

## INFLUENCE OF POLYPHOSPHORIC ACID MODIFIED BITUMEN ON RECYCLED ASPHALT PAVEMENT (RAP) PROPERTIES

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### ABSTRACT

*The addition of polyphosphoric acid (PPA) into bitumen has been a common practice for more than a decade, especially in the United States and Canada. Some of those pavements will be, or have already been rehabilitated, thereby producing recycled asphalt pavement (RAP) material containing PPA. This raises the legitimate question of the general recyclability of PPA modified bitumen and whether or not it performs as well as conventional polymer-modified RAP when utilized in hot mix asphalt. A research study was conducted to evaluate the performance of bitumen mixtures modified with various percentages of laboratory produced RAP. Laboratory aging procedures were used to produce RAP using three bitumen binders; Styrene-Butadiene-Styrene (SBS) only, PPA + SBS, and PPA only with all three bitumen binders performance grading (PG) out to a PG76-22. The three different laboratory RAP materials were mixed with a PG76-22 SBS modified bitumen binder to produce bitumen mixtures with RAP percentages as high as 45%. Bitumen binder characterization, using Multiple Stress Creep Recovery and Linear Amplitude Sweep testing protocols, were performed to assess the high temperature permanent deformation and intermediate temperature fatigue properties. Mixture characterization, using the Asphalt Mixture Performance Tester, Flexural Beam Fatigue, and Tensile Strength Ratio, provided an assessment of the overall mixture properties of the various RAP mixtures. The information presented shows that all three RAP types resulted in very similar performance with respect to permanent deformation, fatigue cracking, stiffness, and moisture damage susceptibility, verifying that PPA modified bitumen is as recyclable as SBS modified bitumen materials.*

**Keywords:** Polymer Modified Bitumen, Reclaimed Asphalt Pavement (RAP), Ageing, polyphosphoric acid, Fatigue Cracking

## 1. INTRODUCTION

Polymer modification of bitumen has increasingly become more popular for asphalt pavements, particularly in the United States. The modification of the bitumen have shown to increase rutting resistance, decrease fatigue damage, and reduce the potential for moisture damage. In a recent study, the Asphalt Institute demonstrated that life cycle costs for polymer modified bitumen are an additional 5 to 7 years greater than when using unmodified bitumen (1). Processes for asphalt modification involving natural and synthetic polymers were patented as early as 1843, with field installations placed in Europe in the 1930's and in North America in the 1950's (2). However, initial costs of modified bitumen limited their use in the United States (3). It was not until the late 1980's to early 1990's did the use of polymer modified bitumen start becoming more attractive as greater emphasis was being placed on long term pavement performance (4). By 1997, a survey of the state transportation agencies, circulated and analyzed by Bahia et al. (5) showed that 47 of the 50 states would be using modified binders in the immediate future, with many of the 47 states having already used modified bitumen. This would indicate that modified binders have been used extensively in the United States for almost 15 years.

A recent review of the Asphalt Institute's *Asphalt Usage Report* from 2000 to 2008 indicated that the use of modified asphalts rose steadily from 5.9% of total bitumen usage in the United States in 2000 to 10.6% in 2005, with the percent of modified asphalt usage generally leveling off to approximately 10% of all bitumen usage between 2006 and 2008 (6).

Polyphosphoric acid (PPA) is one of many additives used to modify and enhance paving grade asphalt. The first patent describing asphalt modification with PPA was published in 1973. Since the early 1990s, PPA has also been successfully used across the United States in combination with various polymer modifiers (7,8,9). Research has shown that the addition of PPA alone or in combination with other polymers can successfully increase rutting and fatigue resistance while minimizing stripping potential similar to polymer modified bitumen (10, 11). Studies have also indicated that the addition of PPA may aid in reducing age hardening and oxidative age related stiffening of bitumen and mixtures containing PPA (10, 12). However, even with the literature indicating the benefits of using PPA to modify bitumen and mixtures, some states are somewhat reluctant to specify its use.

