Technical White Paper

Analytical Methods to Characterize Recycled Shingle Binders (RAS) and to Determine Whether High Recycled Shingle Content is Suitable for Hot Mix Asphalt (HMA)

Fundamental Properties of Asphalts and Modified Asphalts III Product: FP 17

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INTRODUCTION

The use of recycled asphalt shingles (RAS) has gained significant attention in recent years as it is both an environmentally and economically attractive proposition. Waste shingles can be classified into two types. One is manufacturer shingle waste, and the other is tear-off shingles. Manufacturer waste shingles are defined as new material that is obtained from a roofing shingle production plant. Manufacturer waste is a relative uniform, predictable (relatively) product and is the most promising source for rapid implementation of recycling. Tear-off waste shingles are those obtained during the removal of existing roofs and make up the bulk of the scrap shingle supply. Tear-off shingles are more readily available, but require more processing for use in hot-mix as they contain various contaminants such as nails, underlayment, insulation wood, demolition debris, and so on. Both types of shingle binders are all "air-blown" during production, a process that incorporates oxygen into the asphalt and further increases the viscosity. Current specification requires that the amount of deleterious material in the RAS must be less than 1.5 percent. This includes anything that is not part of the shingle (AASHTO MP-15). Nonetheless, the tear-off waste shingle has been successfully used in hot mix asphalt (HMA) as much as the manufacturer waste shingle (Button 1995).

Asphalt shingles contain more than 20 percent of liquid asphalt. Besides the asphalt binder, there are hard fine aggregate (granules), mineral filler, polymers and fibers (either fiberglass or organic felt) in shingles. Tear-off shingles usually contain a greater percentage of asphalt than new shingles because of the loss of a portion of the surface granules from weathering. However, the asphalt in tear-off shingles is hardened from oxidation and the volatilization of the lighter organic compounds. Therefore, the asphalt binder in old tear-off roofing shingles is somewhat harder than new asphalt. This hardened binder (high stiffness) could be problematic in cold climate regions such as the northern United States. Several studies have been conducted to evaluate how to enhance the use of recycled asphalt shingles without suffering pavement performance deterioration. The main findings from the literature can be summarized as follows (Newcomb 1993; Grzybowski 1993; NAPA 1997; McGraw et al. 2007; Button 1995; Tighe et al. 2008; Scholz 2010; Uzarowski et al. 2010; Cascione et al. 2011; Foxlow et al. 2011):

- Recycled asphalt shingles (~5 percent) have been reused effectively in HMA.
- Use of waste shingles can result in significant cost savings by avoiding disposal and landfill cost, and by reducing the amount of virgin asphalt binder required in HMA.
- Laboratory tests have shown that the use of shingles can improve resistance of HMA to high temperature rutting.
- When used in small amounts (<5 percent), there is no significant effect of manufacturer shingle binder on low temperature properties of HMA.

- Mixing and compaction temperatures of HMA with RAS may need to be increased in the laboratory and in the field to accommodate the relatively stiff modified mixtures. Standard compaction temperatures may yield higher air voids than desirable.
- The use of an appropriate softer virgin binder may be required to maintain the fatigue and low temperature performance of the mix.
- Short term field performance of shingle modified HMA is reported to be reasonably fair.

Current specifications (AASHTO MP-15; AASHTO PP-53; ASTM D255; ASTM D3462) in most state DOTs allow up to 5 percent of manufacturer shingles be applied to HMA. The primary reason for this limited use is the uncertainty of the long term performance of RAS-modified materials. Current research estimates that 13 million tons of used shingles are generated each year in the United States (FHWA 1997; Huber 2011), and historically about 95 percent of this valuable solid waste has ended up in landfills. However, the potential cost savings for incorporating this waste in HMA is from around $1.0 to $2.801 per ton for a mix that includes up to 5 percent shingles (NAPA 1997).

The economic savings on the cost of HMA could be substantial if higher waste shingle content could be employed in HMA, particularly when considering the long-term trends on cost of asphalt cements and aggregates. The “green advantage” and societal aspects are also of important consideration.

The continuing challenges to utilizing RAS are quality control and quality assurance of the final product and identifying mix designs that meet the requirements of specifying agencies. Integrating the volumetric properties of RAS into the volumetric design requirements for HMA is one such challenge. In addition to the volumetric problems, one of the critical components in the research of RAS has been to identify the composition of the manufacturer and tear-off asphalt shingles.

To enhance the use of RAS and obtain confidence in the long term, as well as the short term, performance of pavements including RAS, it is important to understand the fundamental properties of extracted shingle binders as well as the interaction between old shingle binder in the recycled shingles and the fresh binder in the new mix. It is equally important to evaluate the diversity of chemical compositions and properties possibly encountered from a wide variety of RAS sources to acquire a sense of the robustness of the formulation recipes that could come out of the first point.

This study aims at evaluating the relationship between rheological properties and typical chemical properties for extracted shingle binders. The information obtained from this study will enable manufacturers and end users including the Heritage Research Group (HRG), to better understand the effect of shingle binders on the properties of HMA, to adjust the fresh binder selection, and further enhance the application of shingles in HMA.

EXPERIMENT DESIGN

Two types of RAS, manufacturer and tear-off, were used in this study. RAS binders were extracted from these two RAS sources by using 85 percent toluene/15 percent ethanol. Note that the standard AASHTO extraction procedure does not provide enough time to remove solvent from extracted shingle binders, as shingle binders have been air-blown, are very stiff, and contain a significant amount of fillers. It was therefore decided to extend the time of the AASHTO solvent removal procedure to ensure solvent-free shingle binders were produced. An additional 1 hour at high temperature (175°C) was applied for shingle binder recovery. A typical virgin binder that is used in Texas was mixed with the extracted RAS binders at 10, 30, 50, and 70 weight percent. A binder that is used to generate manufacturer shingles is also used in this study for comparison purposes.

The mixing procedure is described as follows. The desired amount of RAS binder was added into virgin binder to generate a total binder amount of 4 grams. The blend was heated to 160°C for one hour, and then stirred using a metal spatula for 5 minutes without nitrogen present. The RAS blend binders were then stored in a refrigerator before being subjected to analytical tests.

Numerous analytical techniques were applied to characterize RAS binders. These techniques include (1) dynamic shear rheometer (DSR) for visco-elastic properties and/or blending behavior, if possible, (2) high-performance gel permeation chromatography (HP-GPC) for molecular weight distributions, (3) automated flocculation titrimetry for compatibility, (4) SARA separations (ASTM D4124-09) for compositional measurements, (5) Asphaltene Determinator (AD) for additional compositional measurements, and (6) infrared spectrometry (IR) for aging characteristics via measuring the carbonyl and sulfoxide contents.

The rheological properties of the virgin binder and its blends were measured using 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, 80, 100, and 120°C using 25-mm, 8-mm, or 4-mm parallel plates with 1-mm, 2-mm or 1.75-mm sample gaps. Master curves were constructed by using time-temperature superposition.

Typical chromatographic separation (ASTM D4124) results are included in table 1. Automated Heithaus titrimetry (ASTM D6703) was also performed on the extracted shingle binders and the results are also shown in table 1. Manufacturer and tear-off RAS binders have 34 and 43 percent asphaltene content, respectively, whereas the virgin binder (a typical binder that the contractor used to blend with recycled shingle binders) and shingle binder (the binder that the manufacturer used to make shingles) have only 13 and 29.5 percent asphaltene content. This difference in asphaltene content between shingle and virgin binders is expected. The complex modulus of tear-off shingle binder at a reference temperature of 20°C and frequency of 10 rad/s is 5.39E07 Pa, and 2.11E07 Pa for manufacturer shingle binder at the same temperature and frequency.

