Relationship between Colloidal Index and Chemo-Rheological Properties of Asphalt Binder Modified by Various Recycling Agents

Hamzeh F. Haghshenas, Ph.D.

Research Assistant Professor, Department of Civil and Environmental Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska, USA

Materials and Research Engineer, Nebraska Department of Transportation, Lincoln, Nebraska, USA

*(****Corresponding Author****; 362R Prem S. Paul Research Center at Whittier School, 2200 Vine St., Lincoln, NE 68583-0851; Email: h.f@unl.edu)*

Robert Rea

Assistant Materials and Research Engineer, Nebraska Department of Transportation, Lincoln, Nebraska, 68502, USA, Email: robert.rea@nebraska.gov

Gerald Reinke

Technical Director at Mathy Construction, MTE Services, Onalaska, Wisconsin, USA, E-mail: gerald.reinke@mteservices.com

Martins Zaumanis, Ph.D.

Senior Researcher, Road Engineering/Sealing Components Laboratory, EMPA Swiss Federal Laboratories for Materials Science and Technology E-mail: martins.zaumanis@empa.ch

Elham Fini, Ph.D.

Associate Professor, School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, Arizona, USA; Email: efini@asu.edu

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Abstract:

This paper examines relation between colloidal index (CI) and chemo-rheological properties of asphalt binders modified by five different recycling agents (RAs) including paraffinic oils, aromatic extracts, naphthenic oils, triglycerides/fatty acids, and tall oils. To monitor the change of binder properties, each binder was exposed to different aging conditions. Saturates, aromatics, resins and asphaltenes content of each modified binder, as well as its rheological and low-temperature cracking properties were determined before and after aging. It was found that recycling agents could vary the softening and long-term performance of the modified binders based on their chemical makeup. While all RAs softened the binder, only few could restore binder rheological properties, with only one (aromatic extract) meeting low temperature cracking threshold after aging. The study results revealed a strong linear relation between the CI and the chemo-rheological properties of binders. For instance, the flexural creep stiffness and complex modulus found to inversely related to CI while the phase angle and relaxation constant (m-value) found to be directly related to CI. The study results highlight the source dependency of RAs' efficacy to restore and maintain binder properties after aging.

Keywords: Recycling Agents (RAs); Aging; Saturates-Aromatics-Resins-Asphaltenes (SARA); Colloidal Index (CI); Oxygen Analysis; Dynamic Shear Rheometer (DSR); Bending Beam Rheometer (BBR)

Introduction

The chemical composition of asphalt binders is highly dependent on crude source, refinery process, and additives (e.g., polymers and recycling agents (RAs)); having a direct impact on their rheological properties [1-3]. Asphalt binder is a heterogeneous material and its chemical composition is well described as a colloidal system [4]. In this colloidal system, four fractions can be distinguished and identified as the Saturates, Aromatics, Resins, and Asphaltenes [5], often referred to as SARA fractions.

The SARA classification is based on the polarity and solubility of the four fractions in different solvents [6]. Asphaltenes are high molecular weight and relatively polar components and are often defined as the n-heptane insoluble fraction of asphalt, while the maltene fractions (saturates, aromatics, and resins) are soluble in n-heptane. As the asphaltene fraction increases, the potential for secondary intermolecular bonding also increases. This can result in the formation of stiffer structures within the asphalt, sometimes referred to as “gel” structures. In opposite fashion, when the asphaltene fraction is reduced, it results in a decreased stiffness and more fluid-like behaviour [7].

Researchers have explored correlations and relations between the chemical composition of binders and their rheological properties, since the phenomenological events (e.g., oxidation) change the chemical makeup and compositional properties, consequently affecting the rheological characteristics of the binders [2, 3, 8]. Recently, Haghshenas [6] reported that over time there is a linear correlation between the asphaltene content with other chemical (e.g., carbonyl index) and mechanical (e.g., stiffness) properties of asphalt binders. As a result, characterizing the chemical composition of the binder can to some extent provide significant insights into the understanding of the complex phenomena of asphalt oxidation and rejuvenation/softening, and help researchers and engineers to predict the rheological properties of binders.