Although the literature clearly indicates the benefit of utilizing modifiers in bitumen and mixtures, little to no literature is available regarding how these modified asphalt mixtures behave as RAP. Life cycle cost analysis has indicated that the average expectancy for a typical asphalt overlay is approximately fifteen (15) years (13). Taking into consideration that modified bitumen have shown to provide an additional 5 to 7 years of life before requiring resurfacing (1), it can be assumed that much of the RAP to be produced within the next few years will contain some kind of modified bitumen (i.e. – SBS, PPA, etc.).

## 2. OBJECTIVES

The objective of the study was to evaluate the recyclability of laboratory produced RAP containing two types of asphalt modifiers; Polyphosphoric acid and styrene-butadiene-styrene (SBS). Bitumen mixtures, containing various percentages of RAP produced with PPA and styrene-butadiene- styrene (SBS) were produced and compared using permanent deformation, fatigue cracking, and moisture damage potential tests to provide guidance as to the expected mixture performance of bitumen mixtures containing RAP with bitumen modifiers.

## 3. MATERIALS SUMMARY

### 3.1 Material Characterization

#### 3.1.1 Bitumen

The bitumen used in the study were produced from the neat PG64-22 bitumen binder and modified to achieve a PG76-22 performance grade. The modification type, amount of modifier, and resultant bitumen binder properties are shown in Table 1.

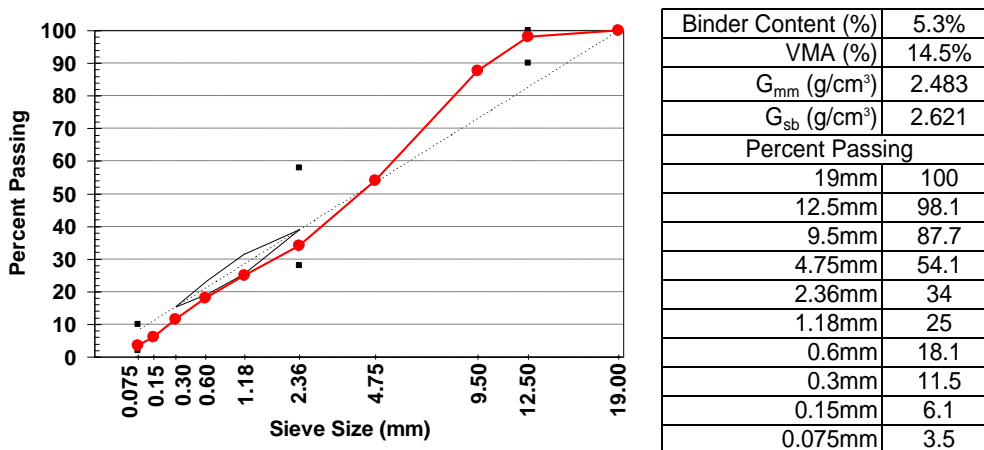
**Table 1 : True Grade Performance High Temperature of SBS and SBS+PPA Bitumens**

Additive/Test Parameter	Binder Modification Type		
	SBS	SBS+PPA	PPA
% SBS	4.25	2.80	0.00
% PPA	0.00	0.60	2.25
% Sulfur	0.10	0.10	0.00
Original DSR, kPa (76°C)	1.767	1.470	1.071
RTFO DSR, kPa (76°C)	2.312	2.719	2.625
BBR Stiffness, MPa (-12°C)	139	148	164
BBR m-slope (-12°C)	0.350	0.350	0.326

**3.1.2 Mixture Design**

The primary aggregate source used to develop the mixture gradation was granitic gneiss from northern New Jersey. The aggregate mineralogy was a combination of pyroxene granite containing bands of magnetite and oligoclase gneiss containing amphibolite. The aggregates were used to develop a coarse-graded, 12.5mm Superpave mix at  $N_{design}$  level of 100 gyrations. Gradation, which was based on a NJDOT approved HMA mixture design. The resultant design volumetric properties are shown in Figure 1. The laboratory produced RAP and the virgin HMA were produced using the identical aggregate gradation and bitumen content. Therefore, modifications to stockpile percentages due to the additional of the RAP were not required to maintain the target aggregate blend gradation shown in Figure 1.