High-performance gel permeation chromatography (HP-GPC) measurements were employed to determine molecular weight distributions of extracted RAP/RAS binders. The method employs a dual detection array system (refractometry and intrinsic viscosity) to determine number and weight average molecular mass. The chromatograph consists of a Waters model 600 pump, a

Waters model 717 autosampler, and a Phenomenex 5µm (300 x 7.8mm) linear/mixed bed column.

Table 1. Fundamental properties of virgin, shingle binders, and extracted RAS binders.

Asphalt	Virgin PG64-22	Shingle Binder	Manufacturer Binder	Tear-Off Binder
Complex Modulus, G*, x 10^7 pa @ 10 rad/s. Tr = 20°C	0.29	1.40	2.11	5.39
Phase Angle, δ degree @ 10 rad/s. Tr = 20°C	59.9	23.0	20.4	13.4
Crossover Frequency, ω_c	3.91 x 10^2	5.02 x 10^{-6}	2.60 x 10^{-7}	2.36 x 10^{-10}
Rheological Index	1.478	4.610	4.621	4.712
SARA Fractions (Iso-Octane), %				
Asphaltene	13.4	29.3	34.8	43.1
Polar Aromatic	40.7	28.2	26.2	21.7
Naphthene Aromatic	35.2	22.3	21.4	16.6
Saturate	7.4	15.0	12.5	11.7
AFT				
P, state of peptization of asphalt	6.67	9.03	6.94	8.38
Pa, peptizability of asphaltenes	0.58	0.62	0.61	0.57
$P_{0,}$ peptizing power of maltenes	2.84	3.47	2.72	3.61
IR Results				
C=O (Absorbance), 1700 cm^{-1}	0.0015	0.1300	0.1604	0.2674
S=O (Absorbance), 1033 cm^{-1}	0.0383	0.0339	0.0551	0.0538

The extracted RAP/RAS binders were also subjected to Asphaltene Determinator analysis to determine if RAS binder asphaltenes contain significantly different compositions than those of SHRP asphalt asphaltenes. The results are shown later in this report in table 4.

Based on the time-temperature superposition of asphalt materials, the curves were shifted over frequency at a reference temperature of 20°C to fit the sigmoidal function. This curve was then used to characterize the performance of an asphalt pavement at various temperature and loading conditions.

RESULTS AND DISCUSSION

Rheology

Figure 1 shows typical complex modulus and phase angle master curves for virgin, shingle, manufacturer, and tear-off binders. It can be seen from figure 1 that virgin binder is much softer

than the shingle binder. Tear-off binder is stiffer than the manufacturer binder at high and low frequencies. Tear-off binder has the lowest phase angle as compared to the other three binders.

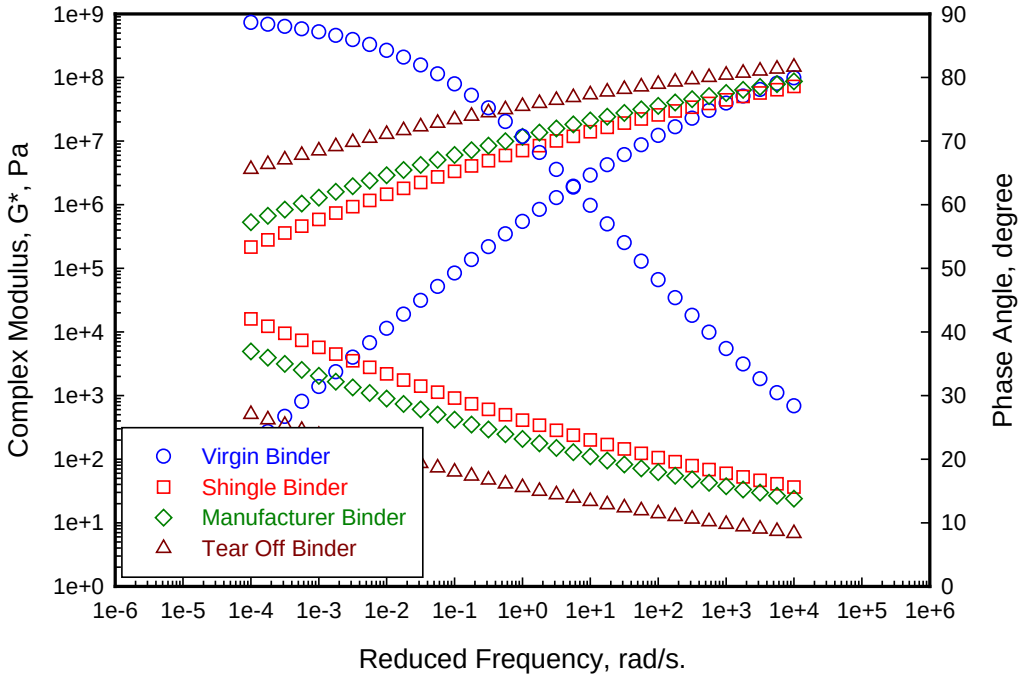

Figure 1. Graph. Complex modulus and phase angle master curves for virgin, shingle, manufacturer, and tear-off binders.

The master curves characterizing the complex modulus (G*) of the virgin binder and its different concentrations of manufacturer and tear-off shingle binders are presented in figures 2 and 3, respectively. A comparison of these curves indicates that as more RAS binder is added to the virgin binder, the curves shift upwards at the low frequency end of the curve with a slight upwards shift at the high frequency end of the curve. This trend indicates a stiffening of the binder at higher temperatures and/or lower frequencies as more RAS binder is added to the virgin binder which translates to an increased resistance to permanent deformation. The modest increase at the high frequency end of the curve indicates that as more RAS is added to the virgin binder, the binder has the potential to become stiffer at lower temperatures.

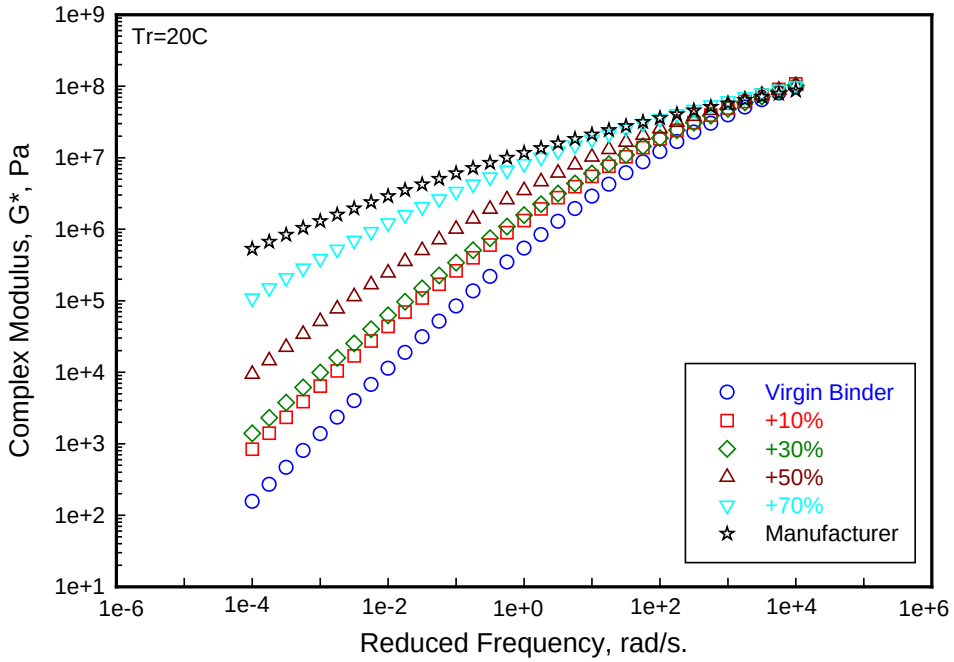

Figure 2. Graph. Complex modulus master curves for virgin binder and different concentrations of manufacturer shingle binders.

