Technical White Paper

Aging Characteristics of RAP Binders—What Types of RAP Binders Suitable for Multiple Recycling?

Fundamental Properties of Asphalts and Modified Asphalts III Product: FP 15

March 2015

Prepared for
Federal Highway Administration
Contract No. DTFH61-07-D-00005

By
Shin-Che Huang, Will Grimes, Troy Pauli, Ryan Boysen,
Steve Salmans, and Fred Turner
Western Research Institute
3474 North 3rd Street
Laramie, WY 82072
www.westernresearch.org

Western Research INSTITUTE

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF TABLES

AGING CHARACTERISTICS OF RAP BINDERS—WHAT TYPES OF RAP BINDERS SUITABLE FOR MULTIPLE RECYCLING?

INTRODUCTION

The use of recycled asphalt pavement (RAP) has become relatively common practice in most states as it is both an environmentally and economically attractive proposition. A survey conducted by the Federal Highway Administration's RAP Expert Task Group shows that the average RAP content in hot mix is only 10 to 20 percent as used in the United States, even though specifications allow up to 30 percent. The primary reason for this limited use is the uncertainty of the long term performance of RAP materials (Copeland 2008).

Some states have used RAP in Marshall mix designs with success (Kandhal 1997; Decker 1997; Terrel et al. 1997; Huffman 1997; Kearney 1997). Others have tried to use RAP in Superpave® mixture design (McDaniel and Shah 2003; Mohammad et al. 2003; Daniel et al. 2009). Some highway agencies, when using low percentages of RAP, do not consider the aged asphalt in RAP in the total asphalt content and properties, and therefore, consider RAP as a "black rock". The question of whether RAP, at any percentage, should be considered as "black rock" has not been answered conclusively even after more than 30 years of application. The current Superpave® system does not provide any guidelines for characterizing asphalt binders extracted from RAP, nor are there any test procedures available for recycled hot-mix asphalts. Furthermore, the interaction between new and old asphalt binders in the mixtures containing RAP has not been studied extensively and the physico-chemical interaction is still not well understood.

Current agency specifications typically indicate that 15 percent RAP, or less, by weight of mix may be added without changing the virgin binder grade. When the RAP content of a mix is between 15 percent and 25 percent by weight, the virgin binder grade must be adjusted to account for the stiffening effect of the old (recycled) asphalt binder. When RAP content is above 25 percent of a mix, a detailed design is necessary to select a virgin binder with appropriate properties (McDaniel and Anderson 2001). Several researchers have shown that RAP does not act like "black rock" when it is used at higher percentages (McDaniel and Anderson 2001; Peterson et al. 2000; Soleymani et al. 2000; Buttlar and Dave 2005; Kim et al. 2007; Guthrie et al. 2007; Karlsson and Isacsson 2003). Current NCHRP project 09-46 entitled "Improved Mix Design, Evaluation, and Materials Management Practices for Hot Mix Asphalt with high Reclaimed Asphalt Pavement Content (09-46)" is intended to develop a mix design and analysis procedure for hot mix asphalt (HMA) containing a high percentage of RAP. Additionally, NCHRP 09-46 research provides a specification for the use of a high RAP-percentage in HMA, and eventually to afford satisfactory long-term performance for high RAP content pavements. Another NCHRP project, 09-43; "Mix Design Practices for Warm Mix Asphalt," considered developing a preliminary volumetric mix design method for WMA that is also applicable to the use of recycled asphalt pavement in warm mix asphalts.

How RAP responds to oxidative aging has been a major concern in the development of a selection criterion for virgin and recycled asphalts. It is well known that oxidative aging not only leads to increased stiffness, but also causes changes in the chemical composition of asphalt binders. When an asphalt ages, the relative amount of non-polar molecules is reduced. This reduction occurs due to the conversion of non-polar molecules to oxygen containing polar groups. The increased associations among polar molecules change the nature of the asphalt and leads to increased stiffness and slower stress relaxation rates. Oxidation is an irreversible process mainly controlled by the reactivity of the binder, temperature, pressure, and the amount of oxygen available. As a result, the blended virgin and RAP binder will have a different aging susceptibility than that of the virgin binder.

Understanding the response of virgin/RAP binder blends to oxidative aging is important to the selection criterion for virgin and recycled asphalts. It is essential to understand the fundamental properties of recycled asphalt binder as well as the interaction between the old binder in the recycled asphalt and the fresh binder in the new mix. The objective of this study is to investigate chemical and rheological properties as a function of oxidative aging at pavement service temperatures in RAP and RTFO virgin asphalt blends for the case where all of the RAP is used in blending.

EXPERIMENT DESIGN

Two RAP sources from Manitoba (Man) and South Carolina (SC) were used in this study. RAP binders were extracted from these two RAP sources by using 85% toluene/15% ethanol. Properties of the extracted RAP materials are listed in table 1. The SHRP asphalts AAC-1 and AAA-1 were mixed with the extracted RAP binders at 15 and 50 percent for the aging study.

The mixing procedure is described as follows. The desired amount of RAP binder was added into neat asphalt binder. The blend was heated to 150°C for one hour, and then shaken using a paint shaker for 15 minutes. The sample was then placed back in the oven for 30 minutes and then shaken again for another 15 minutes. This procedure was repeated twice. The blend was then placed in the oven for an additional 15 minutes before cooling. The RAP blend binders were then poured into individual pans used for aging in a forced draft oven at ambient pressure and at 60°C for different durations ranging from 2 days, 2 weeks, 4 weeks, 8 weeks, and 12 weeks.

The rheological properties of unaged neat asphalts and laboratory aged asphalts and blends were measured using either a Rheometrics RDAII or an ARES rheometer. Data were obtained in the region of linear strain at frequencies of 0.1 to 100 radians per second and temperatures of -20, 0, 20, 40, 60, and 80°C using 25-mm, 8-mm, or 4-mm parallel plates with 1 mm, 2 mm or 1.75 mm sample gap. Master curves were constructed by using time-temperature superposition. The Christensen-Anderson model (Christensen and Anderson 1992) was used to shift all temperatures to a reference temperature of 20°C. Table 1 shows the properties of the two RTFO asphalts and two extracted RAP binders. DSR measurements were used to calculate the PG grade of each binder including low temperature grades. The four binders AAA-1, AAC-1, Manitoba RAP binder, South Carolina RAP binder are graded as PG61-33, 69-33, 91-28, and 95-18. Typical saturates, aromatics, resins, and asphaltenes (SARA) chromatographic separations (ASTM D4124) results are also included in table 1. Manitoba and South Carolina RAP binders have 31 and 34 percent asphaltene contents, respectively, whereas asphalts AAA-1 and AAC-1 have only 20 and 14 percent asphaltene content. This difference in asphaltene content between aged and unaged binders is expected. The complex modulus of Manitoba RAP binder at reference temperature of 20°C and frequency of 10 rad/s is 5.48E06 Pa and 19.6 E06 Pa for South Carolina RAP binder at the same temperature and frequency. Note that Manitoba RAP represents "young" RAP and South Carolina RAP represents "old" RAP in this study.

Table 1. Fundamental properties of neat asphalts and extracted RAP binders.

Asphalt	AAA-1	AAC-1	Man RAP Binder	SC RAP Binder
PG: based on DSR (SHRP report)	61.2-33 (58-28)	68.7-33 (58-16)	91.0-28	95.3-18
Complex Modulus, G*, x 10^6 pa @ 10 rad/s. Tr=20°C	1.13	1.51	5.48	19.6
Phase Angle, δ degree @ 10 rad/s. Tr=20°C	62.4	60.9	45.7	37.0
SARA Fractions, %				
Asphaltenes	20.0	14.0	31.3	34.1
Polar Aromatics	36.0	38.0	30.4	29.7
Napthene Aromatics	27.0	29.0	19.8	17.2
Saturates	14.0	17.0	14.2	13.8
AFT				
P	4.73	4.58	2.05	3.19
Pa	0.51	0.59	0.55	0.62
P_0	2.06	1.88	0.92	1.21
IR Results				
C=O (Peak Height)	0.0276	0.0393	0.1409	0.1448
S=O (Peak Height)	0.0497	0.0530	0.1168	0.1126

RESULTS AND DISCUSSION

Rheological Properties

Influence of RAP Binders

The RAP blend binders were investigated to observe how their rheological properties change after forced draft oven aging. The aging experiments were performed for durations of up to 12 weeks at 60°C. Our intention is to explore the features of the oxidative aging with respect to time and temperature that occurs in the field pavement and to model the corresponding modulus increase. The Christensen-Anderson model (Christensen and Anderson 1992) was used to shift all temperatures to a reference temperature of 20°C. Rheological parameters such as the rheological index and crossover frequency were applied to characterize the linear viscoelastic properties of materials in addition to the traditional shape of the master curves and/or the location of the master curves.

Figure 1 shows typical complex modulus and phase angle master curves for two fresh asphalt binders and two extracted RAP binders, Manitoba and South Carolina. It can be seen from figure 1 that RTFO-aged asphalts AAA-1 and AAC-1 show similar rheological behavior in terms of their complex modulus and phase angle at either high or low frequencies, although their moduli cross over at some point below 1 rad/s. However, Manitoba RAP binder is much stiffer than the two fresh asphalts and the South Carolina RAP binder shows an even higher complex modulus than that of Manitoba RAP binder and the two fresh binders, especially at low frequencies. By the same token, South Carolina RAP binder has lowest phase angle as compared to Manitoba RAP binder and the two neat asphalt binders at low frequencies (high temperature). Those RAP behaviors are typical features of highly oxidized – aged binders.

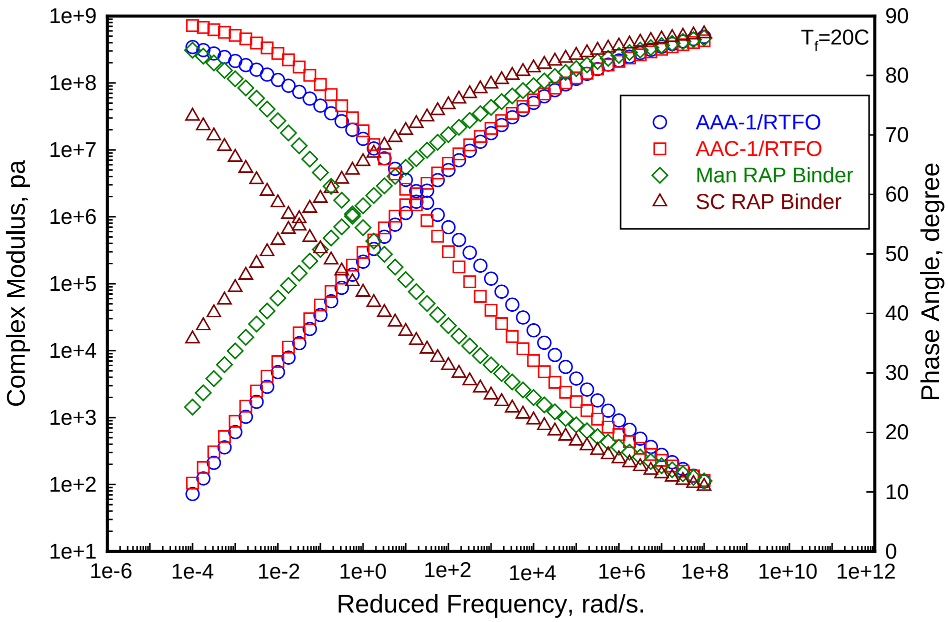

Figure 1. Graph. Complex modulus and phase angle master curves for two RTFO-aged asphalts and two extracted RAP binders.

To investigate how addition of RAP binders influence the relaxation properties of fresh binder, the master curve data for complex modulus and phase angle were used to calculate the relaxation modulus via a prony series mathematical model for all the samples. The prony series has been shown to provide more precise and mathematically efficient approach to calculate relaxation modulus for viscoelastic material than the other models (Ferry 1980). The prony series expression of the relaxation modulus is briefly described as follows:

$$G(t) = G_{\infty} + \sum_{i=1}^{n} G_i e^{-(t/\rho_i)}$$

Where: G(t) = relaxation modulus
G_{∞} = long-time equilibrium modulus
G_i = regression constants
ρ_i = relaxation time
n = number of dashpots in the model

Calculated relaxation modulus as a function of time plots for RTFO-aged asphalts AAA-1 and the blends with extracted RAP binders from Manitoba and South Carolina, as shown in figures 2 and 3, respectively, suggest that addition of RAP binder into RTFO-aged asphalt reduces the relaxation properties. The data also show that the extracted South Carolina RAP binder reduces the relaxation properties more than that of the extracted Manitoba RAP binder.

The plot of the slope of relaxation modulus versus time (or relaxation spectrum width) represents how the asphalt and RAP binder blends relax. The results of this analysis for these samples indicate that addition of extracted RAP binder to RTFO-aged asphalt increases the relaxation time. As more extracted RAP binder is added, the longer the relaxation time, i.e. the slower the material can relax at a given time, as seen from figures 4 and 5. The results also show that the extracted South Carolina RAP binder has more effect on relaxation time than the extracted Manitoba RAP binder.

One of the most common rheological criteria used to characterize the compatibility properties of polymer blends is the modified cole-cole plot (G' versus G" plot). The modified cole-cole plot represents the changes between elastic and viscous components of the complex modulus. When G' is plotted against G", a straight line corresponding to G'=G" can be used to characterize the rheological properties of the blends. Data on the right side and under the straight line indicate a behavior dominated by the viscous or loss component of the modulus, i.e., stress is dissipated by flow. On the other hands, if the data fall on the left side and above the equal-modulus line, it indicates that the elastic mechanisms dominate the behavior of the samples under the testing condition. As expected, at high temperatures the asphalt blends are predominantly viscous, while at low temperatures the materials showed crossover frequency, indicating a transition in the behavior of the blends. This can also be observed in the frequency sweeps.

Figure 6 shows G' versus G" plot for AAA-1 and its different concentrations of Manitoba RAP binder blends. As seen from this figure, the relationship between stored and dissipated energy for blends during shear deformation is linear and the higher the RAP binder content, the more the behavior of the blends departed from the behavior of the neat asphalt but it still remains on viscous mechanism site (right side of the equal-modulus line). This also indicates the molecular structure remains unchanged and no new species formed between the two phases (old and fresh binders). It appears there is a transition in the behavior from viscous-dominated flow behavior at low frequencies (high temperatures) to elastic dominated at high frequencies (low temperatures), especially as RAP binder content increases. Figure 7 shows the same type of plot for asphalt AAC-1 and its Manitoba RAP binder blends. Linear relationship is still observed between G' and G" from zero RAP content to 100% RAP binder, indicating there is no composition dependent on the blends. The same type of plots for AAA-1, AAC-1, and their South Carolina RAP blends are also observed and are shown in the Appendix. These results indicate that the relationship between G' and G" is independent of RAP contents but is asphalt type dependent.

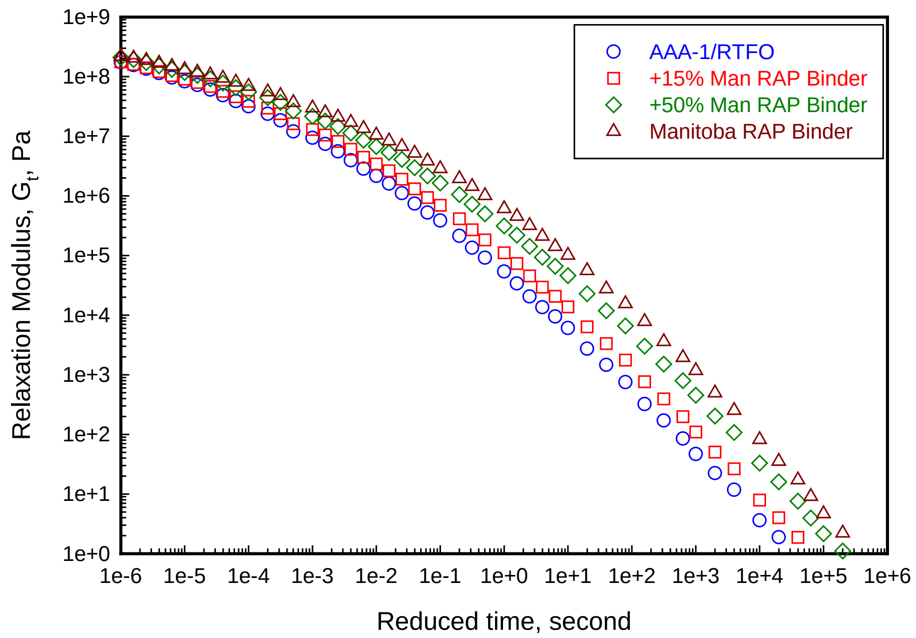

Figure 2. Graph. Relaxation modulus for RTFO-aged AAA-1 and its Manitoba RAP blend binders.

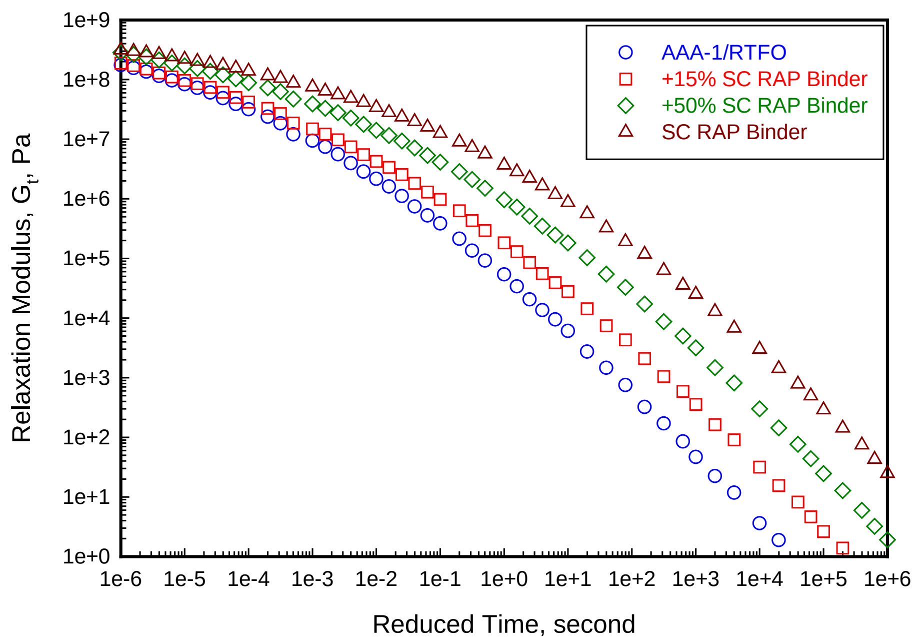

Figure 3. Graph. Relaxation modulus for RTFO-aged AAA-1 and its South Carolina RAP blend binders.