Mixing of the laboratory RAP and virgin materials followed that recommended by NCHRP 9-33, *A Mix Design Manual for Hot Mix Asphalt (HMA)* (10). The RAP was heated in a separate oven set to 110°C (230°F) for no longer than two hours to eliminate potential of changing the properties of the RAP binder (14). The virgin aggregates were heated to 10 to 20°C above the mixing temperature for the PG76-22 bitumen binders. Bitumen mixtures containing 0, 15, 30, and 45% RAP were produced in the laboratory with RAP containing different bitumen binders; 1) PPA only modified, 2) SBS only modified, and 3) PPA and SBS modified. Each RAP type was mixed with the same bitumen mixture, conforming to the job mix formula shown in Figure 2 and using the identical SBS modified bitumen binder used in producing the laboratory RAP. After mixing, the bitumen mixtures were aged in accordance to AASHTO R30, *Mixture Conditioning of Hot Mix Asphalt* and then compacted into performance specimens.



**Figure 1: Gradation and Design Volumetric Properties**

**3.2 Aging Protocol for Laboratory Produced RAP**

In order to manufacture RAP in the laboratory, an accelerated aging process on virgin mixtures was conducted. At first, the aging condition of 100°C for 2 days was proposed based on a literature study concerning the accelerated aging of HMA materials (15). Additional times of 4 and 6 days were also evaluated. Preliminary aging consisted of using a PG64-22 bitumen binder and comparing the extracted and recovered bitumen binder grade to the PG grade of field sampled RAP. A PG64-22 bitumen binder was used as this was the primary PG grade used in New Jersey just prior to the adoption of polymer-modified bitumen binders and was assumed to make up a large percentage of the RAP currently found in New Jersey. In addition, the field sampled RAP came from the same region as the raw aggregates used in the laboratory RAP work in hopes any binder-aggregate interaction during the laboratory aging may mimic that which had occurred in the field.

The laboratory aging results are shown in Figure 2a, b, and c. The PG grade results indicated that 2 days of oven aging at 100°C was not enough to produce a similar PG grade to the field sampled RAP. Based on the test results, it was determined that eight (8) days was required to age the laboratory produced RAP to a condition similar to the field sampled RAP. The final protocol used to produce the laboratory RAP was as follows:

- Mix aggregate and bitumen binder until thoroughly coated;
- Short-term age the loose mix for 2 hours at compaction temperature;
- Place loose mix in oven set at 100°C for eight (8) days; and
- Mix loose mix in pan two times daily (first thing in morning and late afternoon was used for this study).

### 3.2.1 Bitumen Properties After RAP Aging Procedure

After the laboratory RAP aging process, the laboratory RAP was sampled and the bitumen binder was extracted and recovered in accordance with AASHTO T164, *Quantitative Extraction Asphalt Binder from Hot Mix Asphalt*, using Toluene as a solvent, and AASHTO T170, *Recovery of Asphalt from Solution by Absorption Method*, with the deviation of using a higher recovery temperature to compensate for the higher boiling point of Toluene. The bitumen binders were also subjected to the rolling thin-film oven for eight (8) minutes after the recovery process to remove traces of any solvent remaining in the recovered binders. The continuous PG grade results for the recovered laboratory RAP binders are shown in Table 2.

Test results indicate that extracted and recovered bitumen binder from PPA modified RAP was generally stiffer, while SBS modified RAP appeared to be softest due to laboratory RAP aging procedure. The PG grades above have been found to be typical for RAP sampled and tested in New Jersey (16). It should be noted that the high temperature PG grade needed to be estimated based on the measured test data.

**Table 2: Continuous PG Grade of Modified Binders After Laboratory RAP Aging Procedure**

Additive/Test Parameter	Binder Modification Type		
	SBS	SBS+PPA	PPA
% SBS	4.25	2.8	0
% PPA	0	0.6	2.25
% Sulfur	0.1	0.1	0
Original DSR, kPa (82°C)	9.915	11.116	20.335
Original DSR, kPa (88°C)	5.379	5.951	10.26
RTFO DSR, kPa (82°C)	13.483	17.706	29.715
RTFO DSR, kPa (88°C)	7.386	9.689	15.546
BBR Stiffness, MPa (-6°C)	144	152	
BBR Stiffness, MPa (0°C)	74.2	81.8	94.5
BBR Stiffness, MPa (6°C)			53.6
BBR m-slope (-6°C)	0.283	0.27	
BBR m-slope (0°C)	0.322	0.312	0.287
BBR m-slope (6°C)			0.324
<b>Continuous PG Grade</b>	<b>100-13.4</b>	<b>102.8-5.71</b>	<b>106.1-7.89</b>