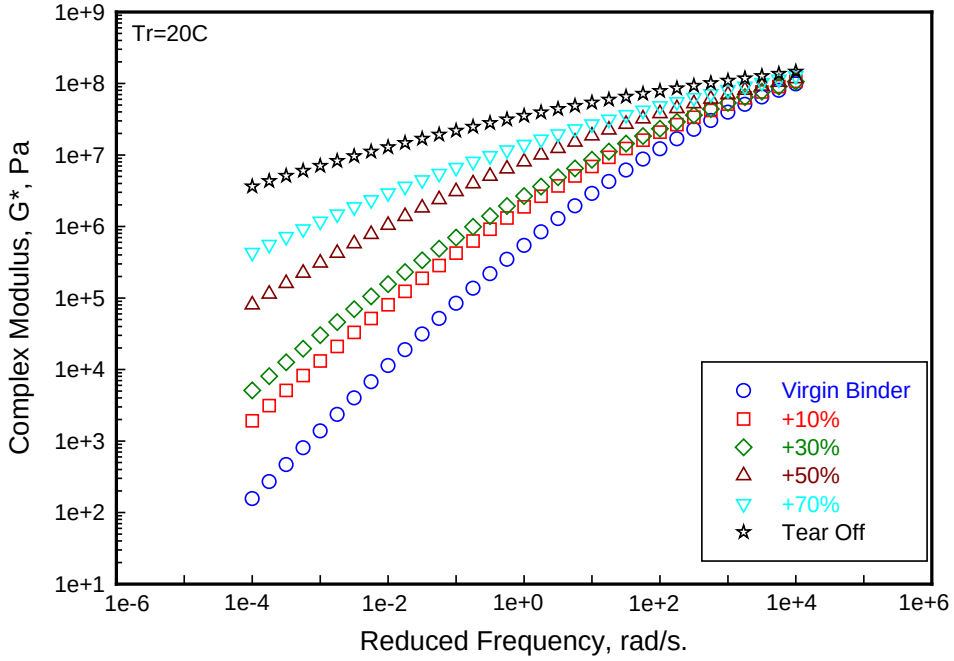

Figure 3. Graph. Complex modulus master curves for virgin binder and different concentrations of tear-off shingle binders.

To investigate how addition of RAS binders influences the relaxation properties of virgin binder, the master curve data for the complex modulus and phase angle were used to calculate the relaxation modulus via a prony series mathematical model for all the samples. The calculated relaxation moduli as a function of time for the virgin binder and its blends with extracted RAS binders from manufacturer and tear-off shingles are shown in figures 4 and 5, respectively. The plots show that addition of RAS binder into virgin binder slows relaxation.

Figure 6 shows another rheological parameter, the rheological index, as a function of RAS content for virgin binder. 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 exhibit a higher elastic modulus. As seen in figure 6, the addition of RAS binder into virgin binder increases the rheological index, and that the tear-off RAS added to virgin binder increases the elastic properties more than manufacturer binder to the same virgin binder. The rheological index increases linearly as RAS contents increase. R-squared of 0.98 and 0.93 are observed for tear-off shingle and manufacturer, respectively.

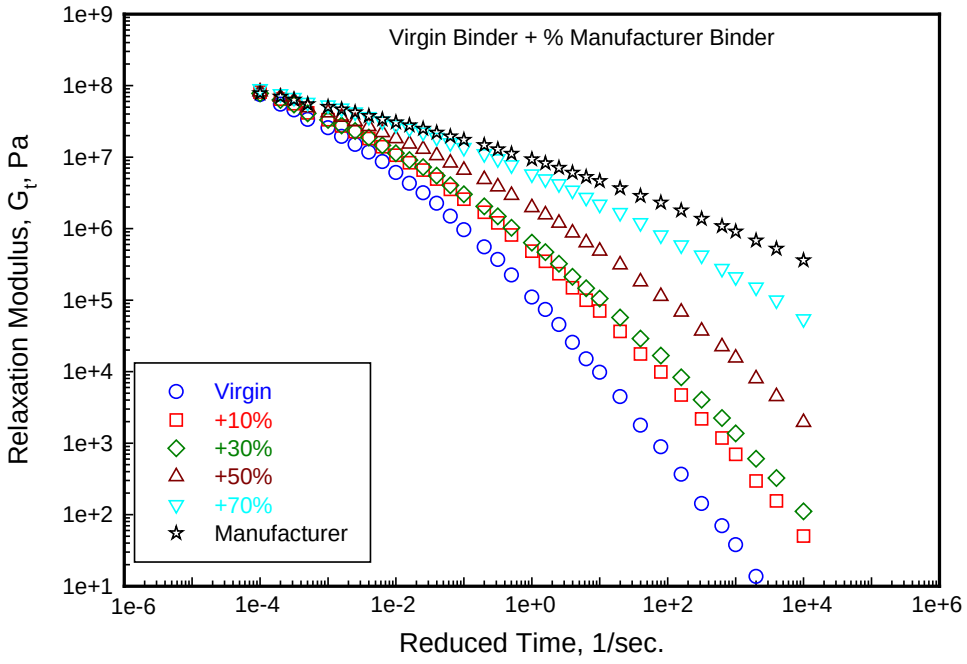

Figure 4. Graph. Relaxation modulus for virgin binder and different concentrations of manufacturer binders.

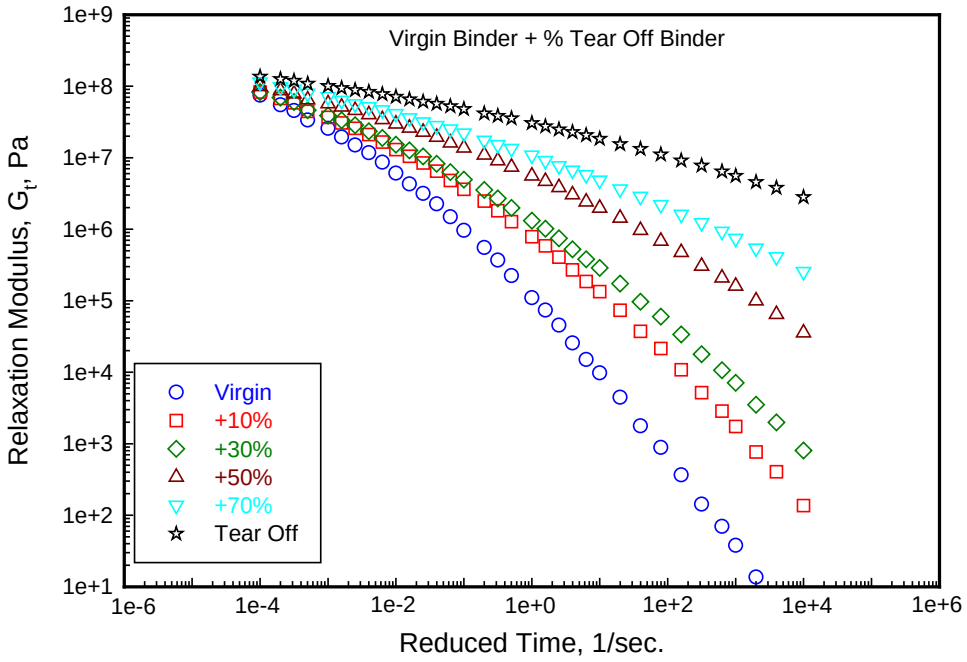

Figure 5. Graph. Relaxation modulus for virgin binder and different concentrations of tear-off binders.