Recycling agents (RAs), either rejuvenators or softening agents, are used to soften the highly aged binder in the reclaimed asphalt pavement (RAP). These RAs are classified based on their origins and processing technologies. Five main categories have been identified by National Center for Asphalt Technology (NCAT 2014), these are (1) paraffinic oils, (2) aromatic extracts, (3) naphthenic oils (4) triglycerides and fatty acids, and (5) tall oils. Although the objective of all these modifiers is to decrease the stiffness of aged materials, their softening mechanism and effectiveness is material dependent and varies significantly with respect to their chemical characteristics [9-14].

A survey of literature reveals that there is limited information regarding the influence of different types of RAs on SARA fractions of asphalt binders [15-18]. In addition, information on the effect of these modifiers on binder's internal stability and their relationship with rheological properties of modified binders, immediately after blending and following the laboratory aging process, is limited in the current literature. Therefore, the objectives of this study are:

1. To define the chemical composition of one control binder (35% virgin binder + 65% lab-made RAP binder) and five RAs modified binders aged under different conditions using SARA analysis, and
2. To investigate the correlation between the rheological properties of the binders characterized by Bending Beam Rheometer (BBR) and Dynamic Share Rheometer (DSR) with their chemical composition.

Materials

Recycling Agents (RAs)

In this study five "typical" RAs were used and labelled by a generic descriptor as Paraffinic Oil: P, Aromatic Extract: A, Naphthenic Oil: N, Triglycerides/Fatty Acids: TF, and Tall Oil: T.

It is worthy to note that the paraffinic oils, aromatic extracts, and naphthenic oils are petroleum derived products, the triglycerides/fatty acids products are derived from seed oils (e.g., soybean, corn, rapeseed), and tall oil products are derived from trees and obtained as by-products of the Kraft pulping process. The chemical properties of the selected RAs are presented in Table 1.

Table 1. Chemical/physical properties of RAs used in this study [11].

Recycling Agent (RA)	(C, H, N, O, S) [1]	(As, Re, Ar, Sa) [2]	Detected Functional Groups Sensitive to Aging Process and/or Moisture	Viscosity (60 °C, cSt)
P	86.7, 10.5, <0.5, 0.5, 0.1	0.1, 0.0, 7.9, 91.9	Not Identified	22.9
A	87.6, 10.3, <0.5, 1.2, 1.0	0.2, 6.4, 84.0, 9.5	Not Identified	123.4
N	87.6, 13.0, <0.5, 0.5, 0.1	0.2, 0.0, 45.1, 54.7	Not Identified	111.1
TF	77.6, 11.7, <0.5, 11.5, 0.2	0.3, 99.7, 0.0, 0.0	Carbonyl, Hydroxyl, Sulfonyl	14.6
T	77.6, 11.7, <0.5, 10.8, 0.1	0.6, 27.7, 71.7, 0.0	Carbonyl, Hydroxyl	35.5

[1] Carbo, Hydrogen, Nitrogen, Oxygen, Sulfur

[2] Asphaltenes, Resins, Aromatics, Saturates

Asphalt Binders

A performance grade (PG) 64-22 was used as the virgin asphalt binder. To prepare binder samples that simulate field aging, the PG 64-22 was conditioned through one standard RTFO plus two standard PAV cycles (i.e., extended lab-aging condition). This method for preparing field aged binders in the laboratory (i.e., lab-made RAP binder) was proposed by Bowers et al. [19] and used by other researchers [20, 21]. Then 65% of the lab-made RAP binder was blended with 35% of the virgin PG 64-22 binder to establish the base binder (denoted by CR) for modification with different RAs. The 65% lab-made RAP binder was selected for this research due to the fact that the Nebraska Department of Transportation (NDOT) is currently utilizing asphalt mixtures containing 50 to 65% Reclaimed Asphalt Pavement (RAP) materials with different RAs.