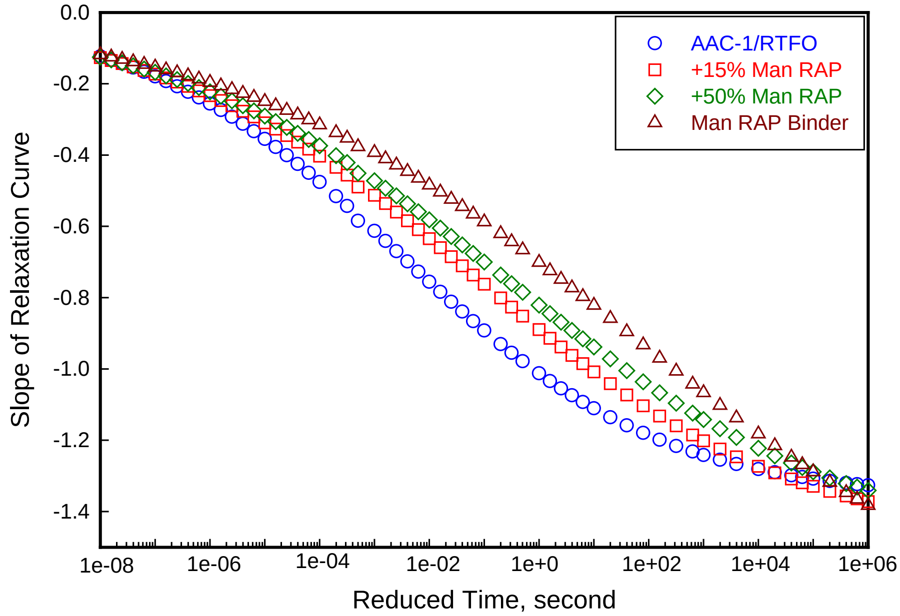

Figure 4. Graph. Slope of relaxation curve for RTFO-aged AAC-1 and its Manitoba RAP blend binders.

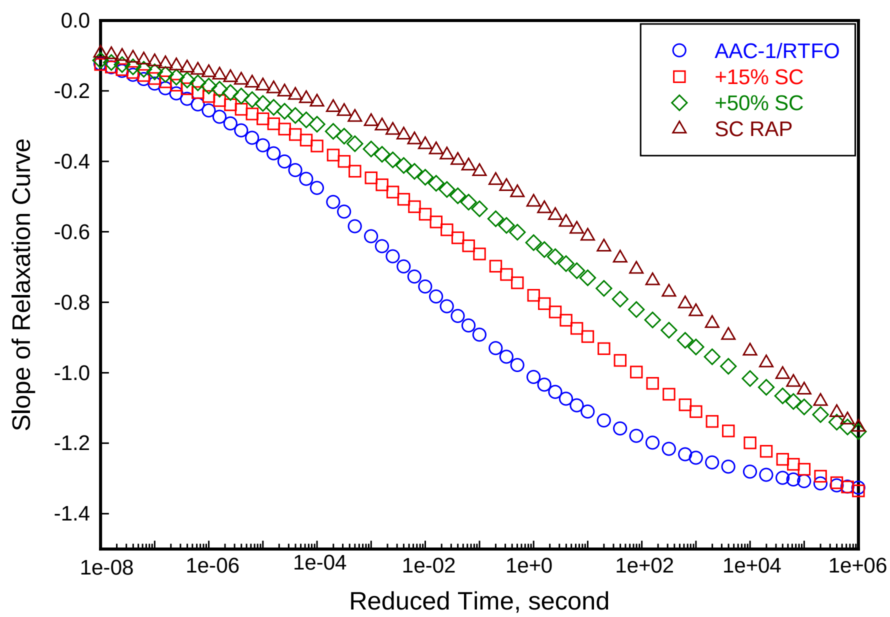

Figure 5. Graph. Slope of relaxation curve for RTFO-aged AAC-1 and its South Carolina RAP blend binders.

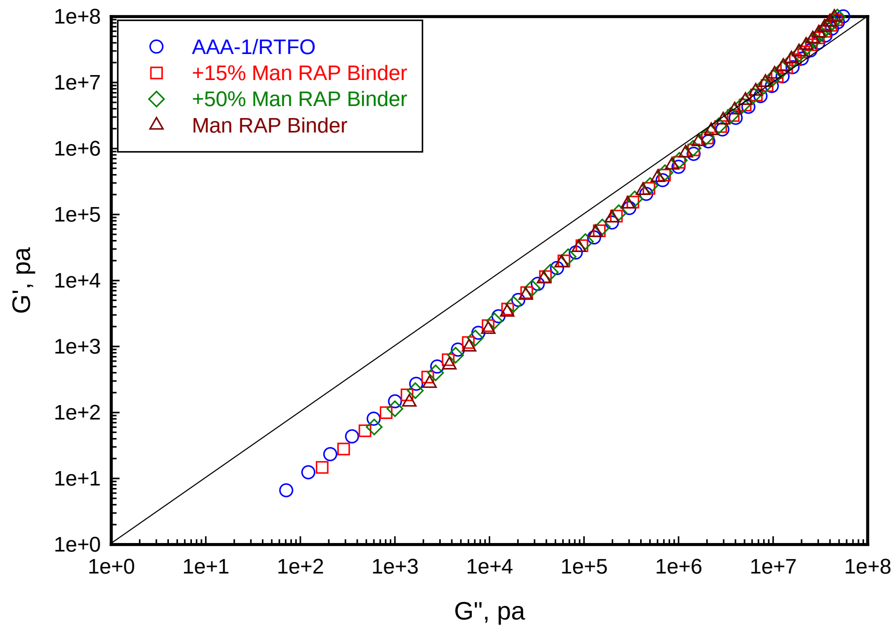

Figure 6. Graph. Relationship between G' (elastic) and G" (viscous) for RTFO-aged AAA-1 and its Manitoba RAP blend binders.

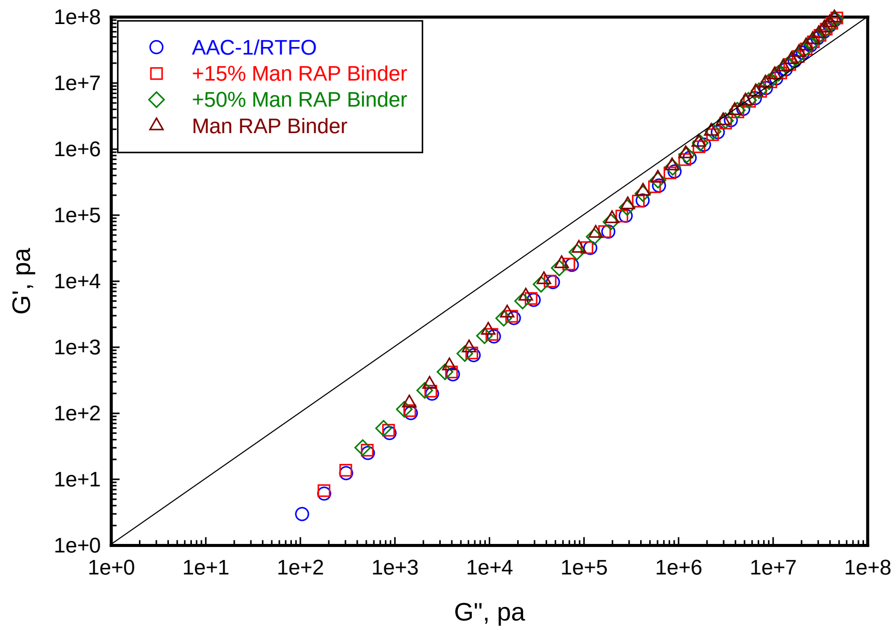

Figure 7. Graph. Relationship between G' (elastic) and G" (viscous) for RTFO-aged AAC-1 and its Manitoba RAP blend binders.

Figure 8 illustrates the variation of crossover frequency as a function of RAP content for both asphalts. Note that the crossover frequency is defined as the frequency where G' is equal to G'' or tan δ is one. The crossover frequency can be thought of as a hardness parameter and indicates the general consistency of asphalt at the selected temperature. As a general trend, the higher the crossover frequency, the more viscous flow the material will demonstrate. As seen from figure 8, the addition of RAP binders into fresh asphalt binders decreases the viscous components of fresh asphalt, and the change of crossover frequency due to addition of RAP binder to RTFO-aged asphalt AAA-1 is greater than the same RAP binder to RTFO-aged asphalt AAC-1.

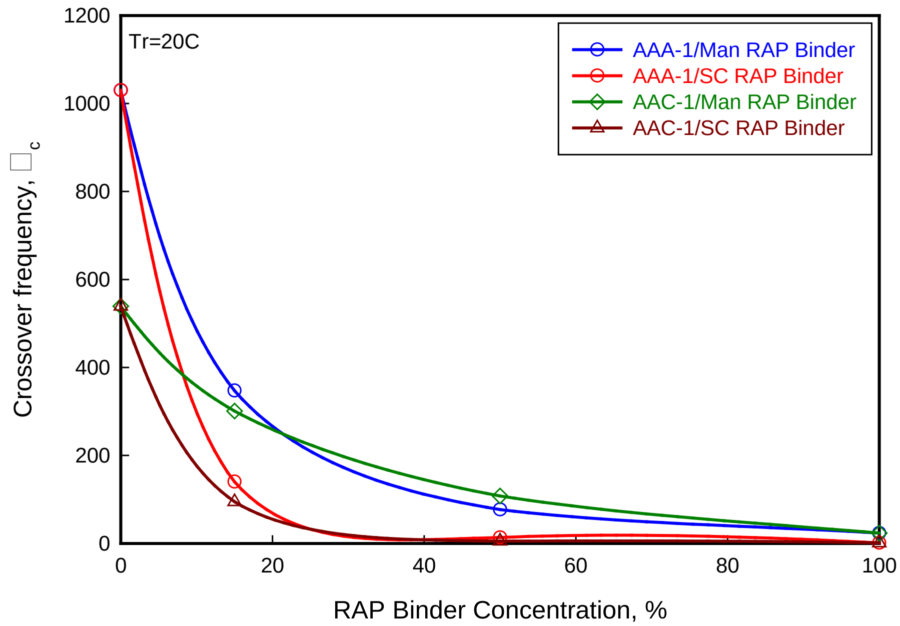

Figure 8. Graph. Crossover frequency as a function of RAP binder concentrations for two RTFO-aged asphalts.

Figure 9 shows another rheological parameter, the rheological index, as a function of RAP content for both asphalts. The rheological index is related to the width of the relaxation spectrum of an asphalt binder. Basically, the rheological index indicates the delayed elastic behavior that an asphalt binder will show. Usually, the higher the rheological index, the flatter the master curve will become, and the asphalt will tend to a larger elastic modulus. As seen from figure 9, the addition of RAP binder into asphalt binders increases the rheological index, and that the same RAP added to asphalt AAA-1 increases the elastic properties more than the same RAP added to AAC-1. This is consistent with the effect observed on crossover frequency.

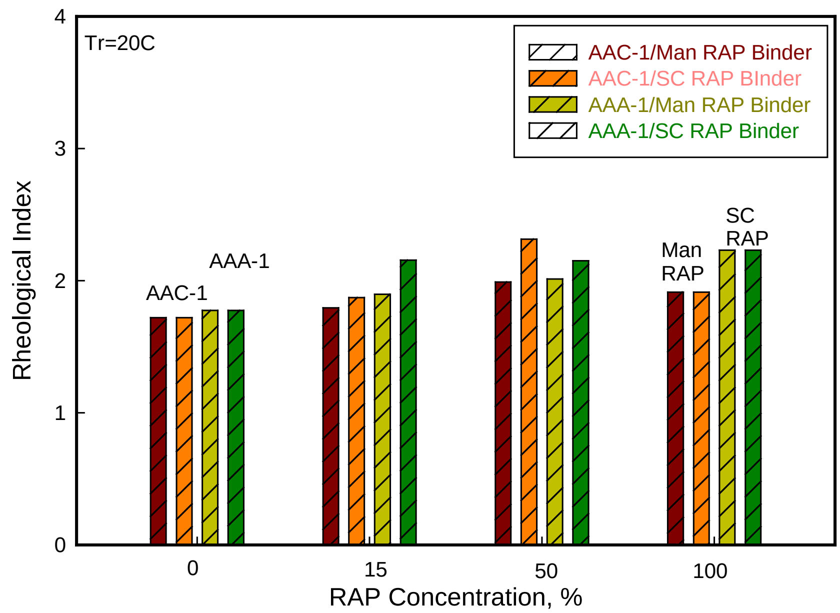

Figure 9. Chart. Rheological index for two RTFO-aged asphalts and their different concentrations of RAP blend binders.

To evaluate how addition of RAP binders influence the PG grade system of fresh asphalts, the measurements obtained from dynamic shear rheometer including 4 mm plate were used to calculate both high and low temperature grades (Sui et al. 2010). Figures 10 and 11 show high and low temperature grades for RTFO-aged asphalt AAA-1 and its RAP blends with Manitoba RAP binder (figure 10) and RTFO-aged AAC-1 mixed with the same RAP binder (Manitoba) (figure 11) at different concentrations. As seen from figure 10, the high temperature PG grade of RTFO-aged AAA-1 was increased from 61°C to 70°C with 15% Manitoba RAP binder and 78°C with 50% Manitoba RAP binder and up to 91°C with 100% Manitoba RAP binder. A linear regression on high temperature grades for RTFO-aged AAA-1 and its RAP blends at different concentrations (0, 15, 50 and 100%) shows a linear relationship, R-squared of 0.99, between PG high temperature grade and RAP content. Further conversion indicates that the approximate changes of PG grade will be 3 PG grades when addition of 50 percent of Manitoba RAP binder is mixed into this particular asphalt (figure 10). A similar regression was also obtained for another RTFO-aged AAC-1 mixed with the same Manitoba RAP binder at different concentrations and is shown in figure 11. It can be seen that the PG grade is changed to only one grade when 50 percent of RAP binder is mixed to this asphalt. The same linear relationships are also observed on the other two blends of RTFO-aged AAA-1 and AAC-1 with South Carolina RAP binder and are shown in figures 12 and 13. The R-squared of these two blends are 0.91 and 0.91, respectively. Further conversion indicates that the PG grade needs to be adjusted up to 4 PG grades when 50 percent of South Carolina RAP binder is going to be mixed into the asphalts. The lower R-squared value (0.91) may indicate less homogeneity in this more aged South Carolina RAP binder.

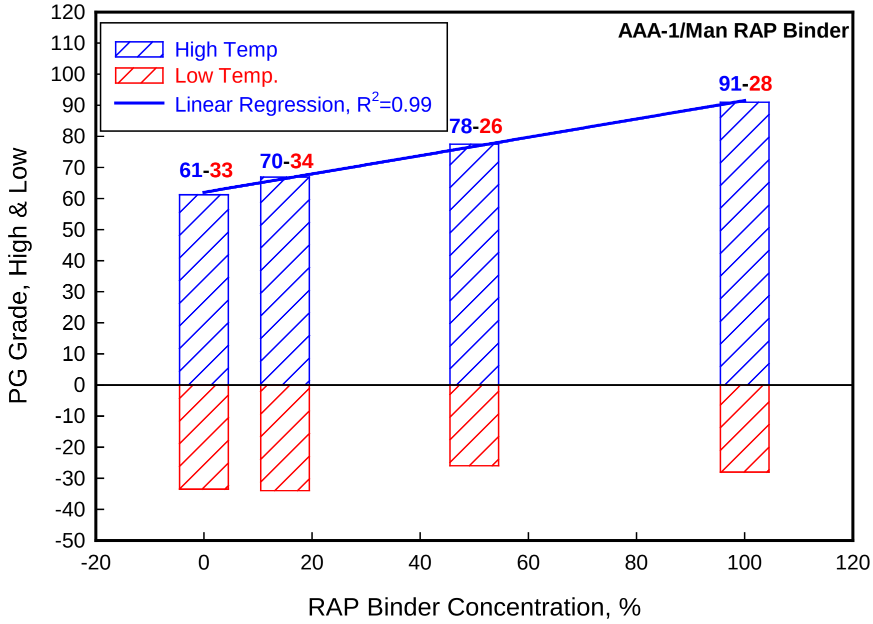

Figure 10. Chart. PG grades for RTFO-aged AAA-1 and its Manitoba RAP blend binders.

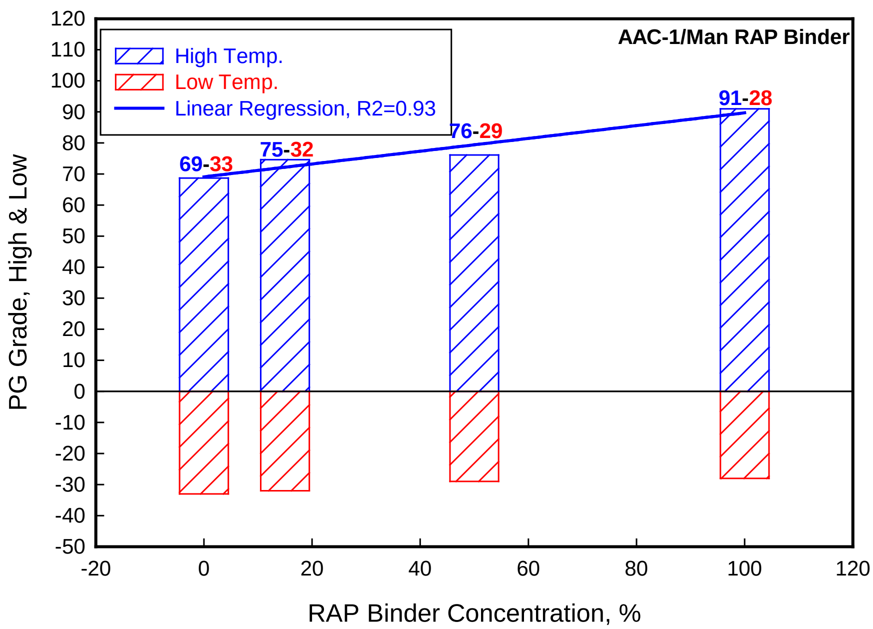

Figure 11. Chart. PG grades for RTFO-aged AAC-1 and its Manitoba RAP blend binders.

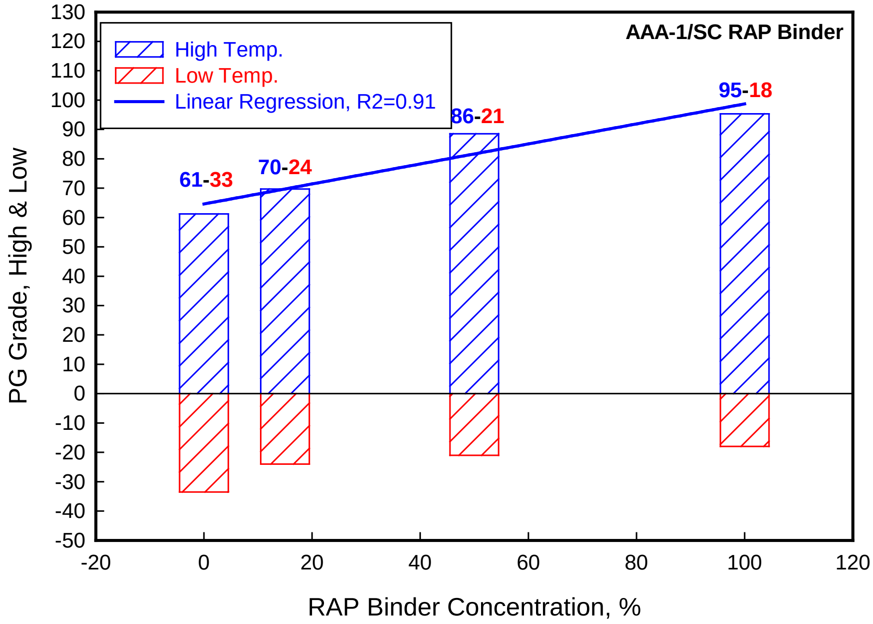

Figure 12. Chart. PG grades for RTFO-aged AAA-1 and its South Carolina RAP blend binders.