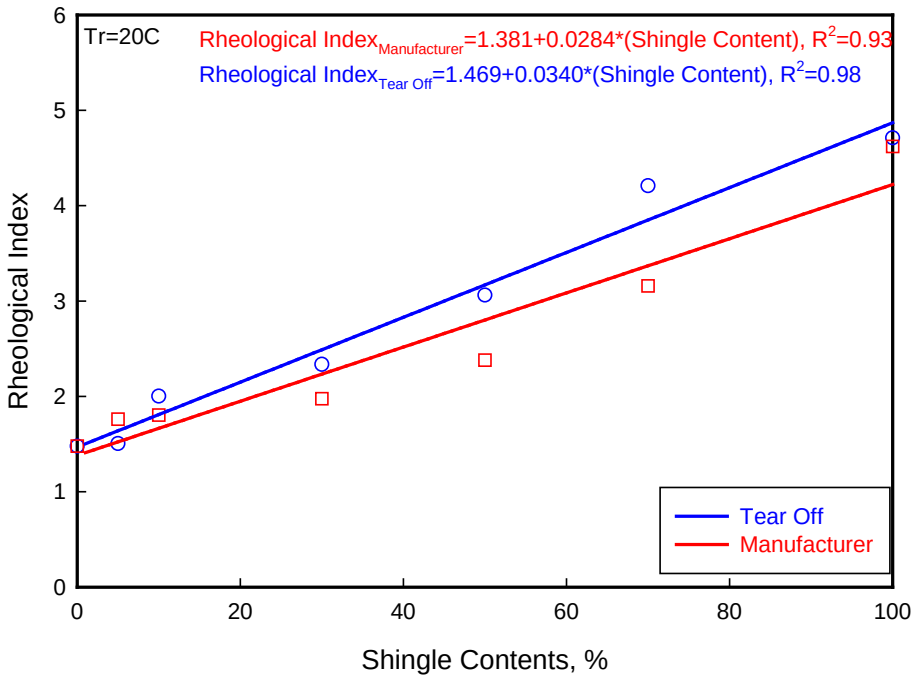

Figure 6. Graph. Rheological index for virgin binder and different concentrations of manufacturer and tear-off binders.

Infrared Spectrometry

Figure 7 shows carbonyl and sulfoxide peak heights as a function of RAS content for virgin binder and its two different types of RAS blend binders. It can be seen that a linear relationship exists between IR results (carbonyl+sulfoxide) and RAS concentrations, as expected. An R-squared value of 0.99 was observed for the relationship of IR results and RAS concentration for both tear-off and manufacturer binders, indicating that addition of RAS binders into virgin binder changes their chemical compositions proportionally and that no specific chemical species form from the blending. Note that the control sample (shown in figure 7) of virgin binder was excluded in the regression analysis because it was not subject to the same mixing procedure as those of binder blends. It is speculated that the control point could fall into the same linear lines if it is subjected to the same mixing procedure.

Figure 8 shows another rheological parameter, the crossover frequency, as a function of RAS content for virgin binder. The crossover frequency is defined as the frequency where G' is equal to G'' or tan δ is one. As a general trend, the higher the crossover frequency, the more viscous flow the material will demonstrate. For comparison purposes, data from the RAP study for Manitoba and South Carolina RAP binders mixed with RTFO-aged AAA-1 and AAC-1 are also included in this figure. As seen in figure 8, the addition of RAS binders to virgin binder reduces the viscous component of the resulting blend much more than the RAP binder does. The crossover frequency of virgin binder is reduced from 391 down to 18.2 when mixed with 10 percent tear-off shingle binder. That is 95 percent reduction on the viscous component.

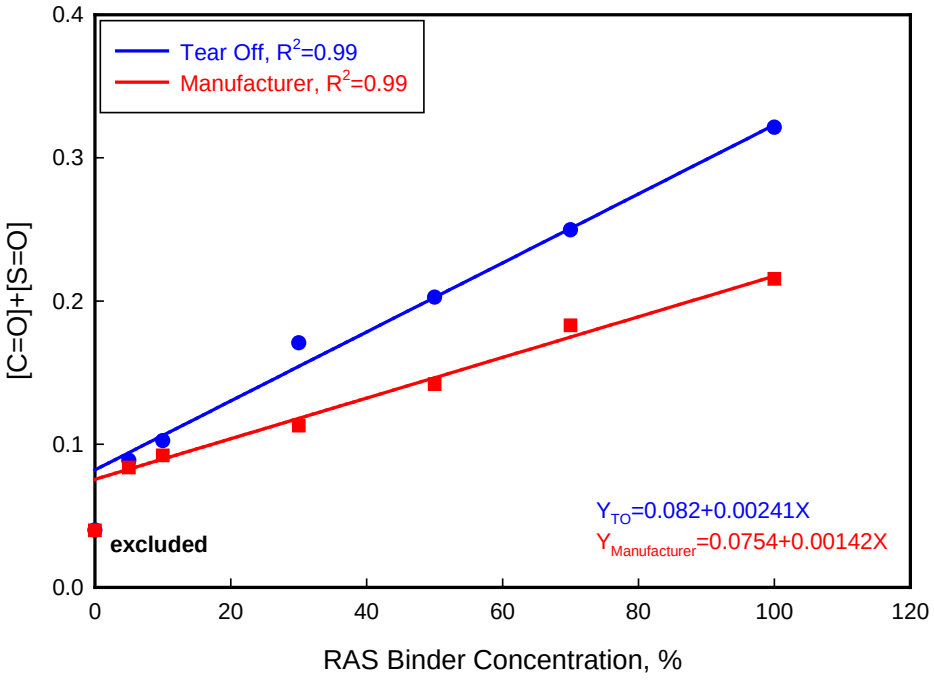

Figure 7. Graph. IR results for virgin binder and different concentrations of RAS blend binders.

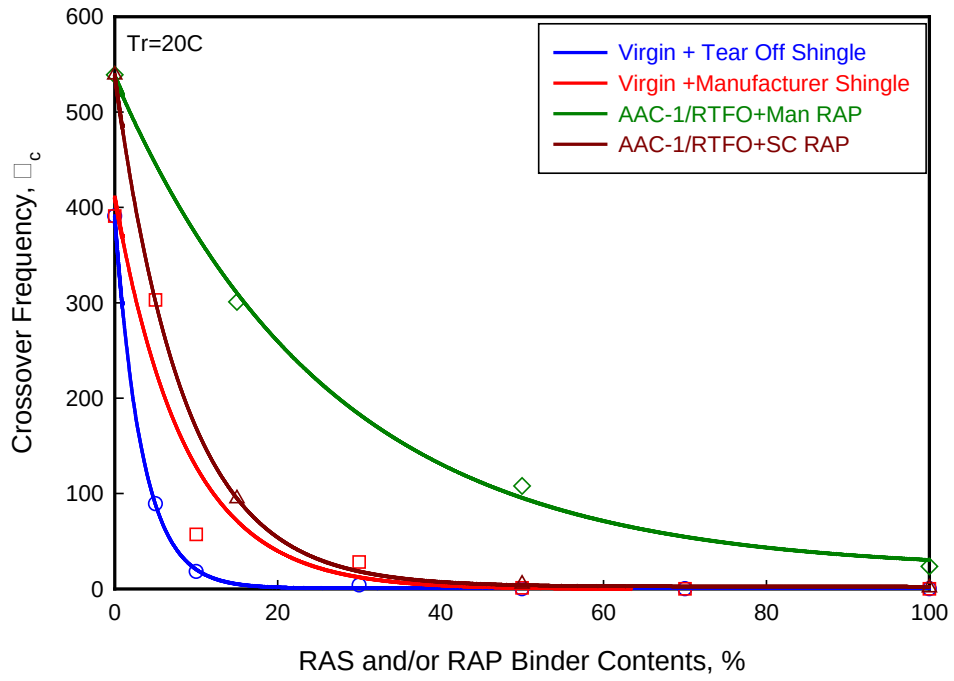

Figure 8. Graph. Crossover frequency as a function of RAP/RAS binder concentrations for virgin and fresh binders.