The optimum dosage of each RA was selected based on a fixed target PG approach. The dosage of each RA was the selected amount required to reduce the base binder (CR: 65% lab-made RAP binder + 35% virgin binder) to the target binder, PG 64-28. The decision to target PG 64-28 was due to this grade being commonly used in the central part of the United States. The blended binders considered in this study for chemical and rheological characterization is shown in Table 2.

Table 2. The asphalt binders used in this study.

Binder Description	Binder ID	Continuous PG
Virgin Binder (PG 64-22)	C	67.3-25.9
Extended Laboratory Aged of PG 64-22 (lab-made RAP binder)	R	89.8-14.4
35% C + 65% R	CR	81.1-18.4
23% C + 65% R + 12% P	CRP	68.2-31.7
21% C + 65% R+ 14% A	CRA	67.1-29.6
21% C + 65% R + 14% N	CRN	66.9-29.6
29% C + 65% R + 6% TF	CRTF	69.5-33.1
27% C + 65% R + 8% T	CRT	67.4-29.9

Experimental Methods

Rolling Thin Film Oven (RTFO) and Pressure Aging Vessel (PAV)

The short-term (RTFO) and long-term aging (PAV) of the binders were performed according to ASTM-D2872 [22] and ASTM-D6521 [23], respectively. In order to examine the long-term performance of recycling agents during the aging process, the modified binders were further subjected to one cycle of short-term aging (RTFO), and either one or two cycles of long-term aging (simulated by PAV) consisting of 20 hrs (1PAV) and 40 hrs (2PAV)) of aging at 100ºC under an air pressure of 2.1 MPa. In this study, the RTFO+1PAV cycle and RTFO+2PAV cycles are referred to as "standard" and "extended aging", respectively.

Bending Beam Rheometer (BBR)

The standard test to determine the performance of binder at low temperature associated with cracking is the Bending Beam Rheometer (BBR). This test is conducted according to AASHTO-T313 [24] on the original and aged binders prepared through RTFO and PAV procedures as explained earlier. The test temperature was set to -18 ºC in order to test for a low temperature PG target of -28 ºC. As explained in the testing standard, the relaxation parameter (m) and flexural creep stiffness (S) at 60 seconds of loading were used for the calculation of low-temperature performance grade of the binders.

Dynamic Shear Rheometer (DSR)

The Dynamic Shear Rheometer (DSR) was used to determine the performance grade of the binder at high-temperature (associated with rutting), and performance-related indices at intermediate temperature often associated with load-related fatigue cracking.

Standard 25 mm diameter plates with 1 mm testing gap were used to determine the critical high temperature PG through measurement of the complex modulus (G^*) and phase angle (δ) at various temperatures and calculating the $|G^*|/\sin\delta$ ratios. The temperature in which the value of $|G^*|/\sin\delta$ is equal to 1.00 kPa [25] is considered as the high (critical) PG temperature.

To assess the performance of binder at mid-temperature associated with cracking, Glover-Rowe (G-R) concept was used. The test is performed at 45 ˚C and 10 rad/s using 8 mm diameter plates with 2 mm testing gap. The G-R parameter is determined using following equation:

$$G - R\ Parameter = G^{*} \times \frac{(\cos\delta)^2}{\sin\delta} \qquad \text{Equation 1}$$

Two Black-space failure envelopes are defined in the G-R concept based on historical field experience. Based on these envelopes, binders with G-R properties less than 180 kPa are believed to be less likely to experience cracking, while binder with G-R parameter above the line equal to 600 kPa expected to experience severe cracking. Binders with G-R parameter between 180 kPa and 600 kPa lines is considered in crack damage risk zone [26].