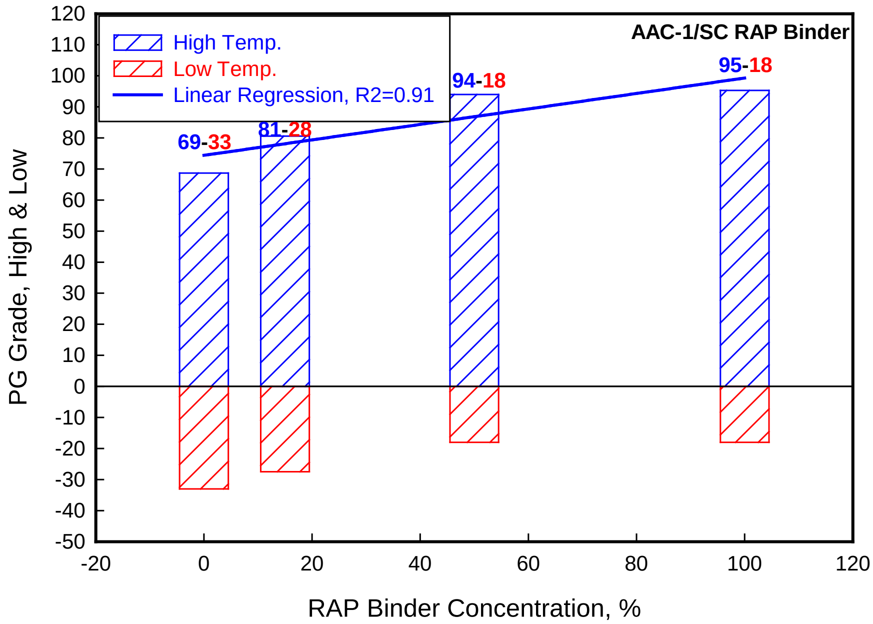

Figure 13. Chart. PG grades for RTFO-aged AAC-1 and its South Carolina RAP blend binders.

The low temperature grade shows some scatter, however, the general trend still can be seen from figures 10 through 13: addition of RAP binder into fresh asphalt increases its low temperature grade from -33 for RTFO-aged AAA-1 to -28 for the Manitoba RAP binder and to -18 for the South Carolina RAP binder. Note that the Manitoba RAP binder was graded as PG91-28, and the South Carolina RAP binder was graded as PG95-18. The linear equations for low temperature grades for all blends are also listed as follows:

$PG_{AAA\text{-}1/Manitoba}$= -33.176-0.0679*(%RAP), R^2=0.572
$PG_{AAA\text{-}1/South\ Carolina}$= -29.496-0.130*(%RAP), R^2=0.74
$PG_{AAC\text{-}1/Manitoba}$= -32.608-0.0511*(%RAP), R^2=0.91
$PG_{AAC\text{-}1/South\ Carolina}$= -30.175-0.147*(%RAP), R^2=0.77

These four figures indicate that different asphalts interact with different RAP binders differently. The interaction between virgin binders and RAP binders contribute to different stiffening effects. The stiffening effect increased by the addition of RAP binders can possibly be explained by the following mechanisms.

Possible mechanism can be that the modulus is increased by virtue of the volume fraction occupied by the increased amount of dispersed asphaltene particles. This part of the modulus increase can be predicted by Einstein law and/or its modifications such as the Pal-Rhodes model. Note that RAP binder is kind of a gel type material. Gel type materials differ from sol type materials because they contain a large number of elements of three-dimensional structure. The interlocking of these structural elements gives the systems an appearance of rigidity. Apparently, the formation of three-dimensional structures can be caused by attractive forces between the individual molecules which are either of the van der Waals type, or in the case of polar molecules caused by hydrogen bonds.

Another possible explanation can be that the modulus is increased by inter-particle attraction force (possible the van der Waals forces) or π-π interactions, which tend to stiffen the asphalt. This mode of modulus increase is enhanced by the apparent particle size and possible retarded by the dispersing action of asphaltenes. But, it eventually produces non-Newtonian flow. All particles are attracted to other particles by certain fundamental forces, the so-called van der Waals or other dispersion forces, where particles are of colloidal dimensions, they make a large number of contacts with each other. A number of these particles associate upon contact as a result of these different forces. Note that the polar molecules may also tend to associate strongly to form organized structures through the continuous phase of the non-polar. This attraction of one polar molecule for another can form three-dimensional intermolecular structures and therefore stiffen the material. The more highly organized structure, the higher the material can resist the external force (better rutting resistance). Of course, the ability to form an organized structure depends on the strengths of the attraction and upon the number of sites where intermolecular attraction occur.

The third possible mechanism can be that the modulus is increased by the formation of a thick and viscous coating about the particles that increases the volume fraction. Asphaltenes are important for the formation of this coating. The coating of the particle by a thick and viscous film increases its effective volume. Then, from the Einstein equation (Einstein 1906), it is clear that this coated particle has a larger effect on stiffness than it would have without its coating. While coating interferes with the van der Waals interactions, it may provide an overriding effect which produces an over-all higher modulus.

In general, asphalts become less Newtonian as the particle concentration is increased. Gel character in the filled systems is therefore increased. The extra gel character will be in part due to particle-particle attractive forces. Nonetheless, further research is recommended to verify the possible mechanisms for the interaction between virgin binders and RAP binders.

The Pal-Rhodes model that was developed from Einstein's colloid theory in terms of accommodating for more concentrated suspensions to account for asphalt flow property was employed to characterize the flow properties of recycled asphalt pavement (RAP) binder blends. The Pal-Rhodes model used for RAP blend binders may be formulated as follows:

$$\eta_{blend} = (\eta_0)\left(1 - K_{blend}(x_a)\right)^{-2.5} \quad (1)$$

Where

η_{blend} = viscosity of blend binder

η_0 = viscosity of maltene fraction (of mixture)

x_a = asphaltene content after blending

K= solvation factor

The viscous property of the continuous maltene (solvent) phase of the blend is defined as

$$(\eta_0) = x_{RAP}(\eta_0)_{RAP} + x_{virgin}(\eta_0)_{virgin} \quad (2)$$

while the asphaltene (suspended) phase assumes these are additive and is defined as

$$(x_a) = x_{RAP}(x_a)_{RAP} + x_{virgin}(x_a)_{virgin} \quad (3)$$

Given the mass fractions of RAP x_{RAP} and virgin x_{virgin} asphalt to be blended, the respective asphaltene contents will be $(x_a)_{RAP}$ and $(x_a)_{virgin}$ and maltene viscosities will be $(\eta_0)_{RAP}$ and $(\eta_0)_{virgin}$, respectively.

Equation 1 indicates that the viscosity of the blend binder can be expressed by a function of maltene and asphaltene fractions of the blend using the Pal-Rhodes model. The viscosity of the maltene fraction of blend can be expressed by a linear function of virgin binder and RAP binder, as shown in equation 2 and asphaltene content of blend binder can be also expressed by linear relationship between virgin binder and RAP binder, as shown in equation 3.

Figure 14 shows asphaltene contents for different asphalts mixed with different concentrations of different RAP binders. Linear relationships exist (R-squared of 0.99 for all four) between asphaltene content and RAP contents, indicating the asphaltene content for blend binders can be calculated from properties of the virgin binder and RAP binder proportionally.

Figures 15 and 16 show the plots of rheological properties versus asphaltene contents of blend binders. Figure 15 shows complex modulus at 10 rad /s. at 60°C versus asphaltene mass fraction (iso-octane) for all blend binders and figure 16 shows phase angle at the same frequency and temperature versus asphaltene mass fractions for all blend binders. Both figures demonstrate that the influence of adding asphaltene content to the blend via addition of highly aged RAP binders has a controlling effect on the rheological properties, indicating that RAP blend binders follow the Pal-Rhodes rule in an additive fashion as well.

To further evaluate the relationship between chemical properties and asphaltene contents of RAP blend binders, the carbonyl and sulfoxide contents obtained from FTIR were correlated to asphaltene content for all blend binders. Figure 17 shows the relationship between iso-octane insoluble asphaltene mass fraction and the sum of carbonyl and sulfoxide contents for two asphalts and their different concentrations of RAP blend binders. R-squared of 0.76 is observed for the relationship.

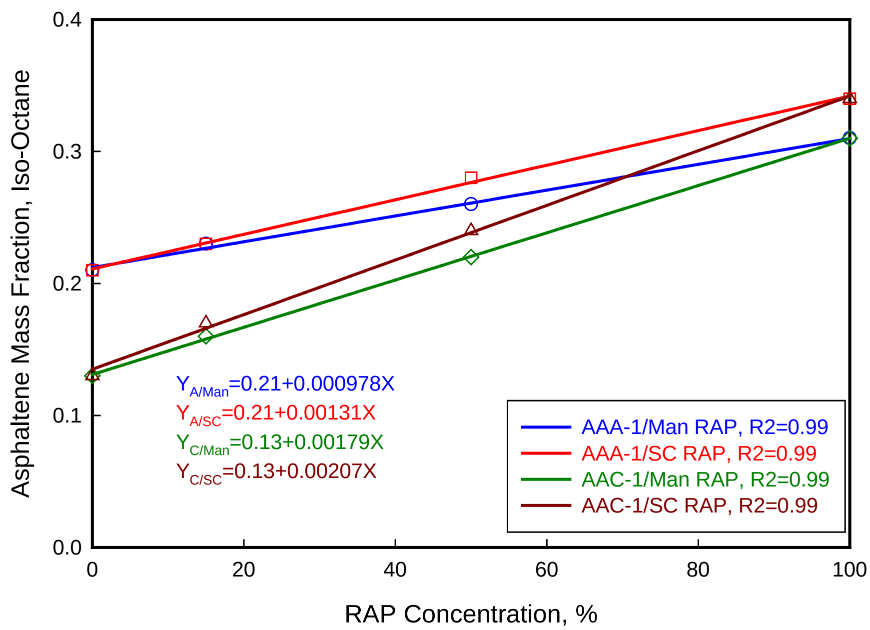

Figure 14. Graph. Asphaltene content versus RAP binder concentrations for two RTFO-aged asphalts and their RAP blends.

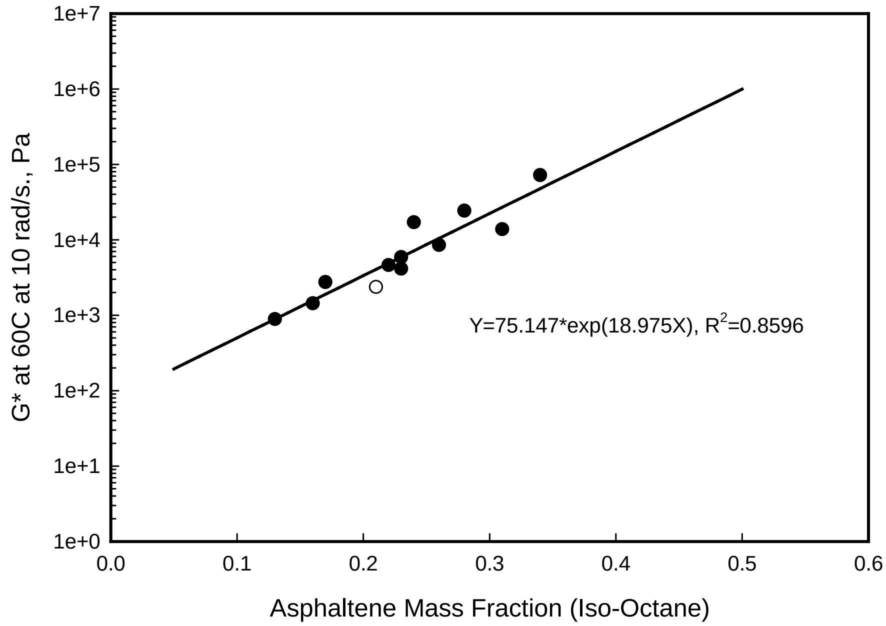

Figure 15. Graph. Relationship between G* and asphaltene contents for RAP blend binders.

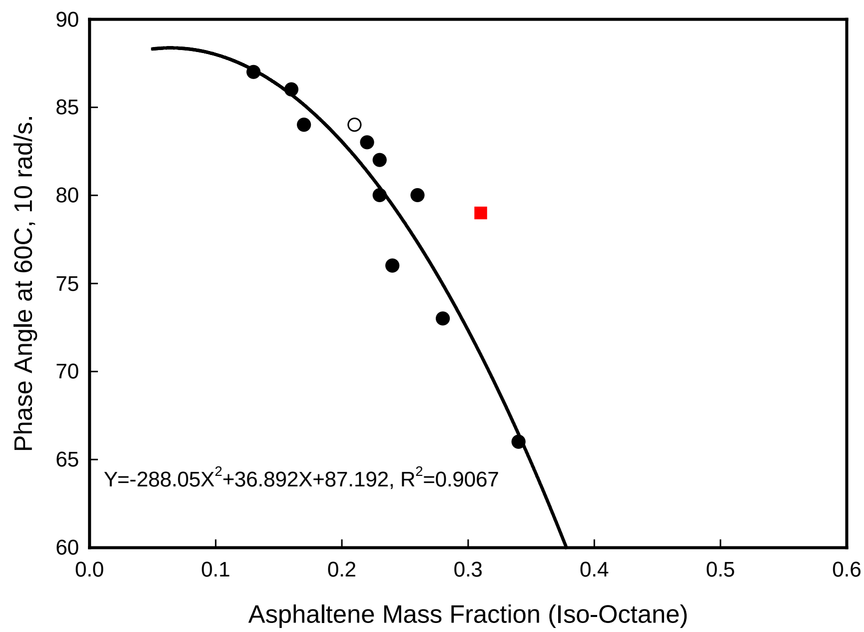

Figure 16. Graph. Relationship between phase angle and asphaltene contents for RAP blend binders.

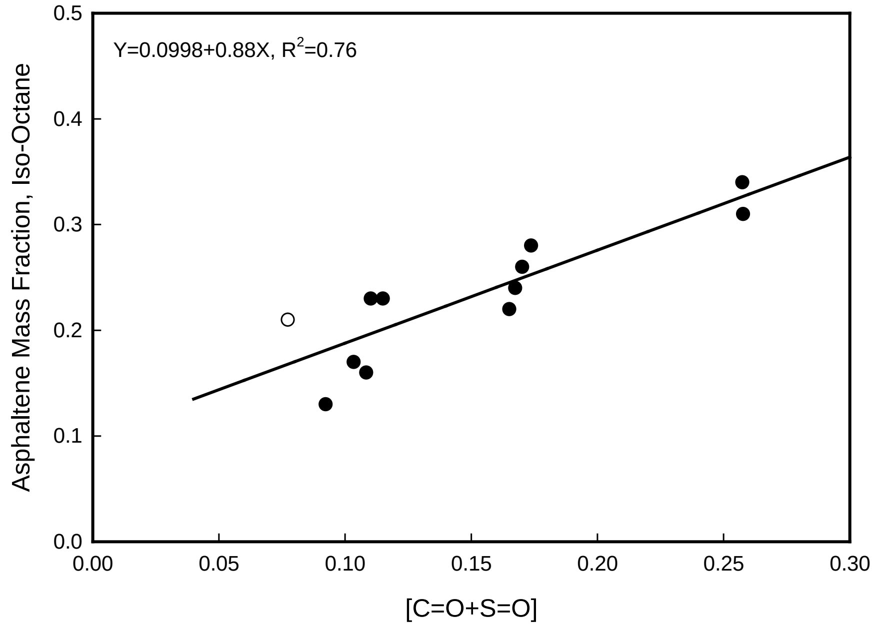

Figure 17. Graph. Relationship between asphaltene contents and IR results for RAP blend binders.

Aging Characteristics of RAP Blend Binders

Aged, blend binders were also removed from the oven after each period of aging time and subjected to IR and rheological testing. Aging kinetic curves in terms of rheological property were reported as follows.

Figures 18 and 19 show typical complex moduli as a function of aging time for two RTFO-aged asphalts AAA-1 and AAC-1 and their RAP blended binders after aging in a forced draft oven at 60°C and 0.75 atmosphere pressure (Laramie, Wyoming). Figure 18 shows the complex modulus at reference temperature of 20°C and at 10 rad/s. as a function of aging times for RTFO-aged AAA-1 and its South Carolina RAP blended binders at different concentrations, 15 and 50 percent. Trends are shown by the solid lines.

A nonlinear regression equation similar to typical aging kinetic model (fast and slow reaction rate) was applied to curve fit the data shown in figures 18 and 19. The equation is shown as follows:

$$G^* = G_0^* \exp\left[M \bullet \left(1 - \exp\left(-k_f \bullet t\right)\right) + k_s \bullet t \right] \quad (1)$$

where G*= complex modulus at given aging time, pa; G^*_0=complex modulus at zero aging time, pa; M= correlation coefficient; k_f=fast reaction coefficient; k_s=slow reaction coefficient; and t=aging time, days.

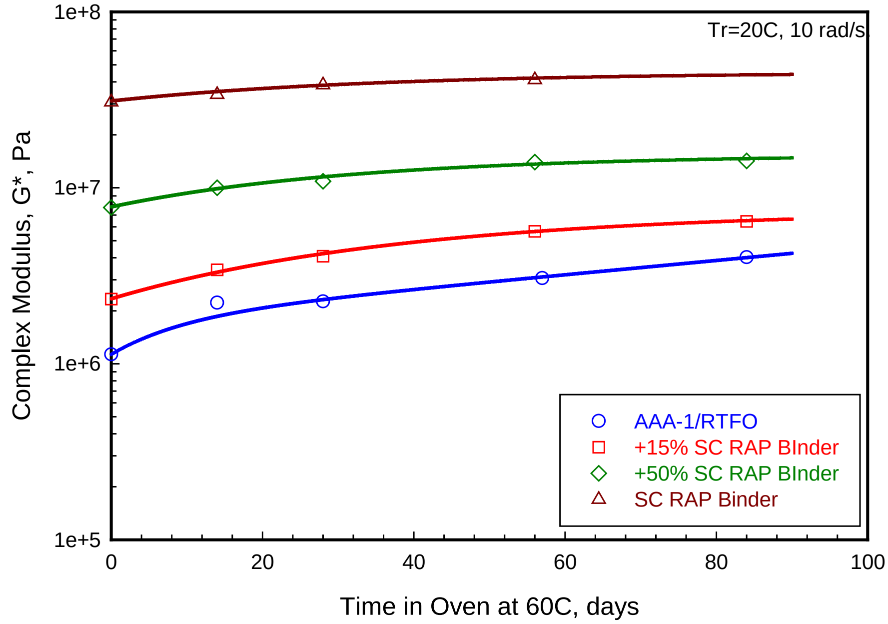

Figure 18. Graph. G* as a function of aging times for RTFO-aged AAA-1 and its South Carolina RAP Blend binders.