In addition, two SHRP asphalts, AAA-1 and AAC-1, used to mix Manitoba and South Carolina RAP binders for the RAP aging study are also mixed with RAS binders at the same concentrations, 15 and 50 percent, to investigate how addition of RAS binders influences the rheological and chemical properties of fresh binders as compared to RAP. A comparison will be conducted when the data is available.

Since asphalt binders in recycled asphalt shingle (RAS) are highly oxidized, it is reasonable to assume that RAS binders contain significant amounts of carbonyl and sulfoxide. Figure 9 shows the relationship between crossover frequency and chemical IR results for virgin binder blended with different concentrations of manufacturer and tear-off shingle binders. Figure 9 indicates that measured IR results have a reasonable relationship with the logarithm of crossover frequency. This also indicates that the change of viscous components due to addition of RAS binders to virgin binder may have resulted from the increase of carbonyl and sulfoxide content in RAS binders.

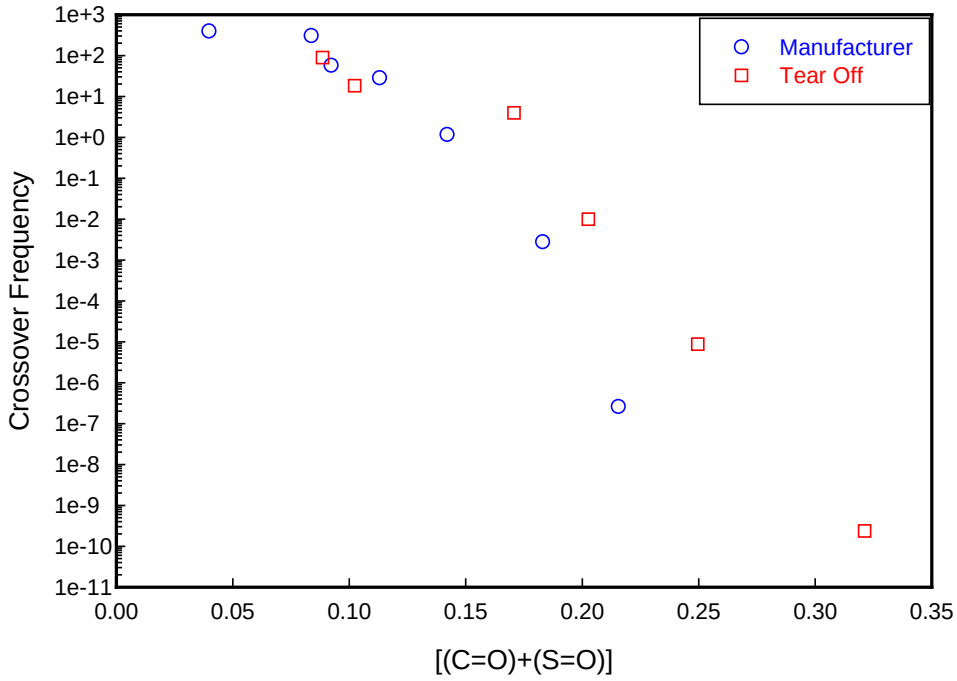

Figure 9. Graph. Relationship between rheological property of crossover frequency and IR results for virgin binder mixed with different contents of manufacturer and tear-off binders.

Thermo-Chemistry

Thermal analysis by temperature modulated differential scanning calorimetry (TMDSC) has 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. The glass transition of RAP modified asphalt binders was measured on a TA Instruments Q2000 differential scanning calorimeter. Temperature Modulated Differential Scanning Calorimetry was used for this study in order to effectively separate the glass transition from other complex overlapped effects such as cold crystallization and enthalpy recovery. To investigate if TMDSC is suitable for characterizing the influence of RAS binders blended with virgin binder, a previous RAP study was further analyzed by using TMDSC. The samples of RTFO-aged AAA-1 and AAC-1 mixed with different concentrations of extracted Manitoba and South Carolina RAP binders were subjected to TMDSC to investigate how addition of RAP binders influences the compatibility of fresh binders.

The sample was first heated and equilibrated at 165°C before cooling down to -90°C. At -90°C, the sample was held isothermally for 5 minutes, which was followed by a heating scan to 165°C. Both the cooling and subsequent heating scans were run at the average scanning rate of 2°C/min with modulation amplitude of 0.5°C every 80 seconds. The limiting fictive temperature T_f' was determined from the reversing heat flow curve during the second heating scan. T_f' was used as the glass transition temperature T_g since it has been widely accepted that T_f' is approximately equal to the glass transition temperature T_g obtained from the cooling scan at the same scan rate

(Datta and Lohse 1996; Gill et al. 1993). Details on how T_f' is determined can be found in another technical white paper, FP-16, and is briefly explained here for reference purpose.

T_f' is found by integrating the heat flow curve and then extrapolating the liquid line to the glass line, a procedure consistent with the method proposed by Moynihan et al. (1976).

$$\int_{T_f'}^{T \gg T_g} (C_{pl} - C_{pg}) dT = \int_{T \ll T_g}^{T \gg T_g} (C_p - C_{pg}) dT \quad (1)$$

where C_{pl} and C_{pg} are heat capacity for the liquid and the glass respectively. C_p is the apparent heat capacity. The limiting fictive temperature T_f', which is equivalent to the glass transition temperature T_g, is tabulated in table 2. Manitoba RAP is softer than South Carolina RAP as indicated by its lower glass transition temperature. For example, T_g of Manitoba RAP is even lower than RTFO aged AAA-1 asphalt binder, while T_g of South Carolina RAP is above that of RTFO aged AAA-1 binder.

Results listed in table 2 indicate that T_g difference between RTFO-aged SHRP asphalt binders and RAP component are relatively small with the largest difference being less than 10°C. Due to the lack of significant difference in T_g and chemical structure of constituent components, the severe incompatibility of those blends, based on TMDSC, cannot be concluded. Extensive data analyses on the TMDSC measurements are shown below.

Table 2. Glass transition temperatures of RAP modified AAA-1 blends and RAP modified AAC-1 blends.

Asphalt Matrix	Manitoba RAP Blends		South Carolina RAP Blends	
	Manitoba RAP, %	T_f', °C	South Carolina RAP, %	T_f', °C
RTFO/AAA-1	0	-22.6	0	-22.6
	15	-26.2	15	-25.3
	23	-24.2	23	-29.1
	30	-25.4	30	-21.1
	43	-23.6	43	-24.5
	50	-27.2	50	-19.4
	75	-26.0	75	-14.3
	100	-26.7	100	-17.8
RTFO/AAC-1	0	-27.2	0	-27.2
	15	-26.0	15	-24.4
	23	-27.7	23	-26.5
	43	-28.7	43	-24.6
	50	-23.8	50	-27.1
	75	-29.7	75	-18.5
	100	-26.6	100	-17.8

The limiting fictive temperature T_f', which is equivalent to the glass transition temperature T_g, is plotted against RAP concentration in figures 10 and 11. The empirical Fox equation, as expressed in equation 2, is used to fit the above mentioned experimental data.

$$\text{Fox: } \frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (2)$$

where component 1 refers to the virgin binder and component 2 is the RAP binder; *w* is the weight fraction of the component.

