [46].

Lower molecular weight of modifiers could be promoting phase compatibility. Rheological test results and $M_n$ distinguish three groups: MABs containing A, D, and E have similar characteristics, MAB containing K has lower expected performance and highest $M_n$, and MABs containing C and G have higher expected performance and lower $M_n$.

The rheological parameters: $\Delta T_c$, GR, and phase angle from black space diagram have consistent trends among all modifiers and are able to distinguish MABs based on their expected cracking performance.

5. Summary and Findings

The focus of this paper is to evaluate the impact of modifiers’ chemical properties on the rheological properties of respective modified binders. Binders blended with various types of modifiers, intended to soften (reduce) the grade of an unmodified binder, were tested at various aging conditions (unaged, RTFO, PAV, 2PAV, and 3PAV). Performance progression indicators were used to predict their long-term performance. Low-temperature cracking susceptibility was assessed using GR and $\Delta T_c$, and intermediate-temperature cracking susceptibility was assessed using black
space diagrams. Chemical characteristics of modifiers were evaluated using elemental analysis, FTIR, GPC, and TLC-FID. The results show that modifier chemistry impacts modified binder performance. The presence of certain elements, chemical functional groups and molecular size can affect the rheological properties of the binder. Following are the findings of this study:

1. Nitrogen-rich modified binders appear to have superior rheological properties. They have higher \( \Delta T_e \), higher phase angles, and lower GR for 2PAV and 3PAV conditions. Hence, it can be assumed that the presence of nitrogen would boost anti-oxidizing properties and reduce susceptibility to cracking. Further research is needed to validate this hypothesis.
2. Sulfur presence may have a detrimental impact on modified binder performance.
3. Lower molecular size/weight of modifiers appears to be related to better cracking resistance potential of modified asphalt binders. Further research towards validating this idea is encouraged.
4. Modifiers A and D have similar chemical characteristics and molecular weight distributions. This suggests that modifier A may have a bio-based origin.
5. The methodology employed in the SARA analysis may not be able to characterize some modifiers. An alternative test method should be considered for some modifiers.
6. Phase angle parameter in conjunction with complex modulus (\( G^* \)) was shown to be sensitive to laboratory aging of modified and unmodified binders. Therefore, such a parameter has potential to identify phase-incompatible asphalt binders, is able to distinguish potential mechanical behavior, and could be associated with field performance.

In conclusion, modifier chemistry was shown to have a relationship with rheological behavior of modified binders. The experimental program presented in this paper can be used to choose modifiers that may control cracking development and could also be used as guidance to engineer asphalt binder modifiers.

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