Saturates-Aromatics-Resins-Asphaltenes (SARA) Analysis

To determine the percentage of the saturates, aromatics, resins, asphaltenes (SARA) fractions of modified binders by different RAs, an Iatroscan MK-6 was employed. In this method, the asphaltenes are first separated from the binders as n-heptane insolubles [27]. The n-heptane soluble portion, referred to as the maltene phase, are then further separated into saturates, aromatics, and resins through a type of thin-layer chromatography, based on elution by different solvents. The eluted fractions are quantified by the Iatroscan MK-6 using a Flame Ionization Detector (FID).

The resulting data has been used to develop indices that have been related to internal phase and colloidal stability of the asphalt binder, often referred to as the binder's colloidal index (CI). The CI has been used to explain to what extent the asphaltene particles are stable within the asphalt binder. The CI is defined as follows [28]:

$$Colloidal\ Index\ (CI) = \frac{Resins\ + Aromatics}{Asphaltenes\ + Saturates} \qquad \text{Equation 2}$$

In the context of Equation 2, a higher CI value is desirable as it indicates the potentially higher stability of the asphaltenes in the binder system [16].

Oxygen Analysis

The oxygen determination using Thermo Finnigan FlashEA™ Elemental Analyzer was made to detect the oxygen content of asphalt binders and RAs. The elemental analyzer pyrolyzes the sample in an inert atmosphere (helium). During the pyrolysis, nitrogen, hydrogen, and carbon monoxide are formed when they contact the nickel-plated carbon catalyst at 1,060 °C and then are separated via a chromatographic column. The elemental analyzer then automatically provides the oxygen percentage.

Results and Discussions

Efficacy of multiple RAs (paraffinic oil, aromatic extract, naphthenic oil, triglycerides/fatty acids, and tall oil) were examined in terms of ability of the restored binder to main its performance and meet performance thresholds even after being aged. Table 3 summarizes the DSR and BBR test results of different binders used in this study. In addition, the SARA fractions of each binder are calculated using Iatroscan and reported in Table 3. The reported values are presented at various levels of conditioning: before aging (original), standard long-term aging, and extended long term aging.

The analysis of CI reveals that, paraffinic and naphthenic oils which are derived from petroleum sources, decreases CI. Considering that paraffinic and naphthenic oils increase the saturate content of the binder, their introduction to binder leads to the reduction to CI according to Equation 2. On the other hand, during the aging process there is an increase in the asphaltenes and a reduction in the aromatics content. As a result, the numerator of Equation 2 is decreased, and the denominator is increased, reducing the CI.

Table 3 shows that aging along with high saturate content of modified binders by paraffinic and naphthenic oils result in the lowest CI. This might be the reason behind the poor extended long-term aging performance of the binders modified by these oils (see Figure 1(b) and (e)) compared to those modified by the other RAs. The poor aging performance of paraffinic oils is also reported in other studies [9, 29-31].

It is hypothesized that the aging properties of RA-modified binders is highly dependent on both the RA's chemistry and compositional properties of the modified binder, such as the colloidal index. The CI of binders treated by petroleum derived aromatics extract (CRA), and bio-derived triglycerides/fatty acids (CRTF), and tall oil (CRT) was higher than that of CR binder before and after being conditioned in standard aging (RTFO+1PAV). Among aforementioned binders (CRA, CRTF, and CRT), the CRA had the lowest rate of loss of CI, m-, and S- value, after RTFO+2PAV cycles (i.e., extended lab-aging condition). This improved performance of binder due to introduction of aromatic extract is evidenced by the treated binder' having the lowest high PG temperature, the lowest Log (G^*), the lowest G-R result and the highest m-value after RTFO+2PAV cycles.