As seen from figure 10, the Fox equation can't satisfactorily describe T_g change of RTFO aged AAA-1 blends with either Manitoba RAP or South Carolina RAP (inset plot).

A similar trend is also found for RTFO aged AAC-1 blends with Manitoba or South Carolina RAP binders in figure 11. The deviation of blends' T_g from the Fox equation is presumably due to the relative closeness in T_g for RTFO aged binder and RAP binder. Further, the possible inhomogeneity caused by the blending process in combination with the small amount (~5mg) of sample for DSC tests, might also contribute to the break-down of the Fox equation.

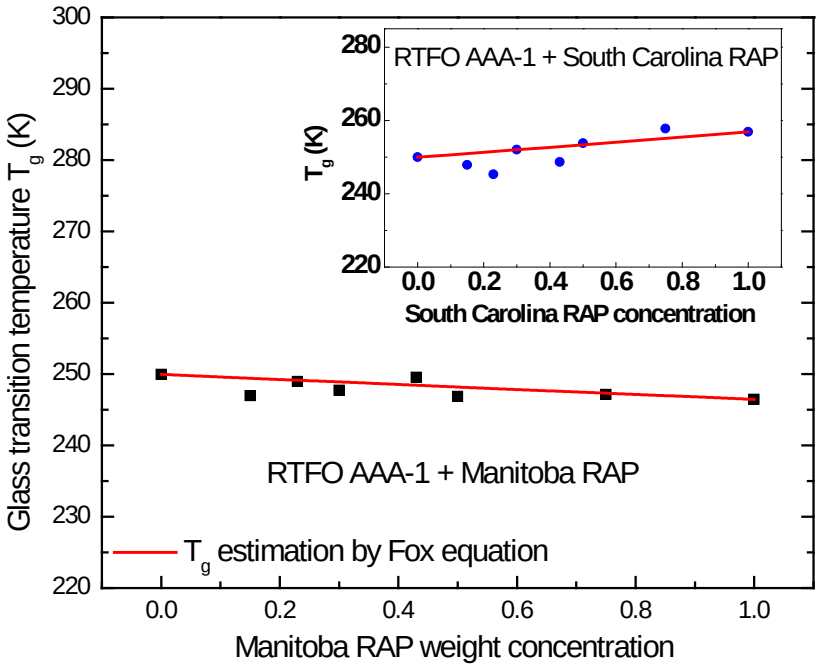

Figure10. Graph. Glass transition temperatures of RTFO AAA-1/Manitoba RAP blends as a function of RAP concentration; the inset is for AAA-1/South Carolina RAP blends.

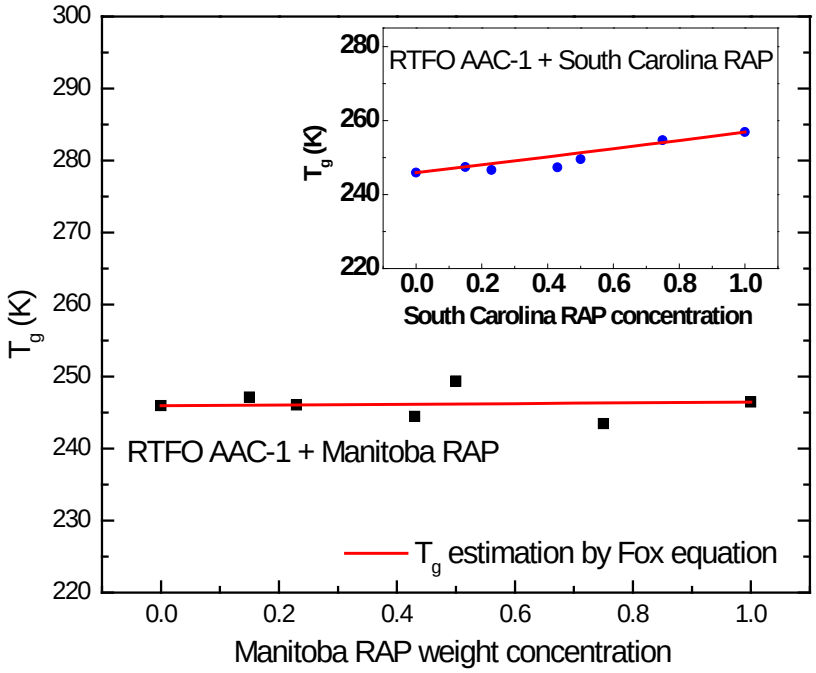

Figure11. Graph. Composition dependence of glass transition temperatures for RTFO AAC-1/Manitoba RAP blends; the inset is for AAC-1/South Carolina RAP blends.

Results shown in figures 10 and 11 indicate that the T_g difference between fresh binders and RAP binders is relatively small with the largest difference of less than 10°C. Again, due to the lack of significant difference in T_g and the similarity in chemical structure of constituent components, the severe incompatibility of those blends is not expected. As shown in figure 12, the broadness of glass transition, as characterized by the temperature derivative of reversing heating capacity, remains unchanged for RTFO aged AAA-1/Manitoba RAP blends. Similarly, no significant glass transition broadening is found for RTFO aged AAA-1/South Carolina RAP blends, as shown in the inset of figure 12.

Figure 13 shows the temperature derivative of reversing heat capacity of RTFO aged AAC-1/RAP blends. At RAP concentrations of up to 50 percent, especially for South Carolina RAP, both the glass transition temperature and broadness are very close to the RTFO aged AAC-1 binder. On the other hand, at 75 percent of RAP, the glass transition temperature and broadness is similar to that of RAP binders. These facts imply that the compatibility of RTFO aged AAC-1 with South Carolina RAP is not as good as RAP blends with RTFO aged AAA-1.

Because the results show that the difference of T_g between RAP binders and RTFO-aged binders is relatively small, it is difficult to characterize RAP binder blends via fictive temperature through TMDSC analyses. It was therefore decided that the TMDSC thermal analysis is not necessary for extracted shingle binders blends.

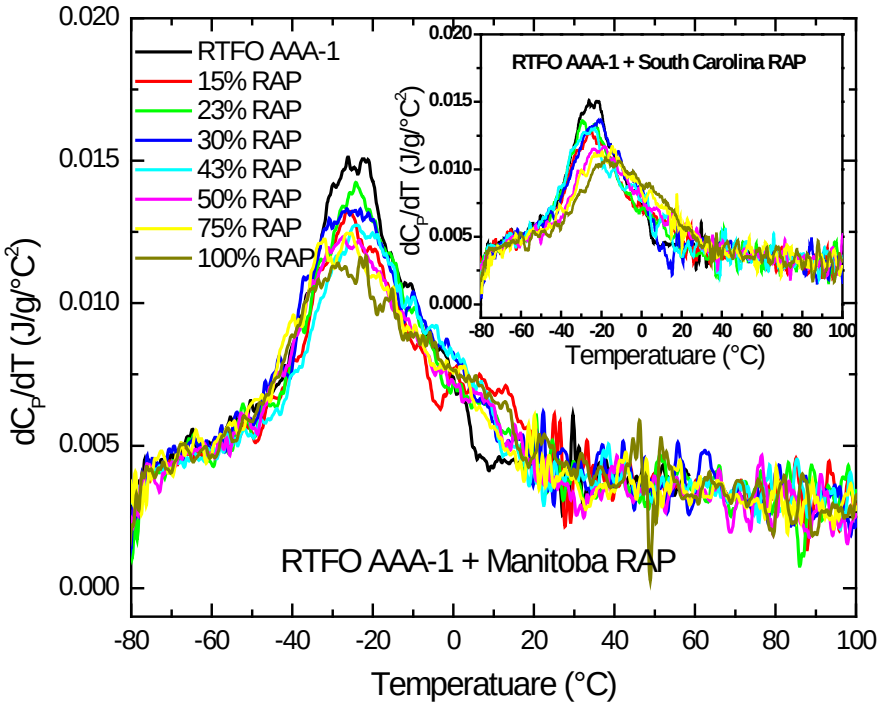

Figure12. Graph. Glass transition broadness of RTFO AAA-1/Manitoba RAP blends; the inset is the same plot for AAA-1/South Carolina RAP blends.