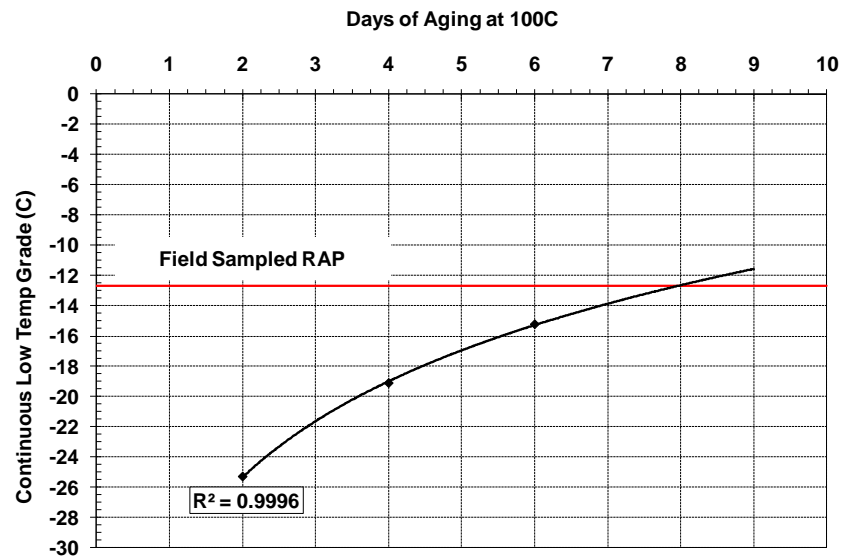
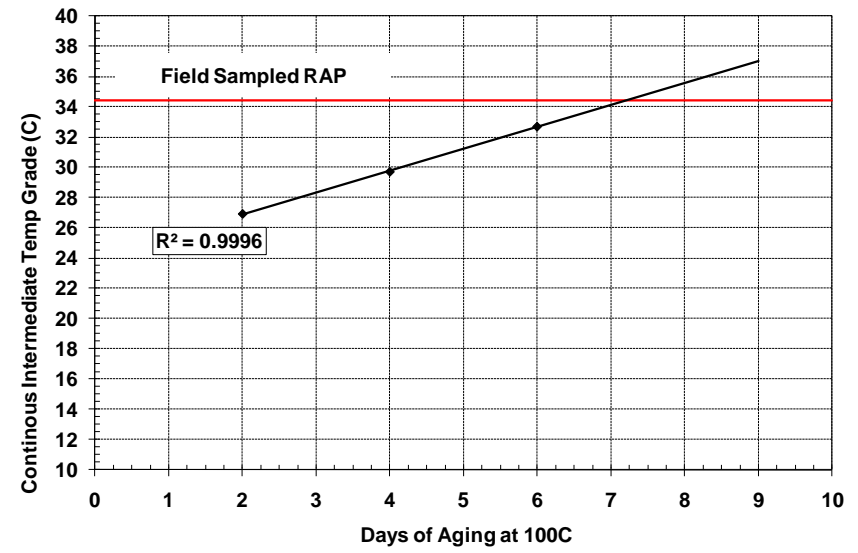
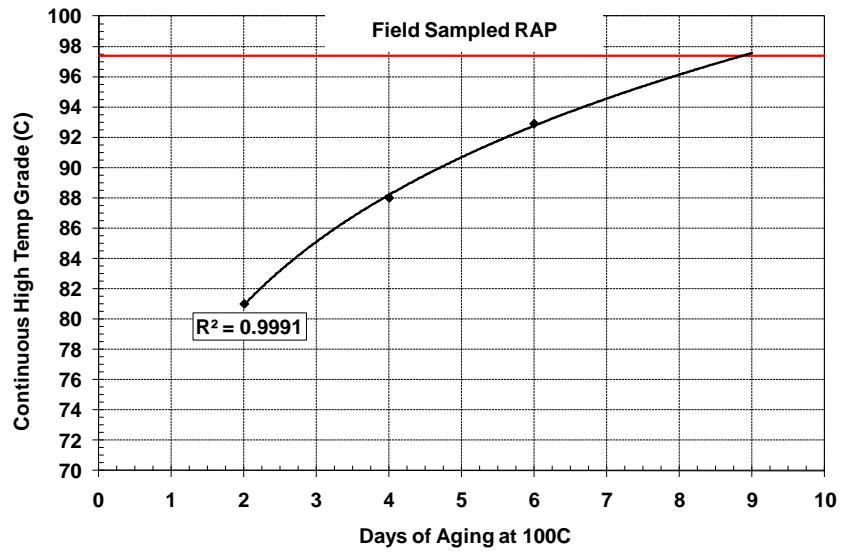