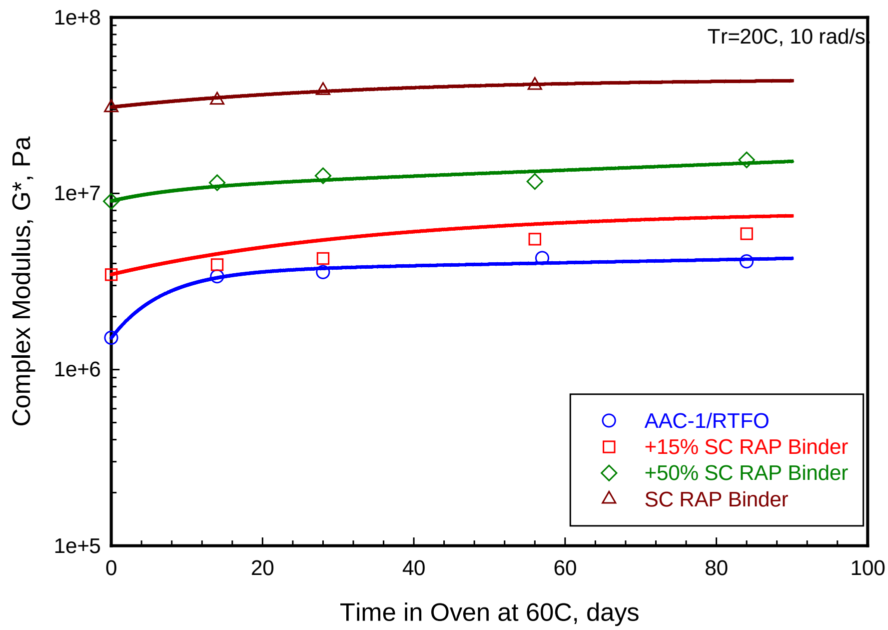

Figure 19. Graph. G* as a function of aging times for RTFO-aged AAC-1 and its South Carolina RAP blend binders.

These curve fittings provide information about how the modulus changes with oxidative aging time, but they do not predict aging temperature response as there is only one aging temperature that was used in this case. The temperature effects of the oxidation aging can be expressed in terms of the magnitude of reaction coefficients, k_f and k_s obtained from the results of the curve fittings and can be used to determine whether they obey the Arrhenius temperature dependency. Nonetheless, these results suggest that stiffness increases as a function of aging time is similar to that of chemical aging kinetic characteristics, fast reaction and constant (slow) reaction. A more detailed mathematical model for complex modulus versus aging time relationship will be presented in the future.

Nonetheless, as expected, addition of 15 percent RAP binder into fresh asphalt increases stiffness slightly, and 50 percent of RAP binder increases stiffness more. South Carolina RAP binder has an approximately 30 times higher complex modulus than RTFO-aged AAA-1 prior to oxidative aging, and it has an almost constant oxidation reaction rate at all aging times.

Figure 20 shows the same type of plot for RTFO-aged AAA-1 and its Manitoba RAP blends. Although the data are scattered, the same general trend still can be observed. The slow reaction oxidation reaction rate of the RAP binder alone also remains constant after certain period of oxidative aging times, as seen from figure 20, indicating this Manitoba RAP binder also reaches a constant reaction rate after short period of aging times in 60°C. Figure 21 shows the same type of plot, complex modulus versus aging times, for RTFO-aged AAC-1 and its Manitoba RAP blend binders. The same behavior observed in RTFO-aged AAA-1 and its RAP blends also occurs in AAC-1, addition of RAP binder to asphalt increases the complex modulus in almost proportional rate, addition of 50 percent RAP binder increases around 3.5 times more than that of 15 percent RAP binder.

The trends seen in figures 18 through 21 show that the stiffness increase as a function of aging time is similar to that of chemical aging, a fast reaction and slow reaction. Several studies (Petersen 1984; Petersen et al. 1993) have reported the stiffness increase with respect to concentration of polar components present in asphalts and increase in asphaltene content with oxidative aging. These authors concluded that when oxidation products are formed as a result of aging, they are immediately engaged in the intermolecular association with neighboring polar materials, and this intermolecular association is believed to increase stiffness. It can be seen that the stiffness increase as a function of aging time for all reblended binders are similar, stiffness increases substantially initially and then levels off after longer aging times. The difference between Manitoba RAP binder and South Carolina RAP binder in terms of their aging kinetic curves can be explained by the fact that Manitoba RAP is softer than that of South Carolina RAP, as seen in table 1.

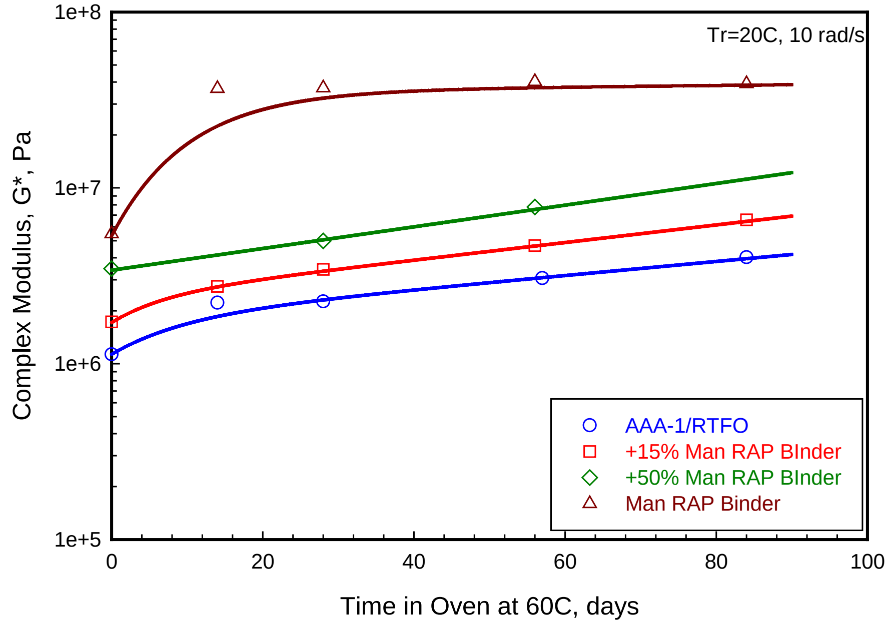

Figure 20. Graph. G* as a function of aging times for RTFO-aged AAA-1 and its Manitoba RAP blend binders.

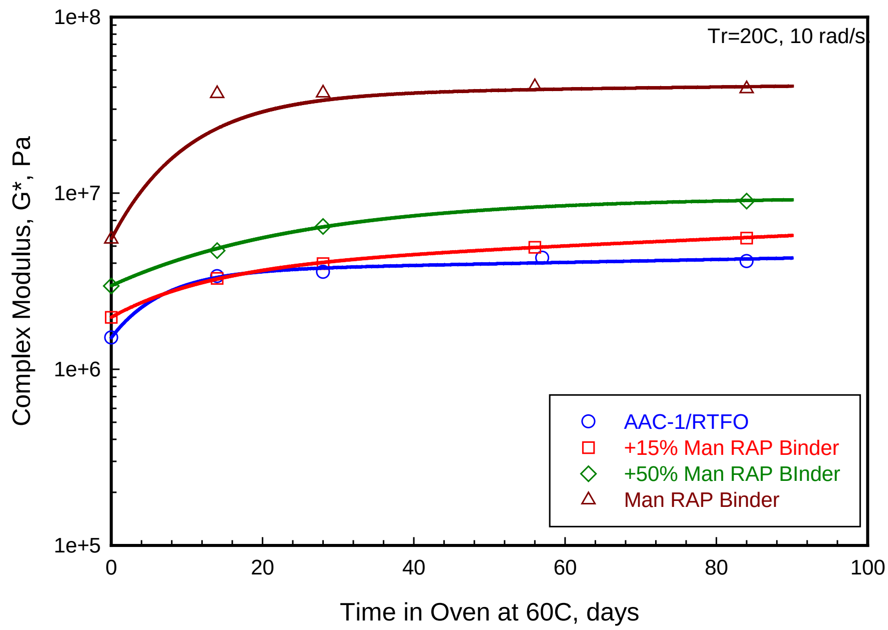

Figure 21. Graph. G* as a function of aging times for RTFO-aged AAC-1 and its Manitoba RAP blend binders.

The prony series used to calculate relaxation modulus for RAP blend binders was also used to laboratory aged RAP blend binders. Figures 22 and 23 show the converted relaxation modulus as a function of time for RTFO-aged asphalt AAC-1 and its Manitoba RAP blend binders, 15 and 50 percent of Manitoba RAP binder, with respect to different aging times, 14, 28, 57, and 84 days, at pavement service temperature of 60°C. As expected that oxidative aging reduces material's relaxation property and addition of 50 percent of RAP binder into neat asphalt reduces more relaxation property than that of 15 percent RAP binder to the same neat asphalt. Figure 24 show the same type of plot for AAC-1 mixed with 15 percent of South Carolina RAP binder with respect to different aging times. This figure 24 indicates that the influence of further laboratory aging on the relaxation property for AAC-1 from South Carolina RAP binder does not show as significant influence as that of Manitoba RAP binder do at the same aging conditions. This can possibly be explained by the fact that South Carolina RAP binder is an old RAP and is a very stiff material. Rheological aging kinetic curves shown in the previous section (figures 18 and 19) have shown that this material has constant aging coefficient reaction rate even further subjecting to laboratory aging.

The important role of phase angle on the aging characteristics of asphalt materials has been proposed by the author previously (Huang and Grimes 2010; Huang et al. 2011), and recently the idea has been extensively applied by the other researchers (Anderson et al. 2011; King et al. 2012). The phase angle indicates the level of viscoelasticity in the asphalt. It is desirable to have a certain level of viscous flow behavior in an aged asphalt to provide for the relaxation of stress. An asphalt exhibiting a higher strain to failure at the same stiffness is more resistant to thermal or fatigue cracking than an asphalt binder with a lower strain to failure at the same stiffness. In other words, it is reasonable to assume that the lower the phase angle at the same stiffness, the more susceptible asphalt becomes to fatigue cracking. Figure 25 shows the relationship between complex modulus and phase angle. The logarithm of the complex modulus and the phase angle are plotted for RTFO-aged AAA-1 and its RAP blends at different contents and aging time. Surprisingly, a linear (R-Squared=0.99) relationship between complex modulus and phase angle for all the aged and unaged AAA-1 samples and its RAP blends is observed. This indicates that the changes in log stiffness are proportional to phase angle for RAP blends at all aging severities. To further validate the log G* versus δ relationship, the same type of plot was applied to the other RAP blended binders. The linear equation for each blended binder is shown as follows:

$$\mathrm{Log}(G^*)_{\mathrm{AAA/SC\ RAP}} = 9.118-0.0502*(\delta),\ R^2=0.99$$
$$\mathrm{Log}(G^*)_{\mathrm{AAA/Man\ RAP}} = 8.971-0.0467*(\delta),\ R^2=0.96$$
$$\mathrm{Log}(G^*)_{\mathrm{AAC/SC\ RAP}} = 8.897-0.0466*(\delta),\ R^2=0.91$$
$$\mathrm{Log}(G^*)_{\mathrm{AAC/Man\ RAP}} =8.944-0.0485*(\delta),\ R^2=0.93$$

Figure 26 shows the same type of plot, logarithm of G* versus δ with respect to different aging times, for all RAP blends together. A strong linear (R-Squared=0.94) relationship can be clearly seen from this figure. The results from the log G* versus phase angle plot suggest that this plot may be used as an alternative approach to characterize material's flow property.

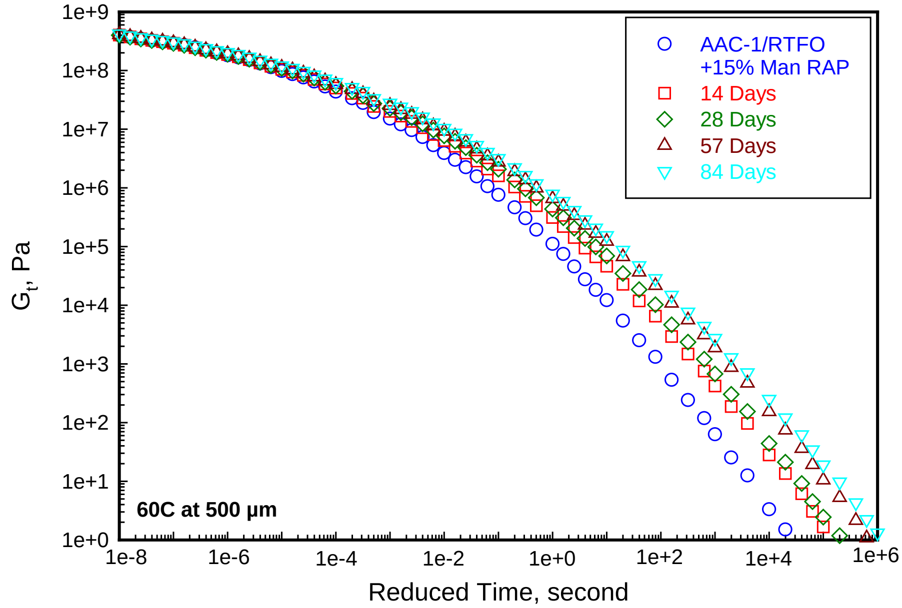

Figure 22. Graph. Gt for RTFO-aged AAC-1 mixed with 15 percent Manitoba RAP binder after aging.

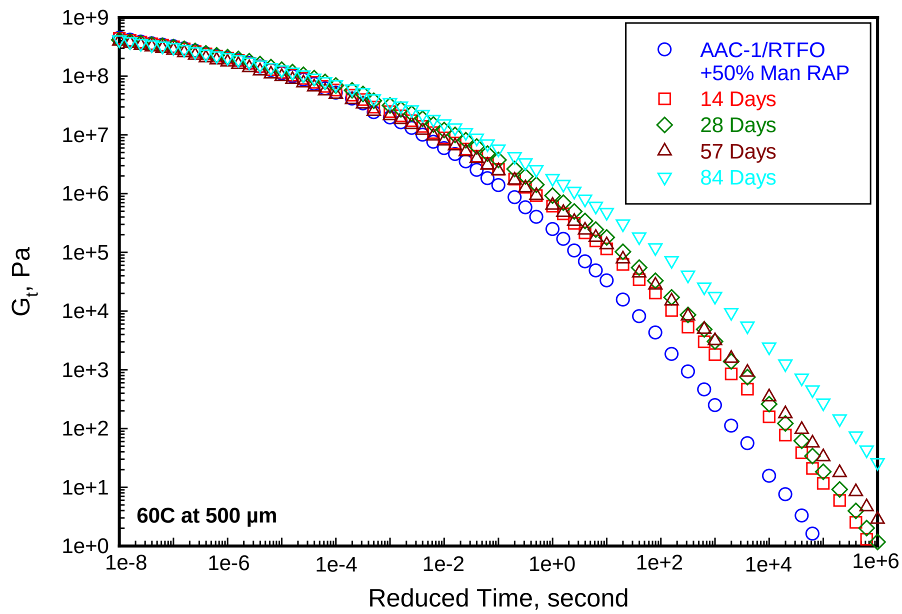

Figure 23. Graph. Gt for RTFO-aged AAC-1 mixed with 50 percent Manitoba RAP binder after aging.

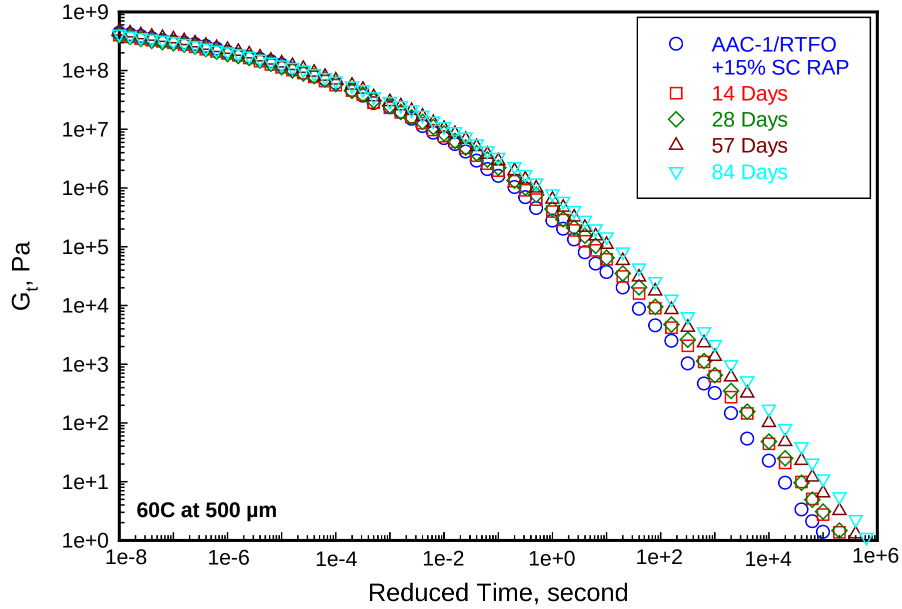

Figure 24. Graph. Gt for RTFO-aged AAC-1 mixed with 50 percent Manitoba RAP binder after aging.

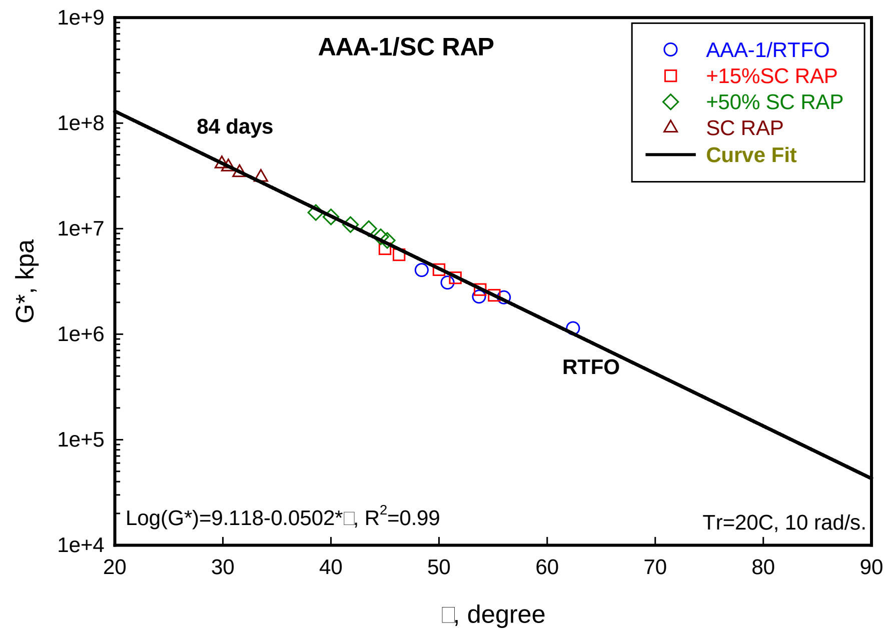

Figure 25. Graph. G* versus phase angle for RTFO-aged AAA-1 and its South Carolina RAP blend binders with respect to different aging times.

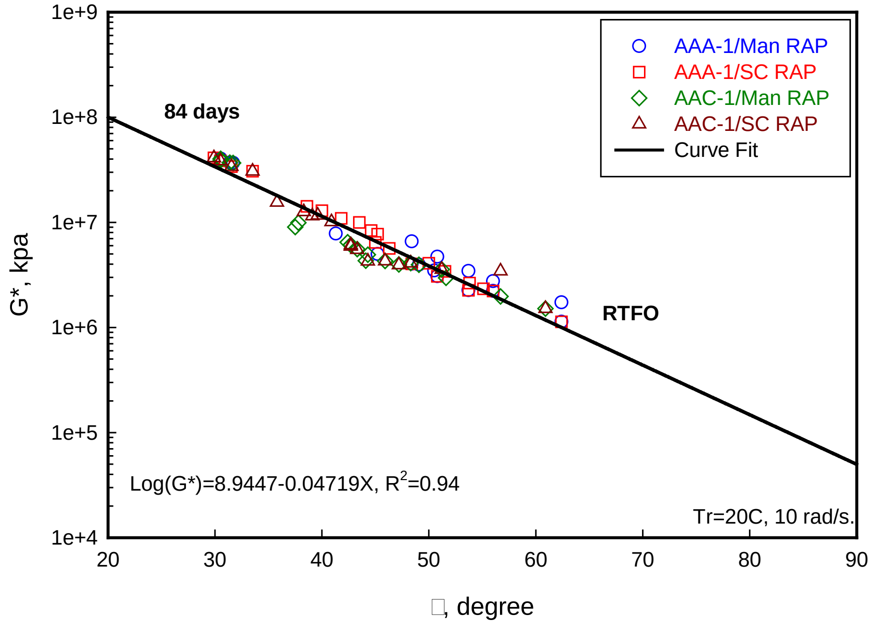

Figure 26. Graph. G* versus phase angle for RTFO-aged AAA-1 and its South Carolina RAP blend binders with respect to different aging times.