It should be noted that to rank the performance of binders based on their CIs, there is a need for a comprehensive sensitivity analysis in terms of correlating property changes with a change in CI. While there has been controversy in the use of the colloidal stability for evaluating bio-based RA, it seems the SARA analysis themselves are acceptable [32]. The naming of SARA is simply a way to categorize solubility of each component. The SARA components themselves are determined based on their solubility and the method is scientifically sound and completely applicable to various materials; for instance, those molecules which are not soluble in n-Heptane are referred to as asphaltene. This includes a large array of highly polar compounds [18].

Table 3. The SARA and rheological test results of asphalt binders in original (unaged) and different aging conditions.

Binder ID	DSR [1, 2]				BBR[2] (tested at -18 °C)		SARA					Oxygen Content (%)
	Continuous High PG Temperature (°C)	*Phase Angle (δ) (°)	*Log (G*) (Pa)	**G-R (kPa)	S-value (MPa)	m-value	Asphaltenes (%)	Resins (%)	Aromatics (%)	Saturates (%)	CI	
Original												
CR	81.5	68.30	5.179	22.32	365	0.249	21.5	27.0	46.8	4.7	2.817	1.37
CRP	65.9	71.50	4.288	2.06	41	0.415	19.2	27.5	41.1	12.2	2.185	1.13
CRA	66.9	75.00	4.401	1.74	128	0.425	18.9	27.9	47.5	5.7	3.065	1.16
CRN	67.6	72.60	4.411	2.41	86	0.407	18.4	27.5	44.0	10.1	2.509	1.18
CRTF	68.9	74.40	4.404	1.90	67	0.448	20.5	31.6	43.1	4.8	2.953	2.04
CRT	67.1	77.30	4.312	1.02	102	0.456	19.0	34.3	41.8	4.8	3.197	2.08
RTFO+1PAV												
CR	93.0	57.60	5.775	202.57	542	0.240	26.3	31.7	37.5	4.4	2.254	1.56
CRP	81.2	55.90	5.115	49.48	81	0.305	24.6	30.7	33.4	11.4	1.781	1.57
CRA	78.1	66.00	4.950	16.16	213	0.336	25.1	30.8	39.1	5.0	2.322	1.62
CRN	81.4	59.00	5.078	36.99	141	0.308	23.9	30.1	36.1	9.8	1.964	1.64
CRTF	82.7	62.30	5.109	31.34	142	0.339	25.6	35.8	34.2	4.4	2.333	2.30
CRT	80.1	67.90	4.975	14.46	222	0.344	25.3	39.0	31.4	4.4	2.370	2.67
RTFO+2PAV												
CR	98.2	53.04	5.996	447.81	560	0.224	28.3	31.5	35.1	5.1	1.994	1.91
CRP	92.3	47.42	5.512	202.19	112	0.254	27.3	28.7	31.6	12.4	1.519	1.88
CRA	85.9	59.40	5.260	54.73	235	0.303	27.8	29.1	39.1	4.0	2.145	1.90
CRN	90.5	49.69	5.541	190.66	162	0.279	25.2	29.8	34.3	10.7	1.786	1.89
CRTF	91.5	56.90	5.471	105.34	184	0.298	29.8	36.4	29.1	4.7	1.899	2.84
CRT	87.7	60.08	5.459	82.53	274	0.299	29.8	38.3	27.2	4.6	1.904	3.03

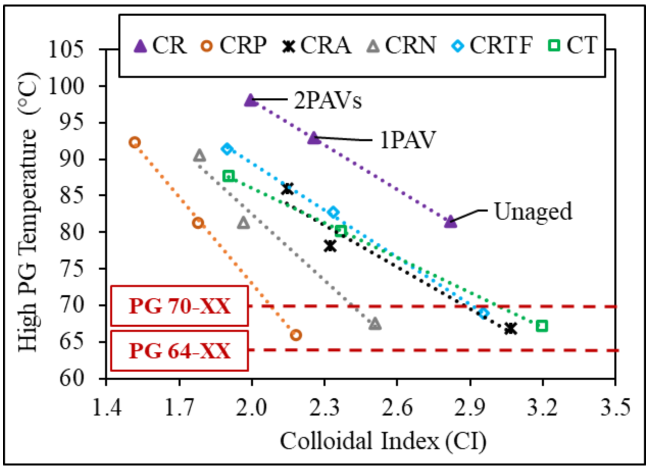
Source: Data from [1]Haghshenas et al. [33] and [2]Haghshenas et al. [10]