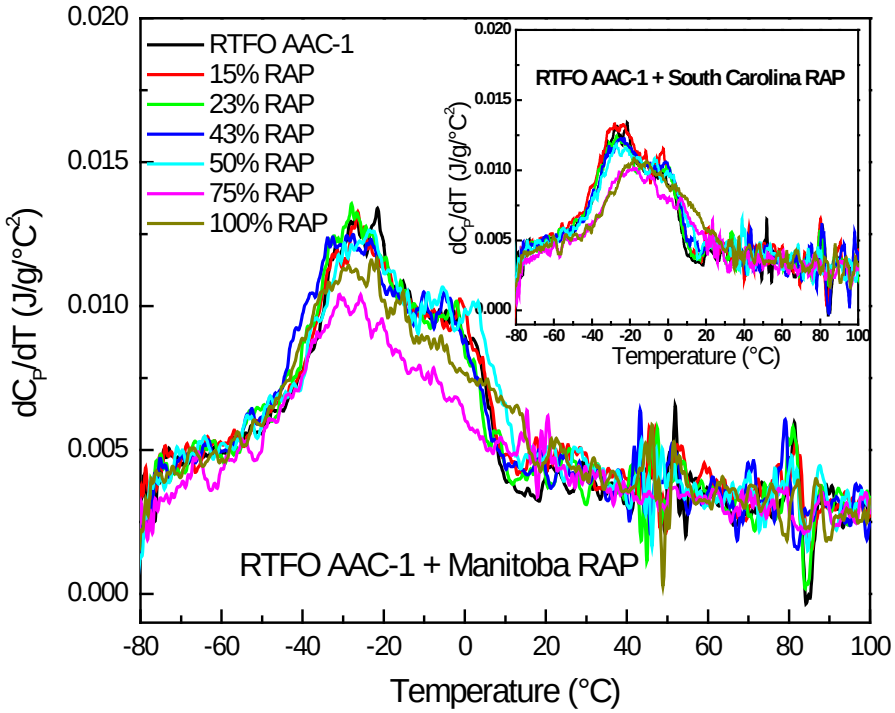

Figure13. Graph. Glass transition broadness of RTFO AAC-1/Manitoba RAP blends; the inset is the same plot for AAC-1/South Carolina RAP blends.

HP-GPC Chromatography

HP-GPC samples were prepared by dissolving 0.0275 ± 0.002 g of material in tetrahydrofuran (THF, HPLC-grade, Alfa Aesar) stabilized with butylated hydroxytoluene in a 2 mL volumetric flask. The solvent flow rate was maintained at 1 mL/min while the column is heated and maintained at 30°C. Downstream from the column, eluate flow is split through a Waters model 2414 refractometer and a Viscotek model 270 capillary bridge viscometer. Standards of naphthalene (MW=128 Da) and polystyrene (MW's=436, 1300, 3000, 10900, 28600, 70600, and 210000 Da) are injected to calibrate column retention times prior to sample analysis. Injection volumes of 190 µL are used for all samples. Waters Chromperfect software is used to record and analyze HP-GPC data.

Weight-average M_w, number-average M_n, and M_p, molecular weight of the peaks, are thus determined, shown below, based on the concentration c_i and molecular weight of the i^{th}-data point of the molecular weight distribution, M_i, relative to the retention peak.

$$\overline{M_w} = \sum M_i c_i \Big/ \sum c_i \tag{3}$$

$$\overline{M_n} = \sum c_i \Big/ \sum \left(c_i / M_i \right) \tag{4}$$

Polydispersity in molecular mass distribution is subsequently determined from the intrinsic viscosity and refractive index responses. It is thus defined as $\mathcal{P} = M_w / M_n$.

Table 3 shows the weight-average molecular weight, number-average molecular weight, molecular weight at the peak, and polydispersity for SHRP asphalt binders, extracted RAP binders, and extracted shingle binders. Table 3 clearly shows that shingle binders have the highest molecular weights. They are almost ten times higher than those of RTFO-aged SHRP core binders. However, it is interesting to mention that the molecular weight of extracted tear-off shingle binder is smaller than that of extracted manufacturer shingle binder. The reason is not known at the present time. However, it is recommended to conduct the same test, HP-GPC chromatography, on each fraction (saturate, asphaltene, polar aromatic, naphthenic aromatic) to investigate the causes.

Table 3. Results of HPLC for SHRP asphalt binders, RAP binders, and RAS binders.

Material	M_n, Daltons	M_w, Daltons	M_p, Daltons	Polydispersity
AAA-1/RTFO	831	3171	634	2.45
AAC-1/RTFO	648	1323	852	2.04
Manitoba RAP Binder	648	1557	516	2.40
South Carolina RAP Binder	712	1787	684	2.51
Manufacturer Shingle Binder	5049	12229	7238	2.42
Tear-Off Shingle Binder	4826	9574	4986	1.98

Bynum and Traxler (1970) used GPC to analyze asphalts extracted from pavement cores. They compared results with GPC chromatograms of samples of the original asphalts used in the pavements. They found that the GPC chromatograms of the asphalts that showed poor resistance to oxidative age hardening differed noticeably from GPC chromatograms of the original asphalts. A bimodal distribution of molecular sizes was observed in the asphalts investigated. Bynum and Traxler noticed that the height of the peak (determined by refractive index) corresponding to the higher molecular size entities increased with extent of oxidative age hardening, and that the size of the second peak decreased. It also was reported that the GPC chromatograms of asphalts of a given specification grade from the same supplier changed with time.

Jennings, Pribanic, and co-workers (Jennings et al. 1988; Jennings and Pribanic 1989; Pribanic et al. 1989; Jennings et al. 1992) have published a number of papers in which GPC chromatograms of asphalts are correlated with pavement performance. One study of Montana pavements manufactured from asphalts obtained from refineries in the state indicates that GPC chromatographic data of original asphalts can predict cracking tendencies in pavements.

Asphaltene Determinator (AD)

The Asphaltene Determinator^{TM} (AD) is a novel automated solubility-based asphaltene separation developed at WRI by Schabron and Rovani (2008). Although high performance liquid chromatography (HPLC) equipment is used, the separation does not involve chromatography. It is strictly solubility-based. This method involves precipitation of a 2 mg portion of a binder sample from the injection of 20 µL of sample solution in chlorobenzene on a polytetrafluoroethylene (PTFE)-packed column. The precipitated material is re-dissolved at room temperature in three steps using solvents of increasing polarity: cyclohexane, toluene, and methylene chloride:methanol (98:2 v:v) (Schabron and Rovani 2008; Schabron et al. 2010; Schabron and Rovani 2011). The detailed separation procedure and discussions of the significance of the various peaks in the separation profile are described in detail in Schabron et al. (2010).