Chemical Properties

As mentioned at the beginning that all unaged and aged RAP blend binders were also subject to typical analytical tests such as FTIR, SARA separation, AFT, and MDSC. They are presented as follows:

The concentrations of carbonyl and sulfoxide were determined using a Perkin Elmer Spectrum 1 infrared spectrometer. The infrared spectrum of an asphalt sample was obtained by dissolving 50 mg asphalt in 1 mL carbon tetrachloride, placing the sample in a sodium chloride cell with a 0.1-cm path length, and recording the spectrum, using solvent compensation, from 4000 to 600 cm^{-1}. The amount of the carbonyl-containing compounds, centered at 1700 cm^{-1} (1680 ~ 1720 cm^{-1}) was estimated using a peak-height method.

Numerous studies of oxidation reaction kinetics have been carried out by different research institutes (Petersen 2009; Liu et al. 1996). Through these efforts, some reaction mechanisms (or pathways) have been elucidated, i.e., aliphatic sulfide to sulfoxide and benzylic carbon to carbonyl. These two mechanisms have long been recognized as two major pathways that cause the increases in viscosity of asphalt binders. These oxidized components and other oxygen containing byproducts of the reactions are polar species that increase the stiffness of the asphalt by molecular interaction with other polar groups. Since asphalt binders in recycled asphalt pavement (RAP) are highly oxidized, it is reasonable to assume that RAP binders contain significant amounts of carbonyl and sulfoxide. Because no chemical reaction is anticipated or assumed to occur between RAP and binder, the relationship between oxidation products (IR results) and RAP binder content should be linear.

Figure 27 shows carbonyl and sulfoxide peak height as a function of RAP contents for RTFO-aged asphalt AAA-1 and its Manitoba RAP blend binders. It can be seen that a linear relationship exists between IR results and RAP concentrations, as expected. Figure 28 shows the same type of plot, sum of carbonyl and sulfoxide as a function of RAP concentrations, for RTFO-aged asphalts AAC-1 and AAA-1 and their RAP blend binders at different concentrations. An R-squared value of 0.97 was observed for the relationship of IR results and RAP concentration, indicating that addition of RAP binders into fresh binders increases their chemical compositions proportionally and that no specific chemical species form from the blending. This may also suggest that an additive blending rule can be made from simple IR analysis.

Figure 29 shows the combination of carbonyl and sulfoxide peak height as a function of aging times at 60°C for AAA-1 and its Manitoba RAP blend binders. The difference in IR results (carbonyl and sulfoxide) between 50% and 15% RAP modified AAA-1 is evident, as expected. The Manitoba RAP binder in this case shows a nearly constant reaction rate, indicating it has passed through its initial spurt stage, and it is in a constant (slow) reaction rate. Figure 30 shows the same type of plot for AAA-1 and its South Carolina RAP blend binders. It can be seen from figures 29 and 30 that carbonyl and sulfoxide formations for the same asphalt blended with different RAP binders show similar rates of reaction at 60°C. The same trend for another asphalt AAC-1 and its two different RAP blend binders with respect to aging characteristics by means of the same chemical properties was also observed and is shown in the figures 31 and 32. Both Manitoba and South Carolina RAP binders show almost constant slow reaction rates. This may indicate that the aging characteristics of RAP binders may be similar in terms of chemical properties regardless young or old and RAP sources. To investigate how much reactive material each blend binder can provide, the Glaser-Petersen dual path kinetic model (Glaser and Loveridge 2012) was applied to calculate the reactive materials for each blend binder. Table 2 shows the calculated reactive materials for each binder. As seen from table 2 that South Carolina RAP binder contains the least amount of reactive material, approximately 0.05 absorbance. While asphalt AAC-1 consists of the highest reactive material (around 0.2 absorbance) as compared to the other binders. This can be easily seen from figure 31, where the oxidation reaction rate of South Carolina RAP binder remains almost constant all the way to the end of aging time of 12 weeks.

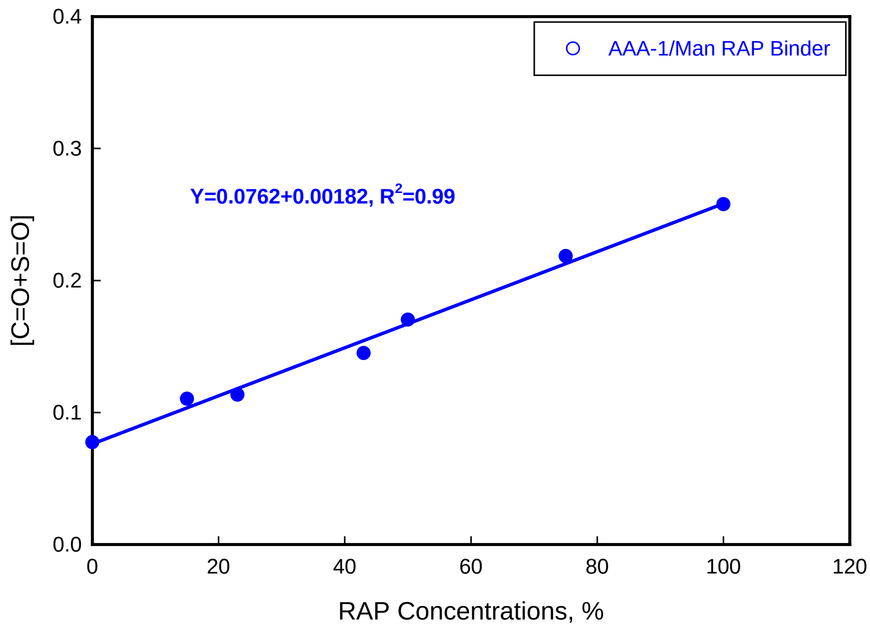

Figure 27. Graph. IR results for RTFO-aged AAA-1 and its different concentrations of Manitoba RAP blend binders.

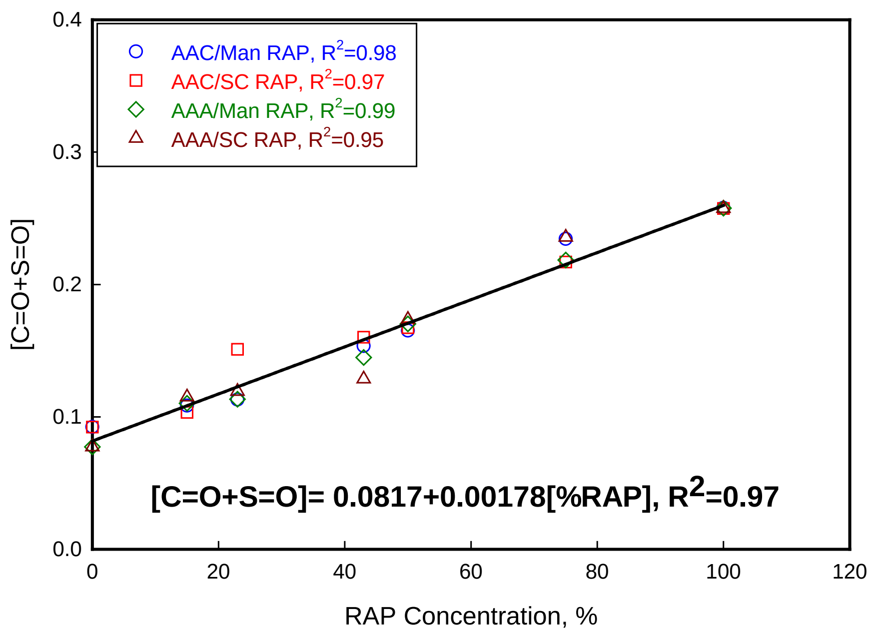

Figure 28. Graph. IR results for RTFO-aged asphalts and their different concentrations of RAP blend binders.

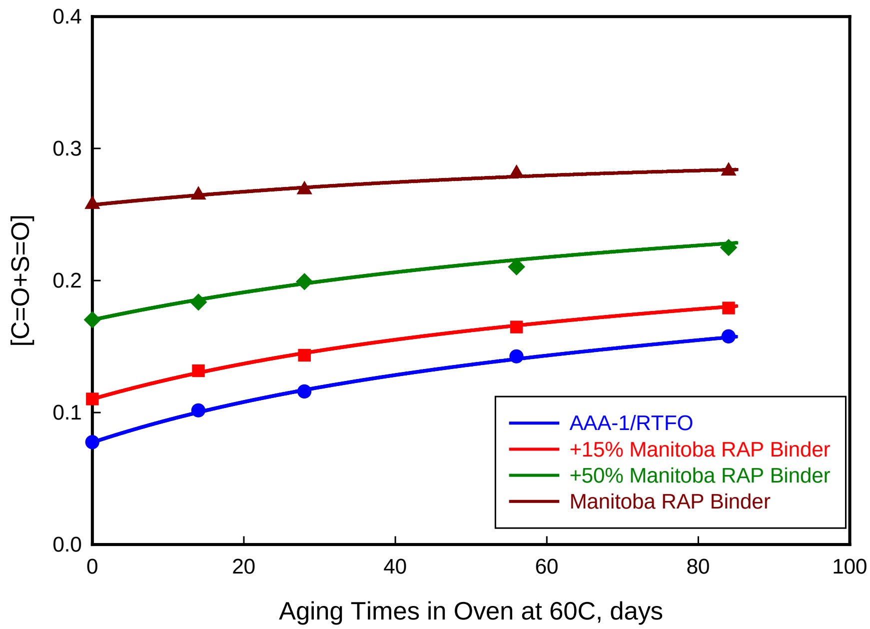

Figure 29. Graph. IR results as a function of aging times for RTFO-aged AAA-1 and its Manitoba RAP blend binders.

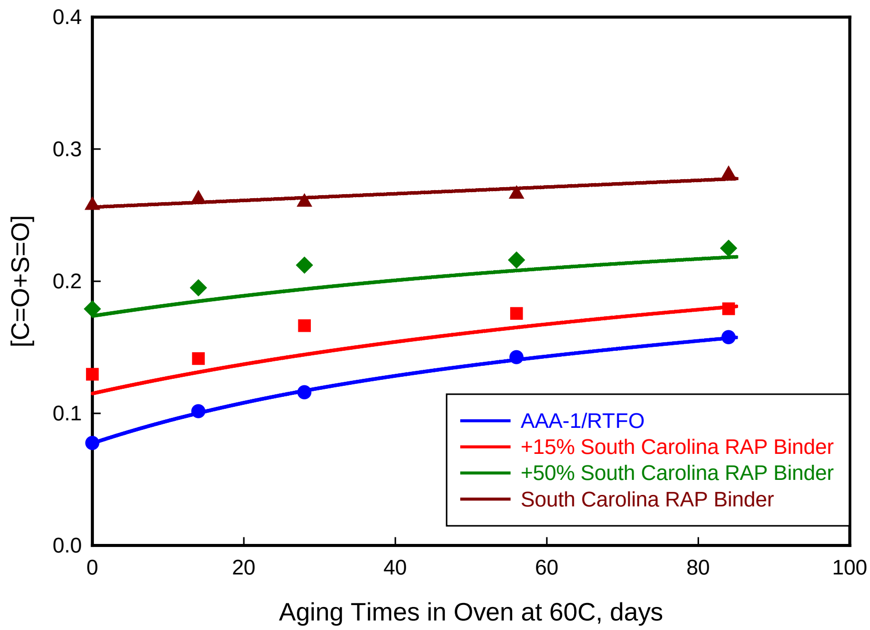

Figure 30. Graph. IR results as a function of aging times for RTFO-aged AAA-1 and its South Carolina RAP blend binders.

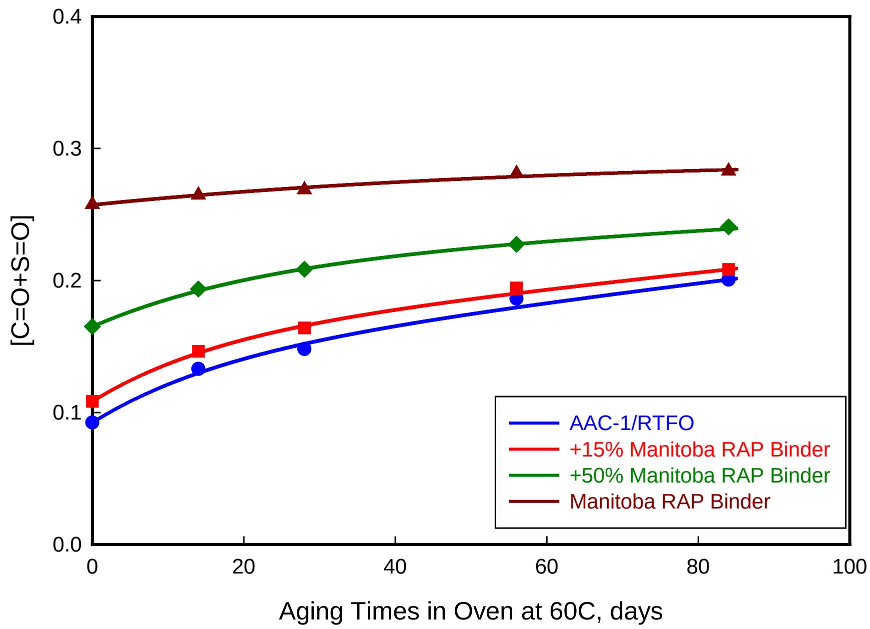

Figure 31. Graph. IR results as a function of aging times for RTFO-aged AAC-1 and its Manitoba RAP blend binders.

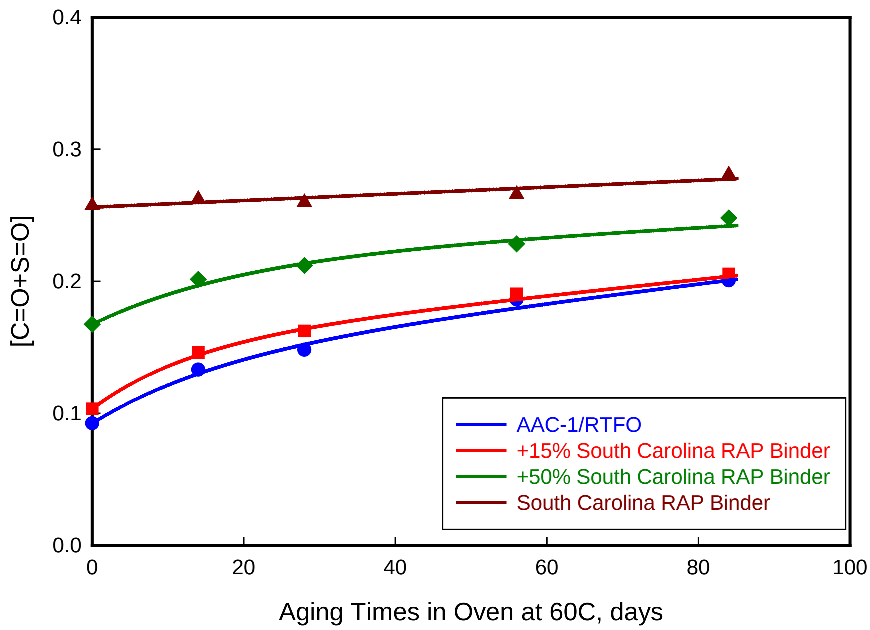

Figure 32. Graph. IR results as a function of aging times for RTFO-aged AAC-1 and its South Carolina RAP blend binders.

Table 2. Calculated reactive materials for asphalts AAA-1 and AAC-1 and their reblended RAP binders.

Sample	Calculated reactive material, absorbance
AAA-1/RTFO	**0.1580**
+15% Manitoba RAP Binder	0.1303
+50% Manitoba RAP Binder	0.0864
+15% South Carolina RAP Binder	0.1075
+50% South Carolina RAP Binder	0.0789
AAC-1/RTFO	**0.1986**
+15% Manitoba RAP Binder	0.1763
+50% Manitoba RAP Binder	0.1241
+15% South Carolina RAP Binder	0.1634
+50% South Carolina RAP Binder	0.1444
Manitoba RAP Binder	**0.0828**
South Carolina RAP Binder	**0.0496**

To verify if RAP binders have reached the constant reaction rate, typical SARA separation (ASTM D4124-01) was conducted on some selected unaged and aged RAP blend binders.

Figure 33 shows typical SARA fractions for two RTFO-aged asphalts, AAA-1 and AAC-1 and two extracted RAP binders. The two RAP binders show significant difference with regard to the four fractions, especially the asphaltene content. Both RAP binders contain approximately 30 percent of asphaltenes.

Figure 34 shows similar type of plot (SARA fraction) for RTFO-aged AAA-1 and its 15 percent Manitoba RAP blend binders before and after 12 weeks of laboratory aging at 60°C at ambient pressure. As expected, the asphaltene content increases after further oxidative aging and the amount of increased (+8%) are approximately equivalent to the sum of the amount of polar aromatic decreased (-3.9%) and the amount of napthene aromatic decreased (-3.9%). This confirms that polar aromatic and napthene aromatic materials are further converted to asphaltene materials due to oxidative aging.

Figure 35 shows another similar plot of SARA fractions for RTFO-aged AAA-1 and its 50 percent of South Carolina RAP blend binders. As seen from this figure that addition of laboratory aging does not change the four fractions of the RAP blend binder statistically. This result agrees with IR results and rheological data.

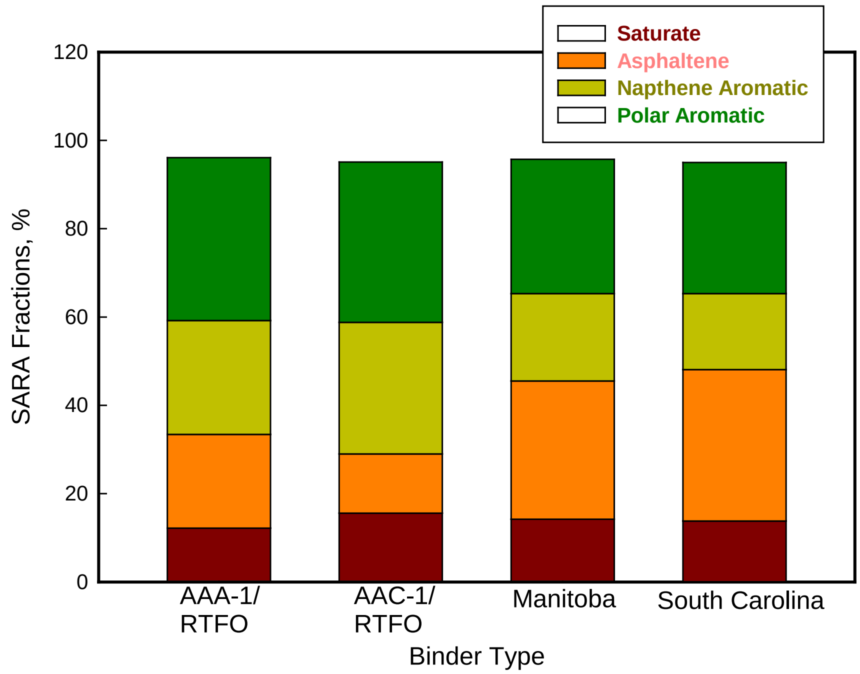

Figure 33. Chart. SARA fractions for two RTFO-aged asphalts and two extracted RAP binders.