Figure 2: PG Grade Results of Laboratory Aged Loose Mix

#### 4. BITUMEN MIXTURE PERFORMANCE TESTING

Bitumen mixture performance testing was conducted on the various mixtures to evaluate how the RAP with different bitumen binder modifications would influence the final material performance. The performance testing included the following:

- Dynamic Modulus: AASHTO TP79
  - Short-term and Long-term aged in accordance to AASHTO R30
- Repeated Load: AASHTO TP79
- Flexural Beam Fatigue: AASHTO T321
- Moisture Damage Susceptibility: AASHTO T283

The mixtures evaluated contained RAP material, composed of the different modified bitumen binders noted earlier in Table 2. Different percentages of the RAP material were mixed with an SBS-modified bitumen to produce the final bitumen mixtures used for performance evaluation. Testing protocols were chosen to provide a comprehensive evaluation of how RAP material, produced with bitumen of different modification types and concentrations, influence the final mixture performance.

##### 4.1 Dynamic Modulus (AASHTO TP79)

Dynamic modulus and phase angle data were measured and collected in uniaxial compression using the Simple Performance Tester (SPT) following the method outlined in AASHTO TP79, *Determining the Dynamic Modulus and Flow Number for Hot Mix Asphalt (HMA) Using the Asphalt Mixture Performance Tester (AMPT)*. The data was collected at three temperatures; 4, 20, and 45°C using loading frequencies of 25, 10, 5, 1, 0.5, 0.1, and 0.01 Hz. Test specimens were evaluated under both short-term and long-term aged conditions in accordance with AASHTO R30, *Mixture Conditioning of Hot Mix Asphalt*.

The collected modulus values of the varying temperatures and loading frequencies were used to develop Dynamic Modulus master stiffness curves and temperature shift factors using numerical optimization of Equations 1 and 2. The reference temperature used for the generation of the master curves and the shift factors was 20°C.

$$\log|E^*| = \delta + \frac{(Max - \delta)}{1 + e^{\beta + \gamma \left\{ \log \omega + \frac{\Delta E_a}{19.14714} \left[ \left( \frac{1}{T} \right) - \left( \frac{1}{T_r} \right) \right] \right\}}} \quad (1)$$

where:

- |E\*| = dynamic modulus, psi
- $\omega_r$  = reduced frequency, Hz
- Max = limiting maximum modulus, psi
- $\delta$ ,  $\beta$ , and  $\gamma$  = fitting parameters

$$\log[a(T)] = \frac{\Delta E_a}{19.14714} \left( \frac{1}{T} - \frac{1}{T_r} \right) \quad (2)$$

where:

- a(T) = shift factor at temperature T
- $T_r$  = reference temperature, °K
- T = test temperature, °K
- $\Delta E_a$  = activation energy (treated as a fitting parameter)

Additionally, the bitumen mixtures were evaluated to determine their potential of aging by evaluating the Aging Ratio between the dynamic modulus properties measured under long-term and short-term aged conditions. As the E\* Aging Ratio goes above the value of 1.0, it represents an age hardening in the mixture's stiffness properties.