Note:

1) Phase angle (δ) and complex modulus (G*) are measured at 45°C at 10 rad/sec.
2) G-R = $G^* \times \frac{(\cos\delta)^2}{\sin\delta}$

It is worth mentioning that all modified binders could satisfy the PG 64-28 requirements (target binder in this study). Figure 1(a) shows that the high PG temperature of these binders in their original state falls between lines of 70 °C and 64 °C which indicates these binders have a minimum true grade (high PG temperature) of PG 64 °C. Figure 1(b) and (c) show that, after standard aging, the S-values and m-values of all modified binders, when tested at -18°C, are less than 300 MPa and greater than 0.300, respectively, and therefore all of these binders meet the low temperature requirements for a PG XX-28 binder.

In order to obtain relationships between chemical and rheological properties and colloidal structure of binders, linear empirical correlations between experimental data are derived, as shown in Figure 1. The main reason for the choice of linear correlations is its simplicity and straightforwardness. Another advantage of linear correlation is the explicitness, i.e., proportionality between parameters and measurements are clearly defined.



(a)

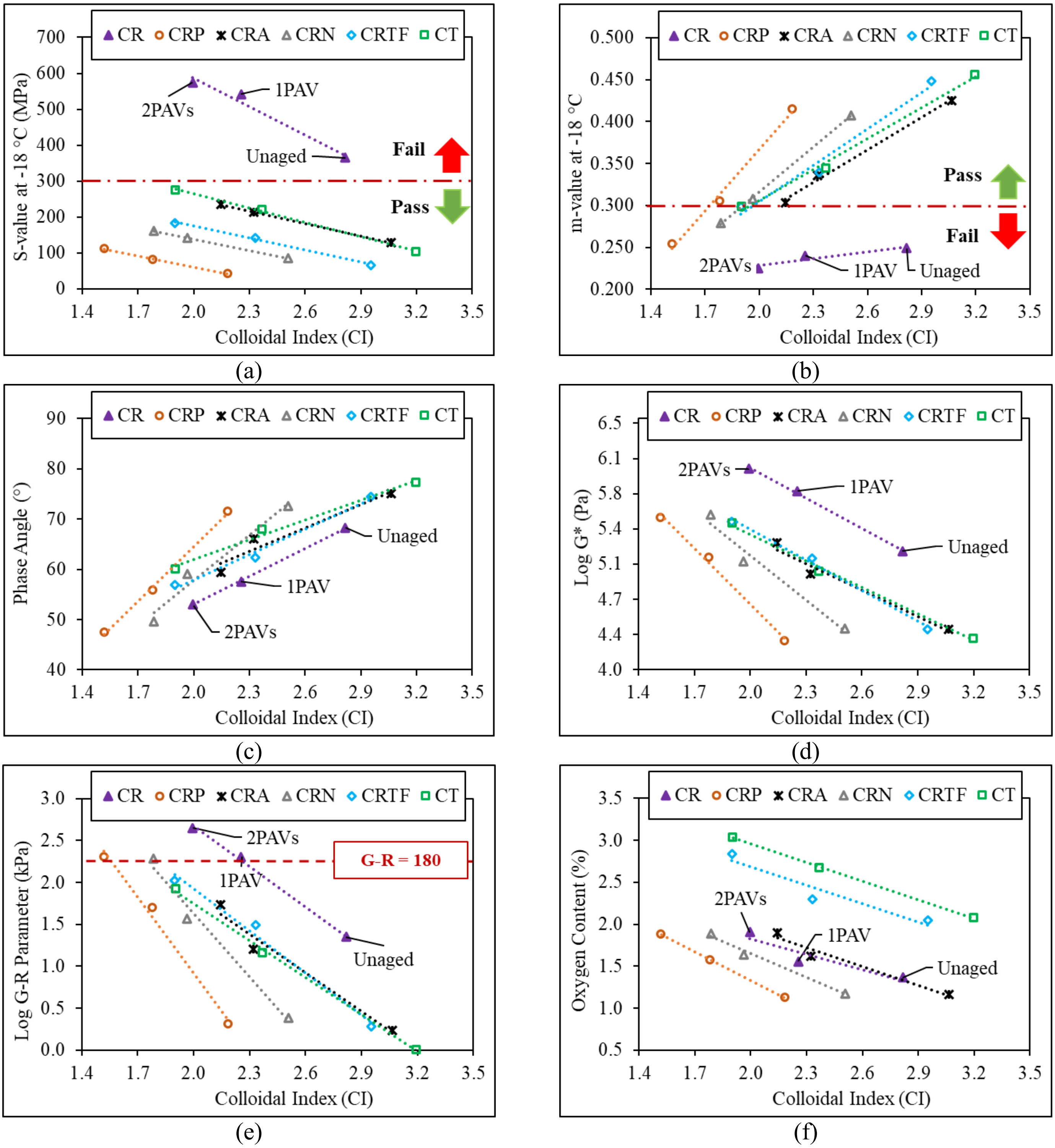


Figure 1. Linear correlation between chemical/rheological properties and colloidal index (CI) at the unaged, standard, and extended aging conditions.

The data reported in Table 3 is used to plot chemical and rheological- properties versus CI for each binder in different aging conditions (see Figure 1) and the linear empirical correlations are shown in Table 4. According to the results presented in

Figure 1 and Table 4, there is a strong correlation between the chemical and rheological properties and the CI of all binders, with the exception of the G-R parameter. Flexural creep stiffness (S-value), high PG temperature, Log complex modulus (Log (G^*)), G-R parameter, and oxygen content with CI are inversely proportional while phase angle and the relaxation constant (m-value) are directly proportional. It means a decrease in the CI of unmodified binder (CR) and modified binders by RAs due to aging, leads to an increase in high PG temperature, Log (G^*), S-value, G-R parameter, and oxygen content which indicates more solid-like behaviour (more brittle) of binder. This decreasing trend in CI consequently decrease both the phase angle and m-value.

Table 4. Correlation between rheological properties and colloidal index (CI) at the unaged, standard, and extended aging conditions.