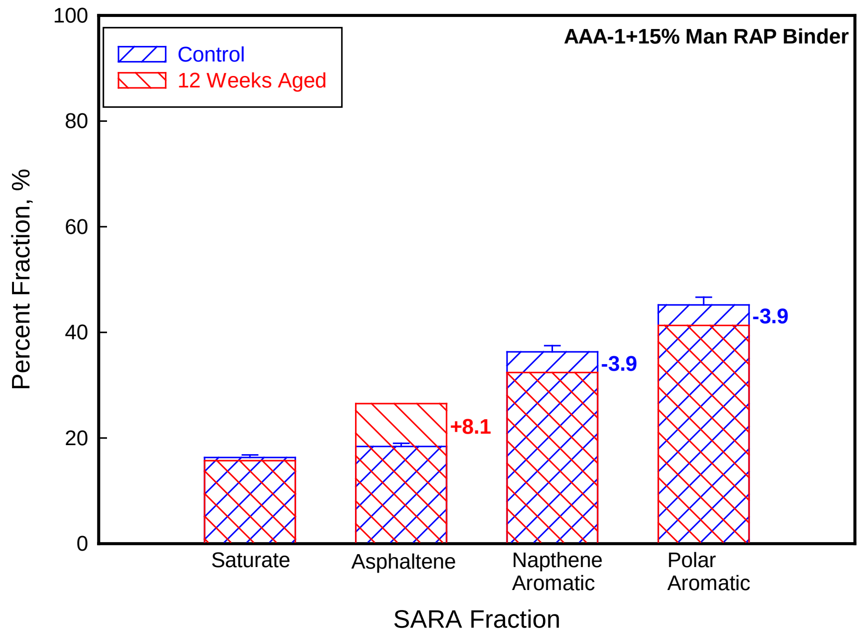

Figure 34. Chart. SARA fractions for RTFO-aged AAA-1 and its 15 percent Manitoba RAP blend binder before and after 12 weeks aging.

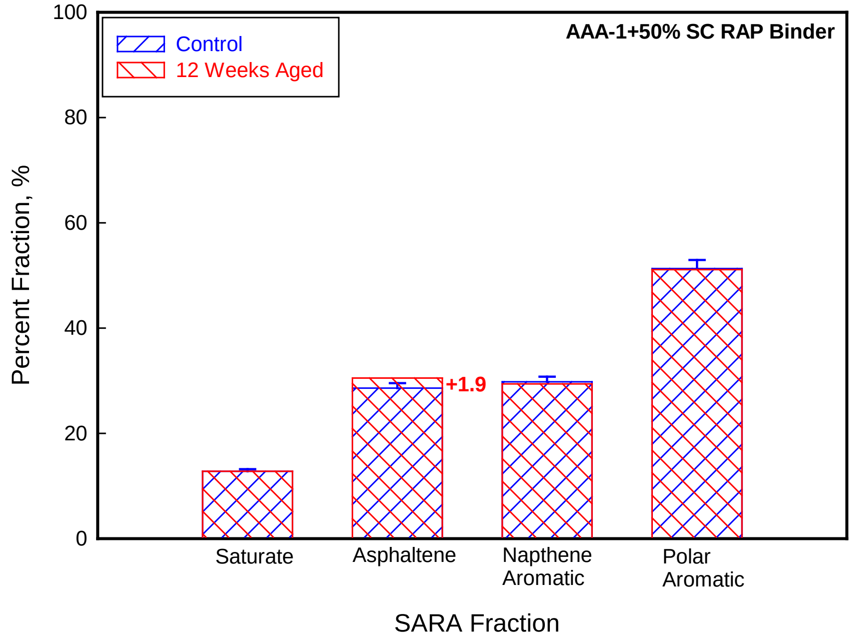

Figure 35. Chart. SARA fractions for RTFO-aged AAA-1 and its 50 percent South Carolina RAP blend binder before and after 12 weeks aging.

Thermal analyses by modulated differential scanning calorimetry (MDSC) have long been used to characterize the low temperature properties of materials. In asphalts and asphalt components, one of the most important features that MDSC can provide is the glass transition, a fundamental property of amorphous (i.e., non-crystalline or semi-crystalline) materials, including asphalt binders. Important glass transition characteristics include: the low-temperature onset of the transition; the high-temperature end of the transition; the glass transition temperature, Tg, as measured by midpoint or inflection; the width of the transition (end minus onset temperature); and the height of the transition, usually in heat capacity units, J/g·K.

Previous MDSC work with aged binders has shown that the onset of the glass transition is insensitive to aging and that the end of the glass transition is very sensitive to aging, moving upwards in temperature as aging severity increases. Given these prior examples, the expectation for RAP blends is that the glass transition end temperature would increase, because aged materials are being added. As shown in figures 36 and 37 this is sometimes, but not always, true.

Figure 36 shows the expected behavior for asphalt AAA-1 blended with the South Carolina RAP binder. AAA-1 exhibits good low-temperature behavior, while the SC RAP binder is a very aged material. The AAA-1 binder and RAP binder have similar onset temperatures (flat line), but end temperatures are very different (higher temperature susceptibility). This figure shows a linear increase in glass transition end temperature with increase RAP concentration. Figure 37 shows a similar plot for AAA-1 blended with the Manitoba RAP. The Manitoba RAP binder has good low-temperature properties for a RAP, and lowers the onset temperatures of the blends while hardly influencing the end temperatures. The changes again appear linear, so the effects are additive.

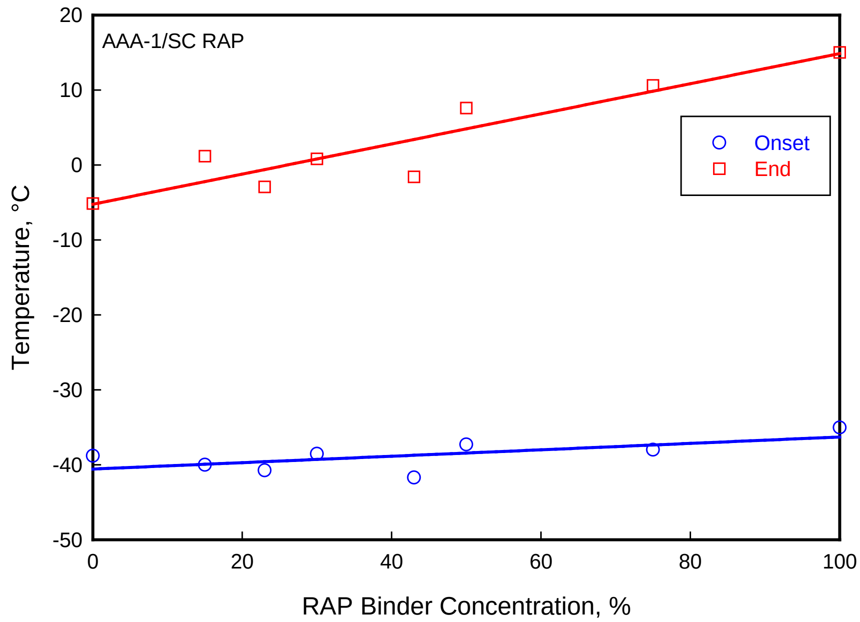

Figure 36. Graph. DSC temperatures (onset and end) for RTFO-aged AAA-1 and its South Carolina RAP blend binders.

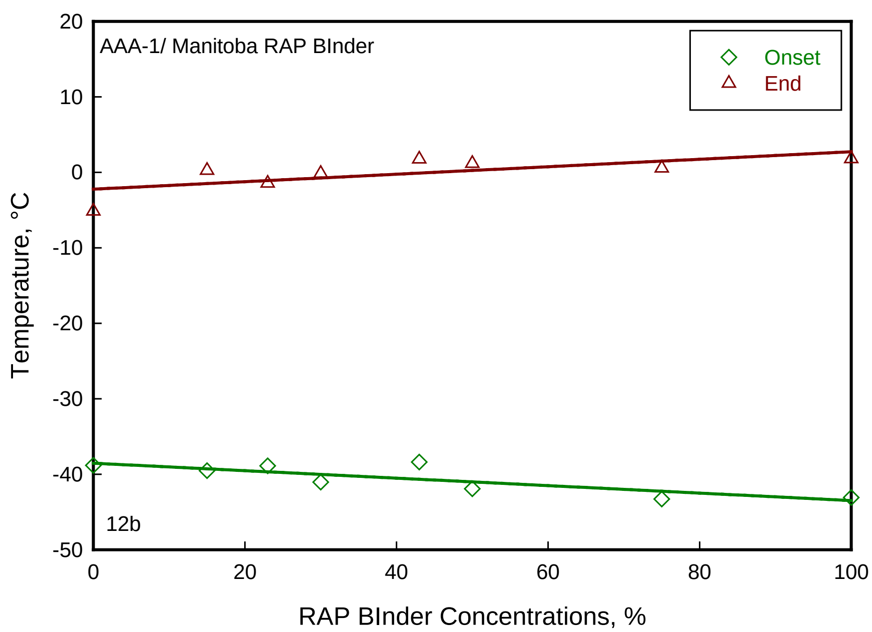

Figure 37. Graph. DSC temperatures (onset and end) for RTFO-aged AAA-1 and its Manitoba RAP blend binders.

Figures 38 and 39 show the same type of thermo plot for another asphalt AAC-1 with both South Carolina and Manitoba RAP binders. Figure 38 shows how asphalt AAC-1 is influenced by addition of the South Carolina RAP binder. Again, the transition end temperature increases linearly with RAP content. The onset temperature varies little with RAP content, but seems to show some nonlinear relationship to RAP content. Figure 39 shows that the Manitoba RAP has the same influence on AAC-1 as it has on AAA-1. The end temperature does not vary significantly with RAP content. The onset temperature decreases linearly with RAP content.

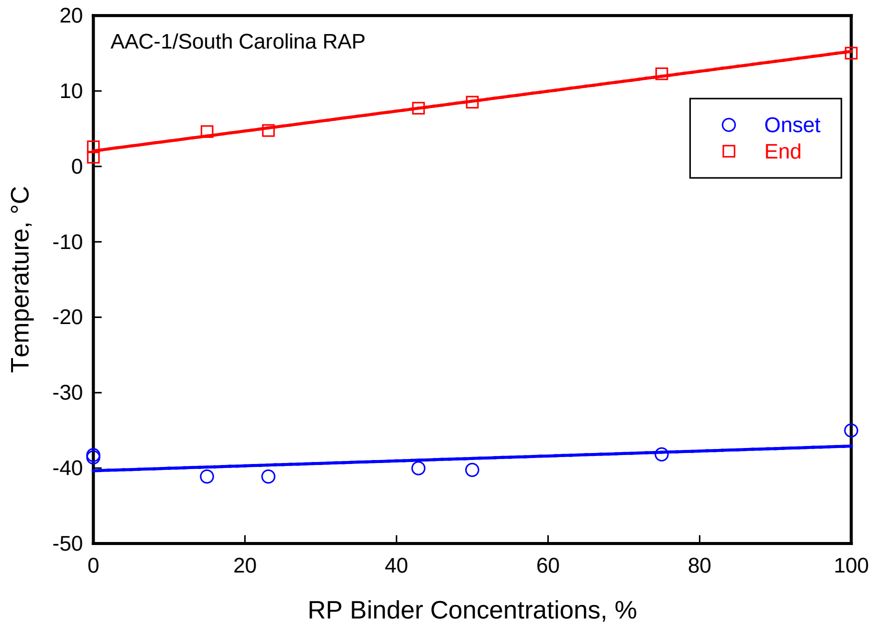

Figure 38. Graph. DSC temperatures (onset and end) for RTFO-aged AAC-1 and its South Carolina RAP blend binders.

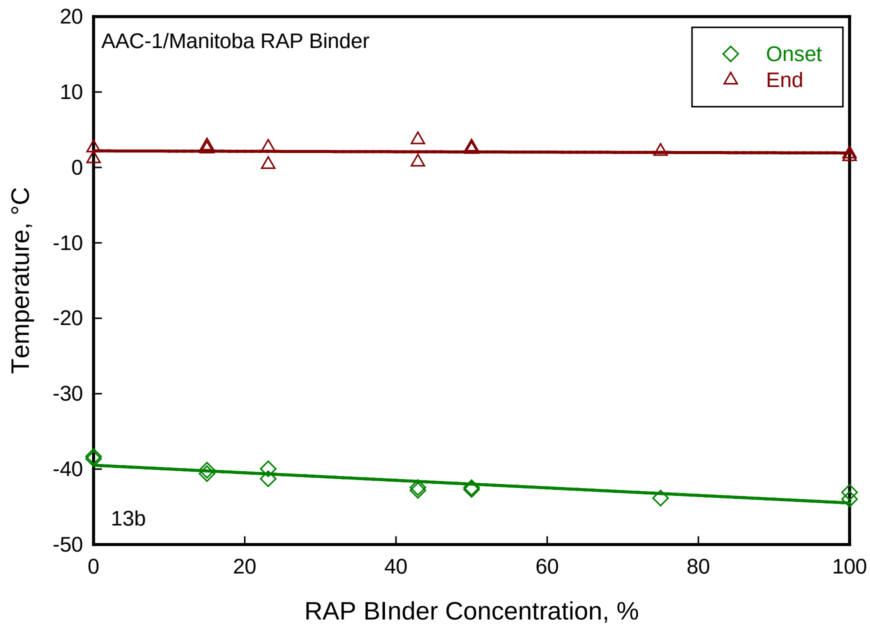

Figure 39. Graph. DSC temperatures (onset and end) for RTFO-aged AAC-1 and its Manitoba RAP blend binders.

CONCLUSIONS

Two chemically and physically different asphalts were mixed with addition of 15 and 50 percent of extracted RAP binders, Manitoba and South Carolina. Several analytical techniques including Dynamic Shear Rheometry, Fourier Transform Infrared spectroscopy (FTIR), and Differential Scanning Calorimetry (DSC) were used to measure physical and chemical properties of unaged and oven-aged blend binders at one atmospheric pressure and at 60°C for different durations.

The results indicate that different virgin binders interact with different RAP binders differently and the PG grade adjustment is asphalt and RAP binder dependent. Some asphalts require higher PG grade adjustments than the others. This finding is different from what the literature recommends (McDaniel and Anderson 2001; McDaniel and Shah 2003). The interaction between virgin binders and RAP binders contributes to different stiffening effects. A few possible mechanisms are proposed to explain the stiffening effect resulted from the addition of RAP binders.

Based on current experiments, the results indicate that there is no chemical reaction (covalent) between RAP binders and fresh binders and that linear relationship exists between oxidation products (IR results) and RAP binder contents. The results also indicate that there is a linear relationship between physical properties (rheological, G* vs. phase angle plot) and RAP contents with respect to long-term oxidative aging regardless RAP sources.

Crossover frequency decreases as RAP contents increase and the rheological index increases as RAP content increases.

The results obtained from rheological test agree with the results received from chemical test (IR). DSC results also agree with what rheology data demonstrated. The linear relationship between complex modulus and phase angle with respect to different aging times at different RAP concentrations indicate that the use of RAP can be dependent on what type of fresh binder being used and that multiple recycling is possible when fresh (virgin) binder can be selected carefully.

The relationship between the complex modulus and aging time for RAP blend binders is similar to that of typical chemical aging kinetic curve for virgin binders, where the stiffness increases substantially initially and then levels off after certain periods of aging times. A nonlinear equation similar to that of aging kinetic model was successfully applied to curve fit the data of complex modulus versus aging times for all RAP blend binders.

The Pal-Rhodes model developed from Einstein's colloid theory, assuming additive amounts of supended solvated asphalts to describe asphalt viscosity, is suitable for characterizing the flow properties of RAP binder blends.

Consideration of the changes in both the complex modulus and the phase angle (modified black plot) of both neat asphalts and blend binders on aging, it is recommended to investigate if a simple additive blending procedure can be used in the field. A field pavement validation study should be conducted to validate the laboratory results. It is also recommended to investigate how material's compatibility influences the blend binder property and its long term performance with high RAP contents.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Federal Highway Administration, U.S. Department of Transportation, for financial support of this project under contract no. DTFH61-07-D-00005. Special thanks are expressed to Dr. J. Claine Petersen for his review and comments. Thanks are also expressed to Ms. Jenny Loveridge, Ms Pamela Coles, and Mr. Gerald Forney for the sample preparation and data measurement. Thanks are also expressed to Ms. Jackie Greaser for preparation of the manuscript.

DISCLAIMER

specific brand names of equipment does not imply endorsement by the United States Department of Transportation or Western Research Institute.

REFERENCES

Anderson, R. M., G. N. King, D. L. Hanson, and P. B. Blankenship, 2011, Evaluation of the Relationship between Asphalt Binder Properties and Non-Load Related Cracking. *Journal of the Association of Asphalt Paving Technologists*, 80: 615-664.

Buttlar, W., and E. Dave, 2005, A Micromechanics-Based Approach for Determining Presence and Amount of Recycled Asphalt Pavement Material in Asphalt Concrete. *Journal of the Association of Asphalt Paving Technologists*, 74: 829-884.

Christensen, D. W., and D. A. Anderson, 1992, Interpretation of Dynamic Mechanical Test Data for Paving Grade Asphalt. *Journal of the Association of Asphalt Paving Technologists*, 61: 67-116.

Copeland, Audrey, 2008, "Sustaining our Highways: A National Perspective on RAP Usage & Best Practices for Recycled Asphalt Pavements," presented at the Pavement Performance Prediction Symposium, July 16, 2008, Laramie, Wyoming.

Daniel, J. S., G. R. Chehab, and D. Ayyala, 2009, Sensitivity of RAP Binder Grade on Performance Predictions in the MEPDG. *Journal of the Asphalt Paving Technologists*, 78: 352-376.

Decker, D., 1997, Hot Mix Recycling: State of the Practice. *Journal of the Association of Asphalt Paving Technologists*, 66: 704-722.

Einstein, A., 1906, Eine Neve Bestimmung der Molekuldimensionen, *Annalen der Physik*, 19: 289-307.

Ferry, John D., 1980, *Viscoelastic Properties of Polymers*, John Wiley & Sons.

Glaser, R. R., and J. L. Loveridge, 2012, Low Temperature Oxidation Kinetics of Asphalt Binders. *Preprints, Div. of Petroleum Chemistry, American Chemical Society*, 57 (1): 9-11.

Guthrie, W. S., D. A. Cooley, and D. L. Eggett, 2007, Effects of Reclaimed Asphalt Pavement on Mechanical Properties of Base Materials. Transportation Research Board, Paper #07-2469.

Huang, Shin-Che, and Will Grimes, 2010, Influence of Aging Temperature on Rheological and Chemical Properties of Asphalt Binders. In *Transportation Research Record: Journal of the Transportation Research Board*, No. 2179, Transportation Research Board of the National Academies, Washington, D.C., pp. 39-48.