AD profiles were obtained with the evaporative light scattering (ELSD) detector and with absorbance at both 500 nm and 700 nm. The ELSD responds more uniformly to a given mass of each of the fractions than other available detectors, so the ELSD data can be used to estimate weight percent of the various fractions. Heptane maltenes elute with heptane, and three components of the asphaltenes are separated by the solvents listed above. The material that elutes with methylene chloride:methanol (98:2 v:v) represents the most refractory, highly pericondensed aromatic pre-coke material in the binder or residuum. The ratio of the toluene peak area to the heptane peak area at 500 nm holds potential for monitoring oxidative aging. This ratio is called the Asphaltene Determinator Asphalt Aging Index (ADAIR) ratio, and it appears to track the aromatization and oxidation of naphthenes and other heptane-soluble molecules into higher pericondensed aromatic structures and oxygenated species in the presence of oxygen, with a concurrent increase in total asphaltene content. This is consistent with the sequential chemical mechanisms for asphalt oxidation as described by Petersen (1998, 2009) and Petersen and Harnsberger (1998).

The Asphaltene Determinator results for the SHRP asphalts, RAP binders, and RAS binders are provided in table 4. The area (related to weight) percent of heptane insolubles increases for a particular asphalt with oxidative aging. By combining peak areas from the ELSD and 500 nm separation profiles, a weight percent estimate of total pericondensed aromatics (TPA) can be determined without using a gravimetric method to determine asphaltenes. Another useful ratio is the AD Asphalt Aging Index ratio (ADAIR), which is the ratio of area of the toluene soluble asphaltene material peak at 500 nm to the peak area of the 500 nm absorbing material in the heptane maltenes fraction. This ratio increases with oxidative aging as more asphaltenes are formed from components present in the maltenes. Both the TPA and ADAIR increase with aging.

The data shown in the table 4 are for different binders. They cannot be compared exactly in the same manner as different degrees of oxidation for a single binder. However, the data show that the binders with the highest values for heptane insolubles (asphaltenes), percent TPA, and ADAIR are the tear-off shingle binder and the manufacturer shingle binder, indicating that these two binders are highly aged materials. The least aged materials are the RTFO-aged AAA-1 and AAC-1 asphalts, as expected. The Manitoba RAP binder and South Carolina RAP binder show significant oxidative aging, but not as severe as the aging of the two shingle binder materials.

Table 4. Results from Asphaltene Determinator (AD) for SHRP asphalts, RAP binders, and RAS binders.

Material	Detector	Asphaltene Determinator, Area Percent				ELSD Area % C7 Insolubles (n-heptane)	Percent TPA	AD Asphalt Aging Index Ratio, T/H
		Heptane (maltene soluble in heptane)	CyC_6 (asphaltene soluble in cyclohexane	Toluene (asphaltene soluble in toluene)	CH_2Cl_2:MeOH (most polar aromatic & asphaltenes soluble in CH_2Cl_2			
AAA-1/RTFO	ELSD 500nm 700nm	90.12 32.51 22.99	3.33 28.70 31.97	6.42 36.93 42.33	0.12 1.87 2.71	9.88	14.64	1.14
AAC-1/RTFO	ELSD 500 nm 700 nm	95.80 45.48 33.55	0.66 18.71 22.09	3.41 32.91 40.04	0.13 2.90 4.32	4.2	7.70	0.72
Manitoba RAP Binder	ELSD 500 nm 700 nm	88.75 29.15 18.72	1.81 20.19 21.86	9.08 46.38 53.46	0.37 4.28 5.96	11.25	15.88	1.59
South Carolina RAP Binder	ELSD 500 nm 700 nm	82.19 22.14 13.98	2.65 18.43 19.38	14.30 52.41 58.27	0.86 7.02 8.36	17.81	22.87	2.37
Manufacturer Shingle Binder	ELSD 500 nm 700 nm	76.29 20.26 12.93	5.71 23.78 25.05	17.78 54.58 60.46	0.22 1.37 1.57	23.71	29.73	2.69
Tear-Off Shingle Binder	ELSD 500 nm 700 nm	71.18 17.42 11.34	6.22 22.14 23.22	22.21 58.34 63.11	0.39 2.10 2.33	28.82	34.90	3.35

To further evaluate how asphaltene particles of RAP/RAS binders disperse in an asphalt, the asphaltene separation based on two different solvents, iso-octane and n-heptane, was used to calculate the asphaltene compatibility index. The asphaltene compatibility index (ACI) is a measure of the dispersibility of asphaltene in an asphalt binder and is defined as follows:

$$\text{ACI} = \frac{Asphaltene_{Iso-Octane}}{Asphaltene_{n-heptane} + Asphaltene_{Iso-octane}} x10$$

Table 5 shows asphaltene compatibility index for all binders. It can be seen (table 5) that asphaltene in shingle binders have the poorest dispersibility as compared to the other binders. This may help explain the results shown above that shingle binders have the highest modulus and stiffness. More research is recommended to further investigate how asphaltenes precipitated from different solvents influence the compatibility of RAP/RAS binder blends.

Table 5. Asphaltene compatibility index for RTFO-aged SHRP asphalt, extracted RAP, and RAS binders.

Asphalt	Iso-Octane Asphaltene, %	n-Heptane Asphaltene, %	Asphaltene Compatibility Index (ACI)
RTFO/AAA-1	20.00	9.88	6.69
RTFO/AAC-1	14.00	4.20	7.69
Manitoba RAP Binder	31.30	11.25	7.36
South Carolina RAP Binder	34.10	17.81	6.57
Manufacturer RAS Binder	34.80	23.71	5.95
Tear-Off RAS Binder	43.10	28.82	5.99

SUMMARY

A commonly used Texas virgin binder was mixed with the addition of 10, 30, 50, and 70 percent of extracted RAS binders, manufacturer and tear-off. Several analytical techniques including dynamic shear rheometry, Fourier transform infrared spectroscopy (FTIR), high-performance gel permeation chromatography (HP-GPC), automated flocculation titrimetry (AFT), SARA separations (ASTM D4124-09), and Asphaltene Determinator (AD) were used to measure chemical and physical properties of extracted RAS binders.

The standard AASHTO extraction procedure did not provide enough time to recover solvent-free shingle binders as shingle binders have been air-blown, are very stiff, and contain a significant amount of fillers. An extended AASHTO procedure was employed to ensure solvent-free shingle binders were obtained.

The results indicate that extracted shingle binders are much stiffer than virgin binder, and the addition of 10 percent of RAS binder into virgin binder reduces the viscous component of the

blend by 95 percent. Crossover frequency decreases exponentially as RAS content increases, and the rheological index increases linearly as RAP content increases.

Extracted shingle binders have high molecular weights as compared to the extracted RAP binders. The weight-average molecular weights of shingle binders are approximately ten times higher than those of RAP binders.

Based on current experiments, the results indicate that there is no chemical reaction (covalent) between RAS binders and fresh binders and that a linear relationship exists between oxidation products (IR results) and RAS binder contents. Tear-off binder has much higher carbonyl and sulfoxide content than that of manufacturer shingle binder. The results obtained from rheological tests agree with the results received from chemical testing (IR).

Temperature modulated DSC was used to investigate the thermal behavior of RAP binder blends. Due to the lack of sufficient difference in T_g and similarity in chemical structure of the binary components, the empirical blending equation can't reasonably describe the plasticization effect. No apparent broadening of glass transition is observed for all blends investigated. In comparison to RTFO aged AAC-1/RAP blends, RTFO aged AAA-1/RAP blends exhibit relatively better compatibility.

Several analytical tests have been successfully applied to characterize extracted shingle binders. It is reasonable to treat shingle binders as highly oxidized asphalt binders. To promote the use of high shingle binder content in HMA, softening agents or recycling agents may be necessary. If recycling agents are used, it is recommended that the compatibility issue between shingle binders and recycling agents should be evaluated.

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DISCLAIMER

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