Binder ID	Equation	R^2
CR	S-value (MPa) = -263.73 CI + 1114.70	0.97
CRP	S-value (MPa) = -105.36 CI+ 270.53	1.00
CRA	S-value (MPa) = -115.34 CI + 481.41	1.00
CRN	S-value (MPa) = -104.20 CI + 346.75	1.00
CRTF	S-value (MPa) = -111.89 CI + 398.89	1.00
CRT	S-value (MPa) = -133.42 CI + 531.64	1.00
CR	m-value = 0.0271 CI + 0.1743	0.99
CRP	m-value = 0.2444 CI - 0.1221	1.00
CRA	m-value = 0.1288 CI + 0.0313	0.99
CRN	m-value = 0.1786 CI - 0.0415	1.00
CRTF	m-value = 0.1446 CI + 0.0154	0.98
CRT	m-value = 0.1234 CI + 0.0589	0.99
CR	Phase Angle (°) = 18.570 CI + 15.902	1.00
CRP	Phase Angle (°) = 36.393 CI - 8.259	1.00
CRA	Phase Angle (°) = 15.566 CI + 27.729	0.94
CRN	Phase Angle (°) = 30.103 CI - 2.365	0.97
CRTF	Phase Angle (°) = 16.802 CI + 24.295	0.99
CRT	Phase Angle (°) = 13.075 CI + 35.844	0.99
CR	Log G* (kPa) = -1.0028 CI + 8.0115	1.00
CRP	Log G* (kPa) = -1.8565 CI + 8.3653	0.99
CRA	Log G* (kPa) = -0.8759 CI + 7.0695	0.97
CRN	Log G* (kPa) = -1.4840 CI + 8.1059	0.97
CRTF	Log G* (kPa) = -1.0210 CI + 7.4396	0.99
CRT	Log G* (kPa) = -0.8767 CI + 7.0988	1.00
CR	High PG Temperature (°C) = -20.283 CI + 138.63	1.00
CRP	High PG Temperature (°C) = -39.415 CI + 151.84	1.00
CRA	High PG Temperature (°C) = -19.041 CI + 124.79	0.94
CRN	High PG Temperature (°C) = -30.215 CI+ 142.87	0.97
CRTF	High PG Temperature (°C) = -21.474 CI + 132.46	1.00
CRT	High PG Temperature (°C) = -15.907 CI + 117.92	1.00
CR	Log G-R = -1.6021 + 5.8751	0.99
CRP	Log G-R = -3.0287 CI + 6.9745	0.99
CRA	Log G-R = -1.5321 CI + 4.9089	0.97
CRN	Log G-R = -2.5198 CI + 6.6672	0.98
CRTF	Log G-R = -1.6748 CI +5.277	0.98
CRT	Log G-R = -1.4658 CI + 4.6791	0.99
CR	Oxygen Content (%) = -0.6052 CI + 3.03	0.86
CRP	Oxygen Content (%) = -1.1200 CI + 3.58	0.99
CRA	Oxygen Content (%) = -0.7447 CI + 3.43	0.96
CRN	Oxygen Content (%) = -0.9500 CI+ 3.55	0.99
CRTF	Oxygen Content (%) = -0.7297 CI + 4.14	0.91
CRT	Oxygen Content (%) = -0.7353 CI + 4.42	0.99

Conclusion

In this study a base asphalt binder (CR) were modified using five different recycling agents including Paraffinic Oil (with an acronym P here): Aromatic Extract (A), Naphthenic Oil (N), Triglycerides/Fatty Acids (TF), and Tall Oil (T). Each modified binder was exposed to short- and long-term aging in the laboratory. Following aging, saturates, aromatics, resins and asphaltenes (SARA) portion of each sample was determined using TLC-FID analysis; SARA data was used to calculate colloidal index (CI) for each binder. Studying the change of CI due to the presence of each recycling agents (RAs), we determined the relationship between CI and rheological properties of binder. Findings of this research can be summarized as follows:

- There is a strong correlation between the CI and rheological properties of modified binder. The flexural creep stiffness (S-value), high PG temperature, Log complex modulus (G^*), Glover-Rowe (G-R) parameter, and oxygen content are inversely related to CI while the phase angle and relaxation constant (m-value) are directly related to CI.
- All RAs softened the CR binder due to a dilution in asphaltene content. The addition of the naphthenic and paraffinic oils decreased the initial CI which can be potentially explained by the higher saturate content in these RAs, while other RAs (A, TF, and T) increased the CI.
- The poor long-term performance of binders modified by naphthenic (N), and paraffinic (P) oils could be justified by a decrease in the initial CI. On the other hand, the CR modified by the aromatic extract (CRA) showed to have the lowest rate of loss of CI, compared to CRTF and CRT, resulting in best low-temperature performance among all binders after RTFO+2PAV cycles.

Recommended Future Studies

The study results showed that there is a strong correlation between the colloidal index and rheological properties of rejuvenated asphalt binder. Future studies are recommended to examine the relation between rheological and microstructure of asphalt in various environmental and aging conditions. Understanding such relationships help engineers and formulators design recycling agents with desirable performance.

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