Huang, Shin-Che, F. Miknis, W. Schuster, S. Salmans, M. Farrar, and R. Boysen, 2011, Rheological and Chemical Properties of Hydrated Lime and Polyphosphoric Acid Modified Asphalts with Long term Aging. *Journal of Materials in Civil Engineering*, 23 (5): 628-637.

Huffman, J., 1997, Full-Depth Pavement Reclamation: State of the Practice. *Journal of the Association of Asphalt Paving Technologists*, 66: 746-759.

Kandhal, P., 1997, Recycling of Asphalt Pavements-An Overview. *Proceedings of the Association of Asphalt Paving Technologists*, 66: 686-703.

Karlsson, R., and U. Isacsson, 2003, Investigations on Bitumen Rejuvenator Diffusion and Structural Stability. *Journal of the Association of Asphalt Paving Technologists,* 72: 463-501.

Kearney, E., 1997, Cold Mix Recycling: State of the Practice. *Journal of the Association of Asphalt Paving Technologists*, 66: 760-802.

Kim, K., S. Amirkhanian, and Y. S. Doh, 2007, Reducing Stiffness of Oxidized Binder in Recycled Asphalt Mixture by Stage Mixing. *Journal of the Association of Asphalt Paving Technologists*, 76: 235-274.

King, G. N., M. Anderson, D. Hanson, and P. Blankenship, 2012, Using Black Space Diagrams to Predict Age-Induced Cracking, Rilem Fatigue Cracking Conference, Delft, NL, June 20-22, 2012.

Liu, M., K. M. Linsford, R. R. Davidson, C. J. Clover, and J. A. Bullin, 1996, The Kinetics of Carbonyl Formation in Asphalt. *Aiche Journal*, 42 (4): 1069-1076.

McDaniel, R., and R. M. Anderson, 2001, Recommended Use of Reclaimed Asphalt Pavement in the Superpave Mix Design Method: Technician's Manual. National Cooperative Highway Research Program, Report 452.

McDaniel, R. S., and A. Shah, 2003, Use of Reclaimed Asphalt Pavement (RAP) Under Superpave Specifications. *Journal of the Association of Asphalt Paving Technologists,* 72: 226-252.

Mohammad, L., Z. Wu, C. Abadi, W. Daly, and C. Daranga, 2003, Investigation of the Use of Recycled Polymer Modif8ed Asphalt Binder in Asphalt Concrete Pavement. *Journal of the Association of Asphalt Paving Technologists*, 72: 551-594.

Petersen, J. C., 2009, *A Review of the Fundamentals of Asphalt Oxidation-Chemical, Physicochemical, Physical Properties, and Durability Relationship*. Transportation Research Circular, Number E-C140, October, 2009.

Petersen, J. C., 1984, Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art. In *Transportation Research Record: Journal of the Transportation Research Board*, No. 999, Transportation Research Board of the National Academies, Washington, D.C., pp. 13-30.

Petersen, J. C., J. F. Branthaver, R. E. Robertson, P. M. Harnsberger, J. J. Duvall, and E. K. Ensley, 1993, Effects of Physicochemical Factors in Asphalt Oxidation Kinetics. In *Transportation Research Record: Journal of the Transportation Research Board*, No. 1391, Transportation Research Board of the National Academies, Washington, D.C., pp. 1-30.

Peterson, R. L., H. R. Soleymani, R. M. Anderson, and R. S. McDaniel, 2000, Recovery and Testing of RAP Binders from Recycled Asphalt Pavements. *Journal of the Association of Asphalt Paving Technologists*, 69: 72-91.

Soleymani, H. R., R. McDaniel, M. Abdelrahman, and M. Anderson, 2000, Investigation of the Black Rock Issue for Recycled Asphalt Mixtures. *Journal of the Association of Asphalt Paving Technologists*, 69: 366-390.

Sui, C., M. J. Farrar, W. H. Tuminello, and T. F. Turner, 2010, New Technique for Measuring Low-Temperature Properties of Asphalt Binders with Small Amounts of Material. In *Transportation Research Record: Journal of the Transportation Research Board*, No. 2079, Transportation Research Board of the National Academies, Washington, D.C., pp. 23-28.

Terrel, R., J. Epps, and J. Sorenson, 1997, Hot in-Place Recycling: State of the Practice. *Journal of the Association of Asphalt Paving Technologists*, 66: 723-745.

APPENDIX

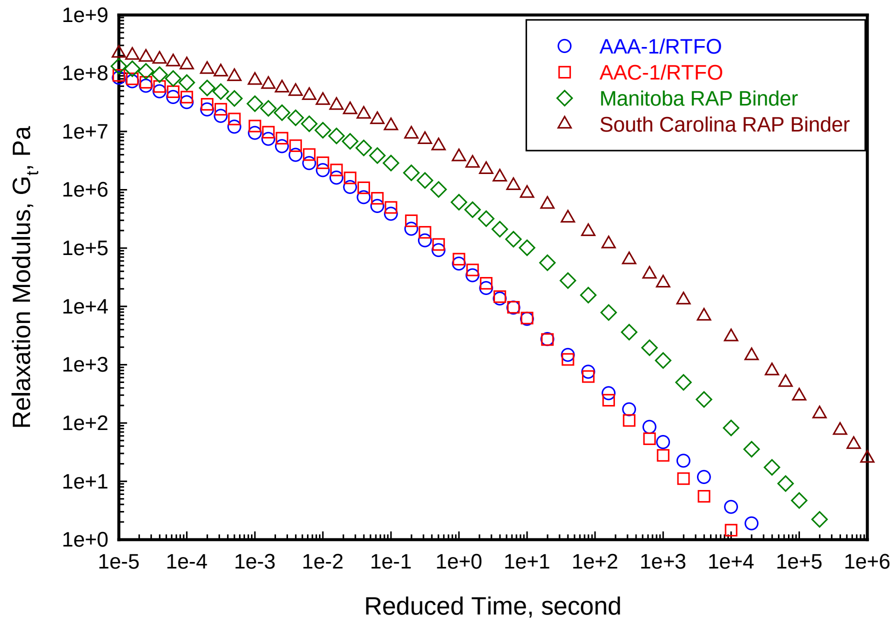

Figure A.1. Graph. Relaxation modulus for two virgin binders and two extracted RAP binders.

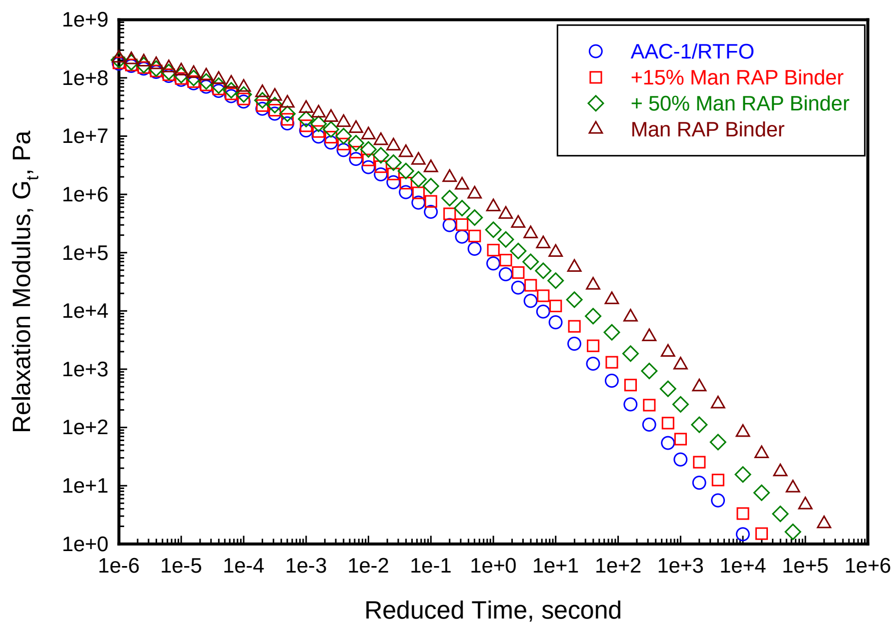

Figure A.2. Graph. Relaxation modulus for RTFO-aged AAC-1 and its RAP blend binders.

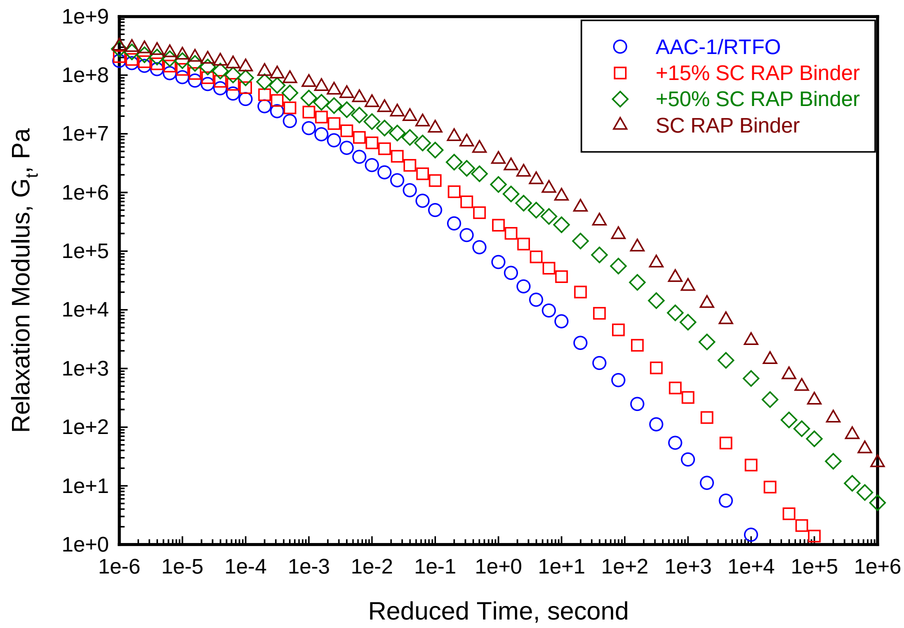

Figure A.3. Graph. Relaxation modulus for RTFO-aged AAC-1 and its RAP blend binders.

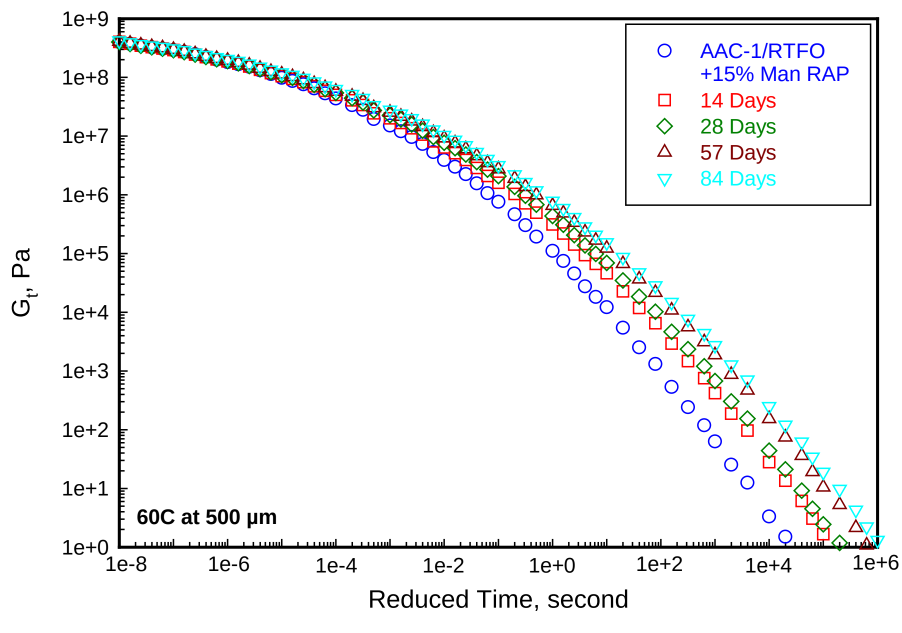

Figure A.4. Graph. Relaxation modulus for RTFO-aged AAC-1 mixed with 15 % Manitoba RAP binder after aging.

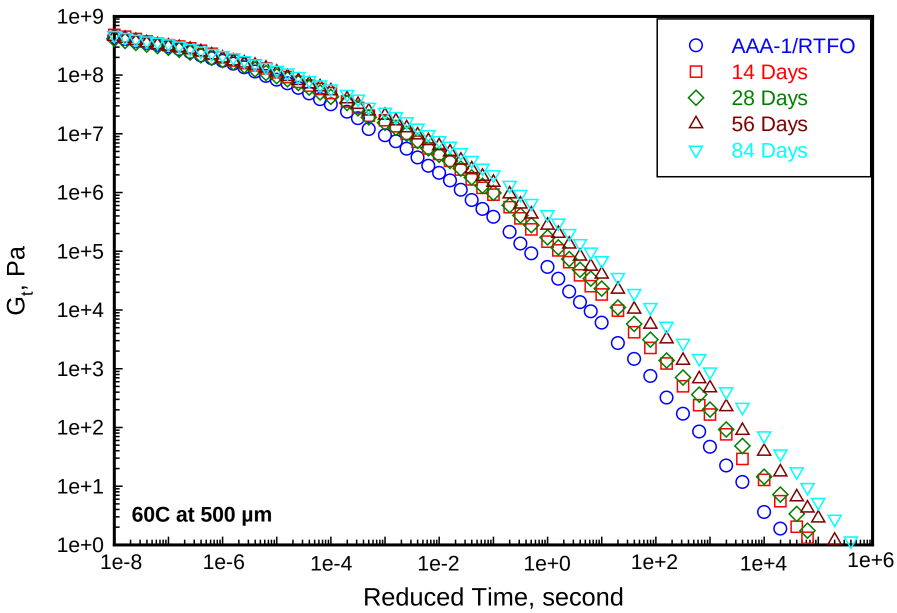

Figure A.5. Graph. Relaxation modulus for RTFO-aged AAA-1 after aging.

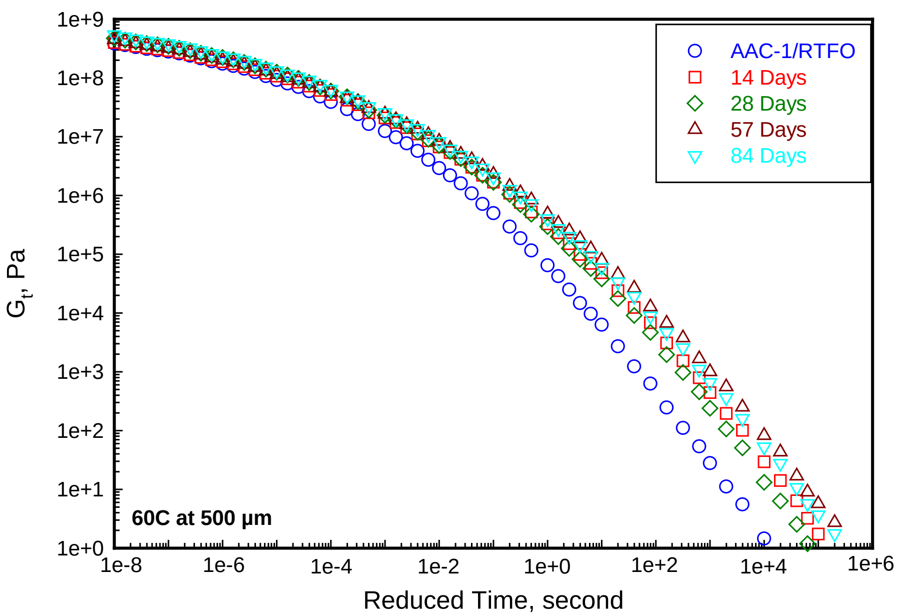

Figure A.6. Graph. Relaxation modulus for RTFO-aged AAA-1 after aging.

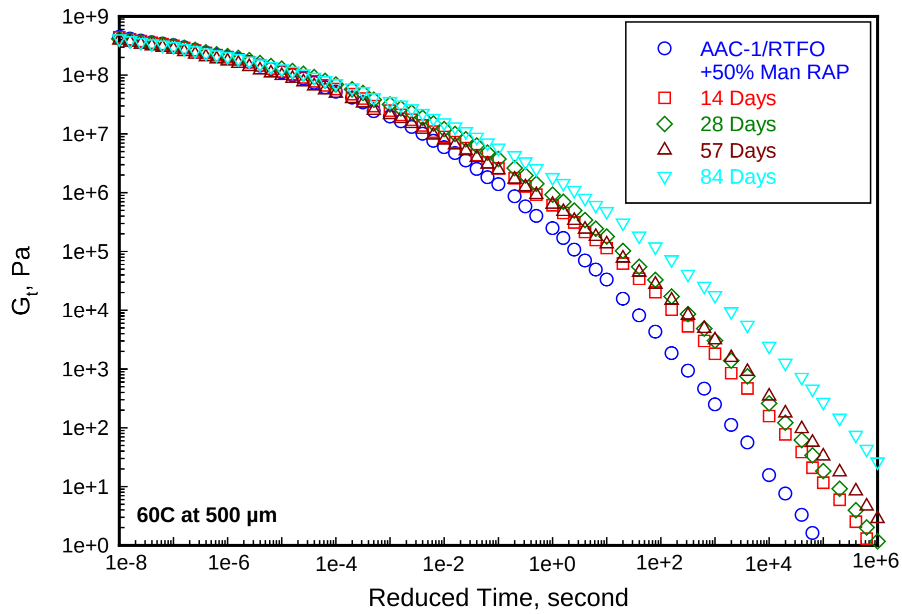

Figure A.7. Graph. Relaxation modulus for RTFO-aged AAC-1 mixed with 50 % Manitoba RAP binder after aging.

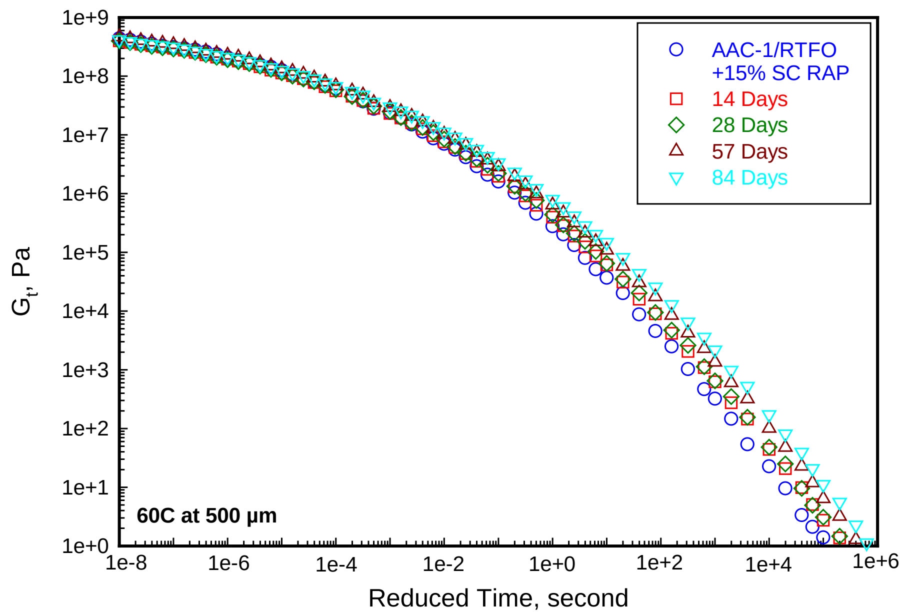

Figure A.8. Graph. Relaxation modulus for RTFO-aged AAC-1 mixed with 15 % South Carolina RAP binder after aging.

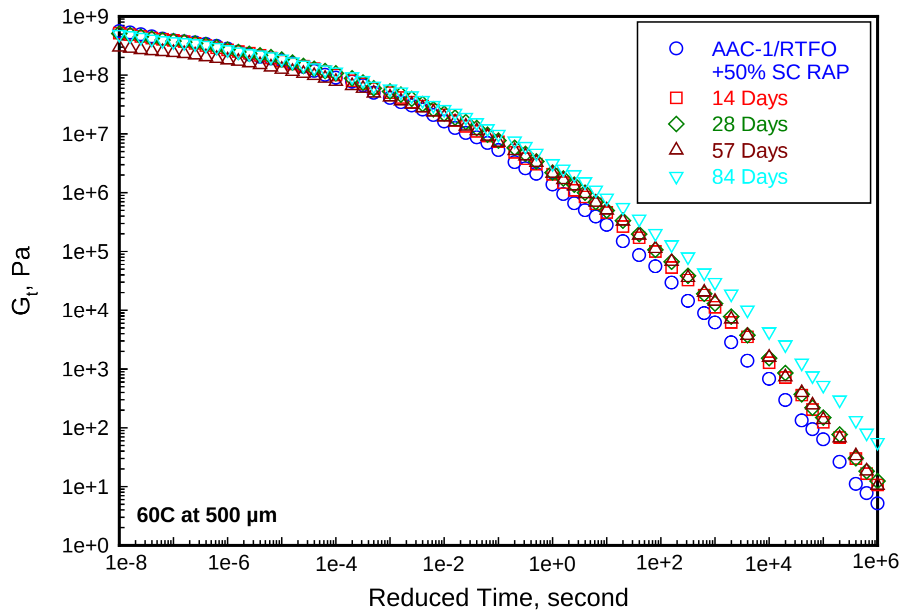

Figure A.9. Graph. Relaxation modulus for RTFO-aged AAC-1 mixed with 50 % South Carolina RAP binder after aging.

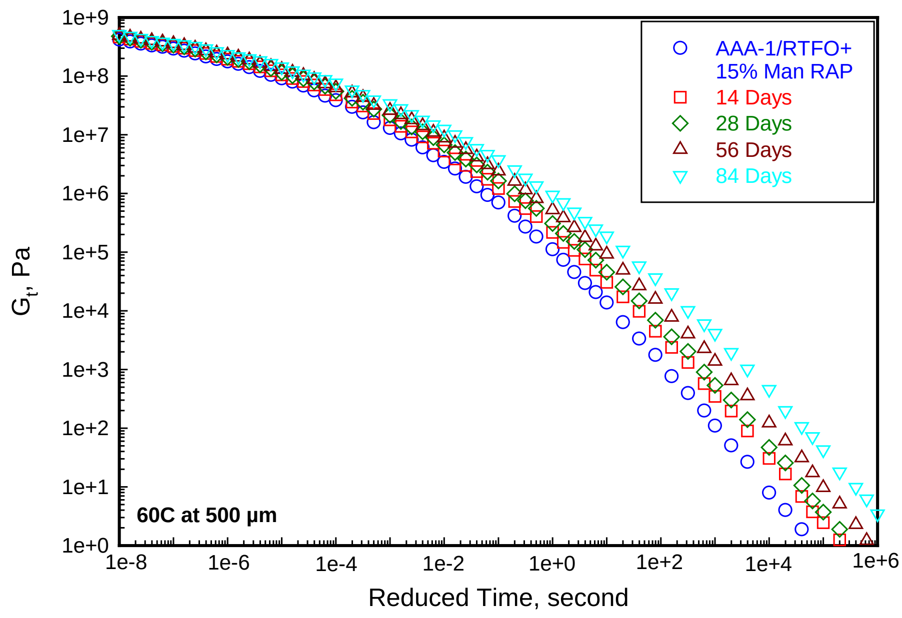

Figure A.10. Graph. Relaxation modulus for RTFO-aged AAA-1 mixed with 15 % Manitoba RAP binder after aging.

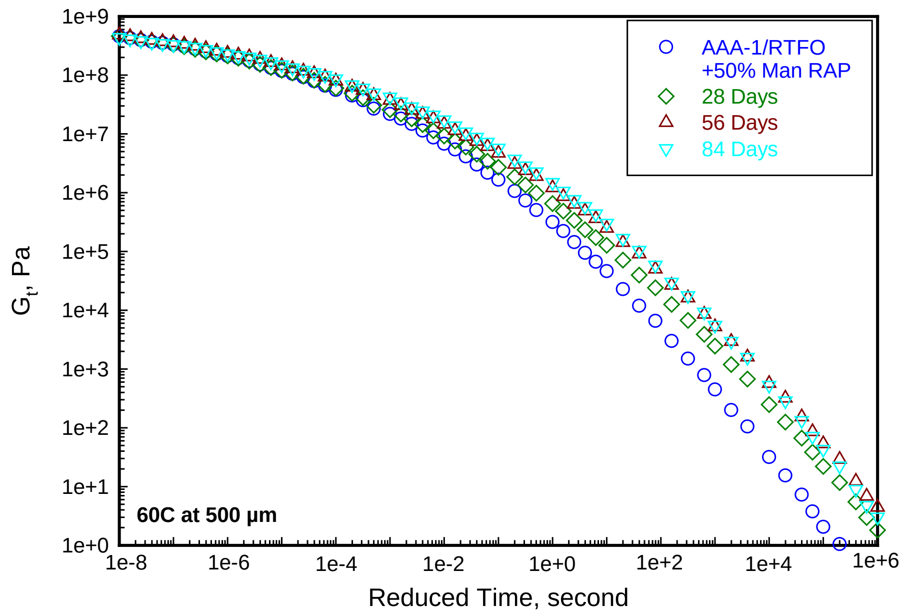

Figure A.11. Graph. Relaxation modulus for RTFO-aged AAA-1 mixed with 50 % Manitoba RAP binder after aging.

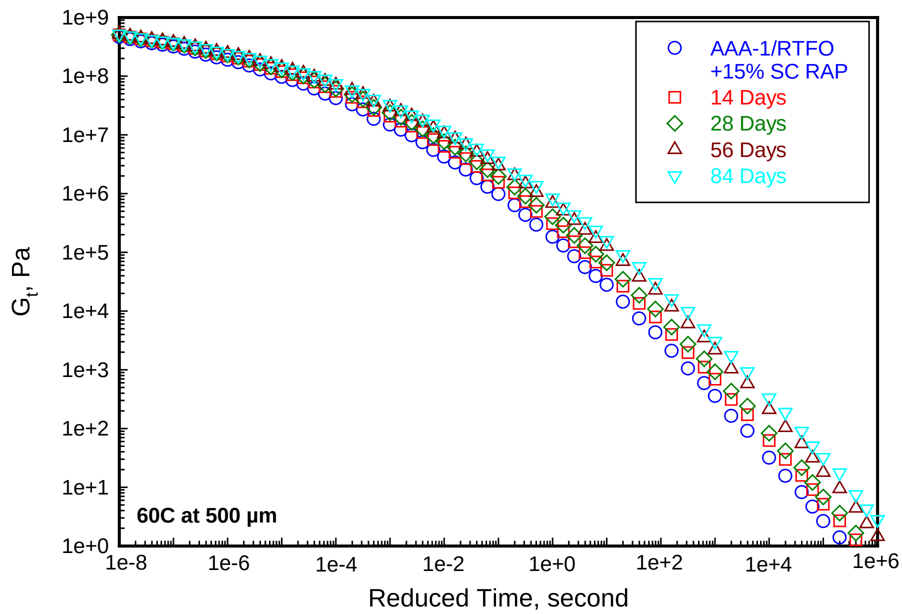

Figure A.12. Graph. Relaxation modulus for RTFO-aged AAA-1 mixed with 15 % South Carolina RAP binder after aging.

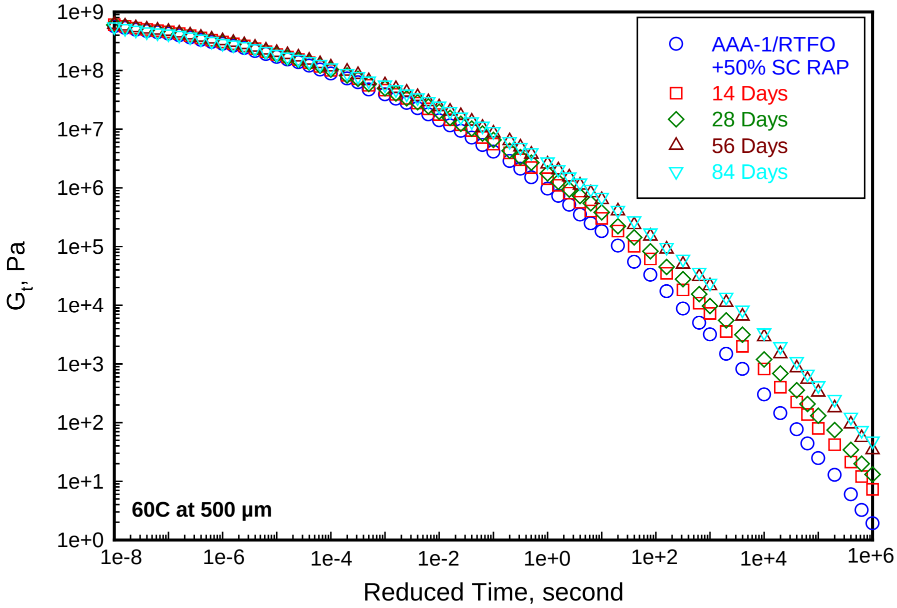

Figure A.13. Graph. Relaxation modulus for RTFO-aged AAA-1 mixed with 50 % South Carolina RAP binder after aging.

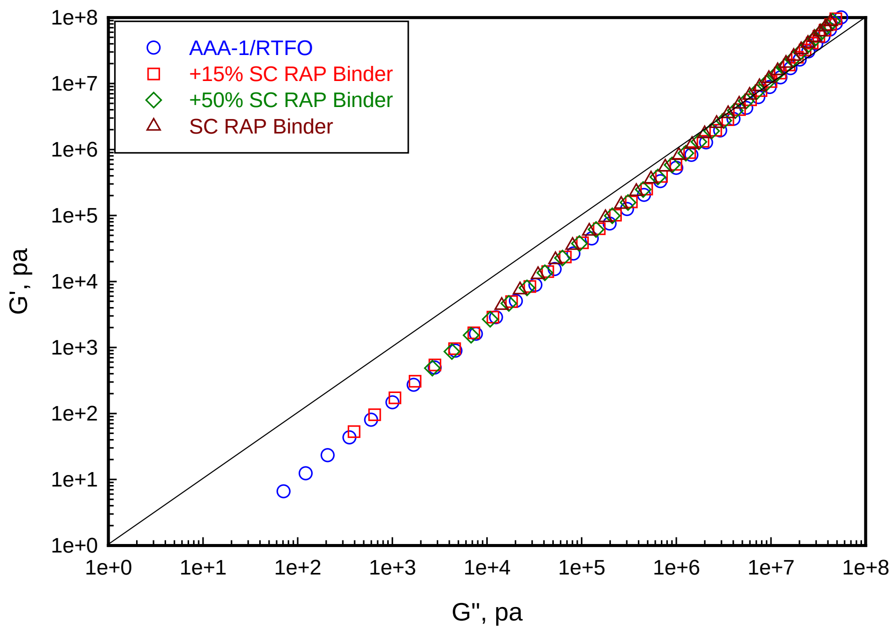

Figure A.14. Graph. Relationship between G’ (elastic) and G” (viscous) for RTFO-aged AAA-1 and its South Carolina RAP blend binders.

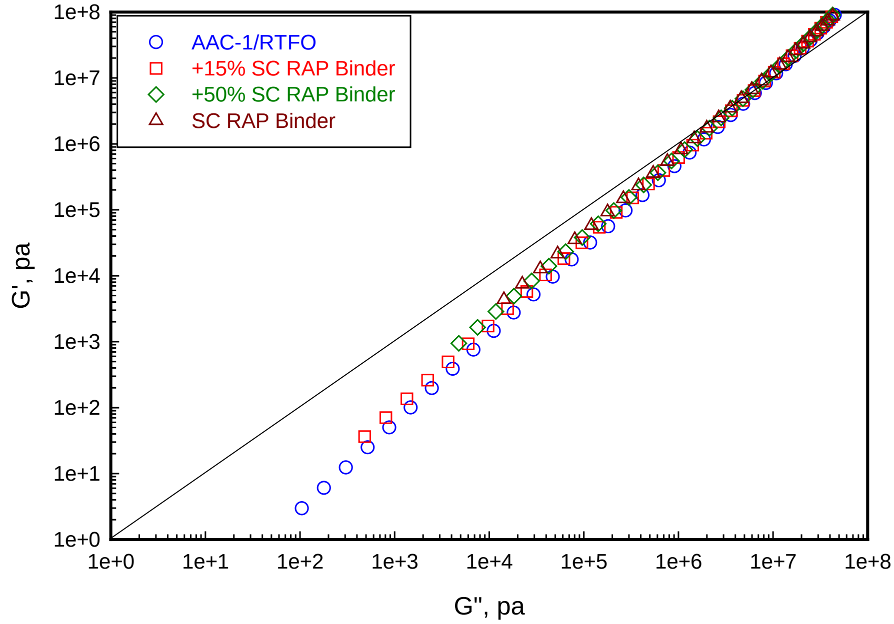

Figure A.15. Graph. Relationship between G' (elastic) and G" (viscous) for RTFO-aged AAC-1 and its South Carolina RAP blend binders.

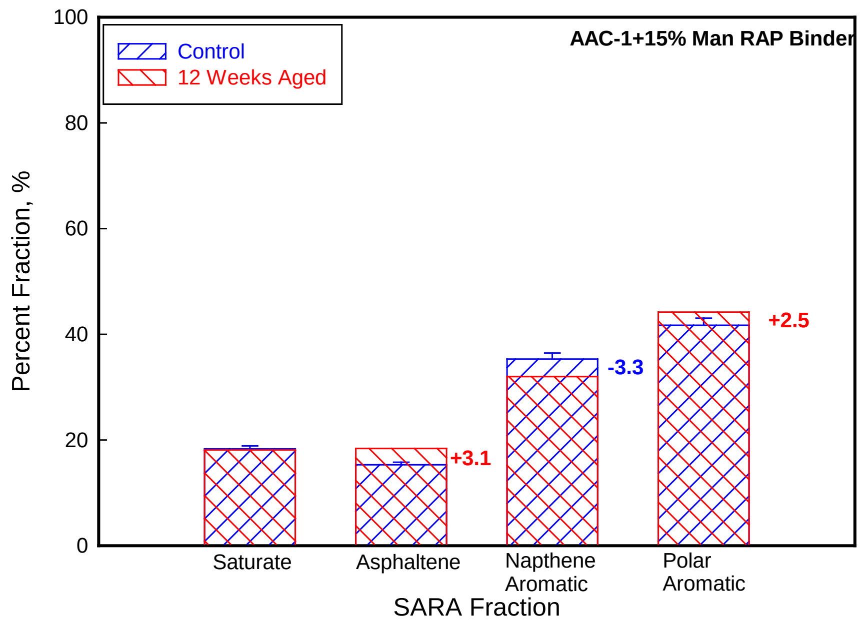

Figure A.16. Chart. SARA fractions for RTFO-aged AAC-1 and its 10 percent Manitoba RAP blend binder before and after 12 weeks aging.

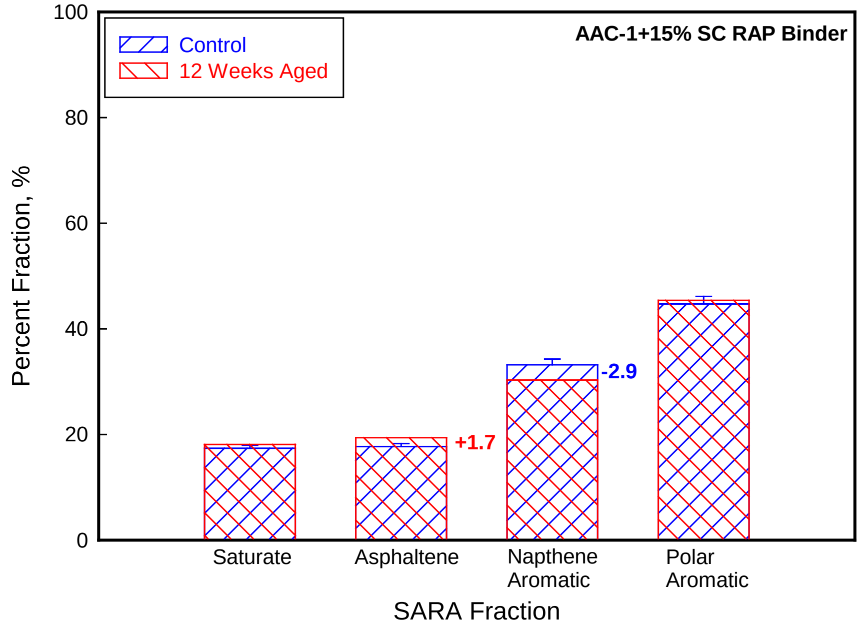

Figure A.17. Chart. SARA fractions for RTFO-aged AAC-1 and its 15 percent South Carolina RAP blend binder before and after 12 weeks aging.

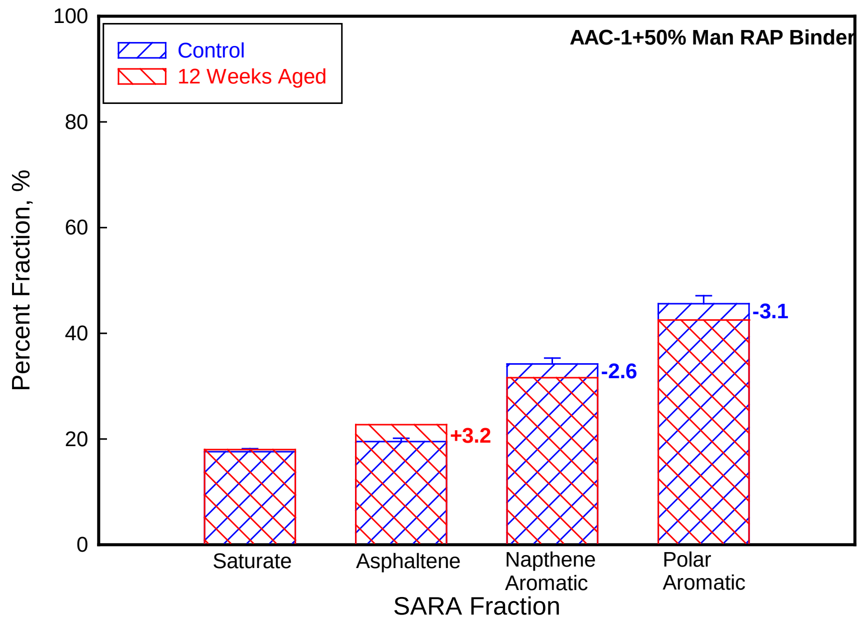

Figure A.18. Chart. SARA fractions for RTFO-aged AAC-1 and its 50 percent Manitoba RAP blend binder before and after 12 weeks aging.