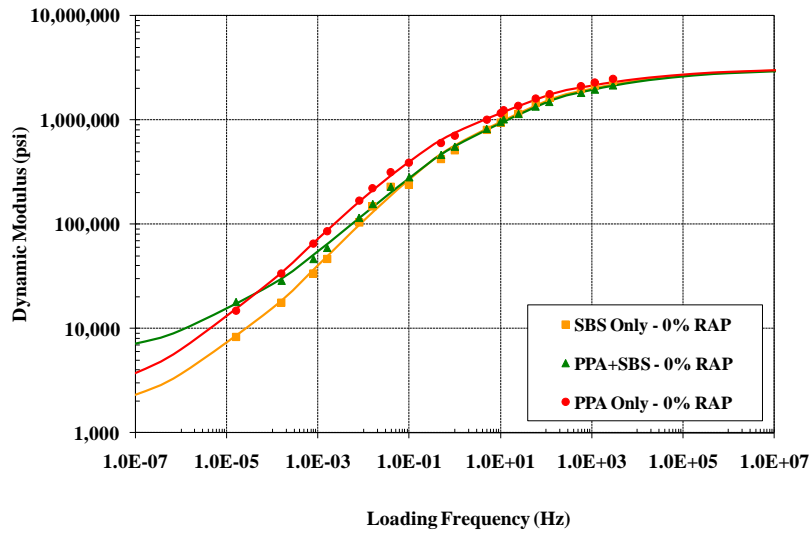
The dynamic modulus master curves for the 0, 15, 30, and 45% RAP mixes for the short-term (STOA) and long-term aged (LTOA) conditions are shown in Figures 3 and 4, respectively. The short-term aged (STOA) results shows that the virgin PPA only modified mixture, the dynamic modulus is highest at all loading frequencies/test temperatures. However, as the PPA modified RAP content increases, it compares favorably to that of the SBS only modified and PPA+SBS modified mixtures. Similar results were found in the long-term aged (LTOA) samples, although the modulus values were much closer at all RAP contents.

The dynamic modulus (E\*) Aging Ratio results are shown in Figure 5. The Aging Ratio results indicate that the PPA only modified RAP mixtures has very similar, if not better, aging characteristics than the SBS only and PPA-SBS modified RAP mixtures. This corresponds to similar findings that have indicated that PPA modified bitumen binders and mixtures are better able to resist general age hardening when compared to other modified bitumens (6, 11).

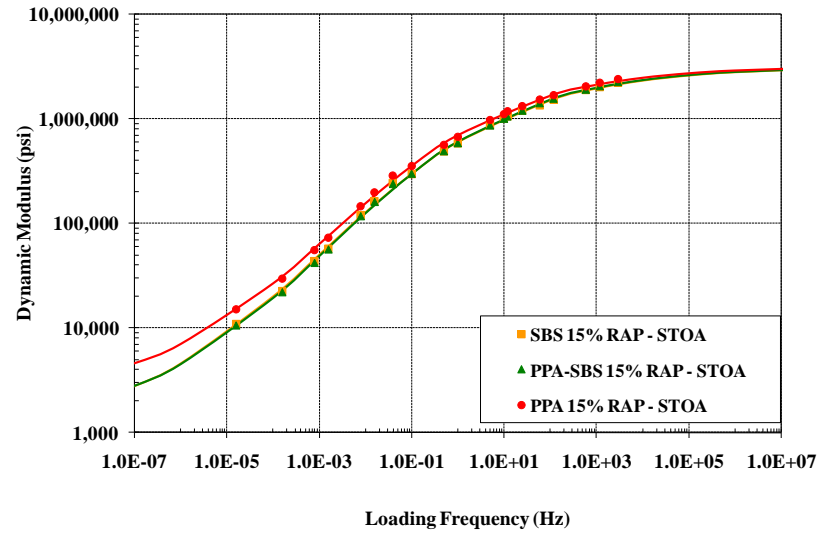
## 4.2 Repeated Load – Flow Number Test

Repeated load permanent deformation testing was measured and collected in uniaxial compression using the Asphalt Mixture Performance Tester (AMPT) following the method outlined in AASHTO TP79, *Determining the Dynamic Modulus and Flow Number for Hot Mix Asphalt (HMA) Using the Asphalt Mixture Performance Tester (AMPT)*. The unconfined repeated load tests were conducted with a deviatoric stress of 600 kPa and a test temperature of 54.4°C, which corresponds to New Jersey's average 50% reliability high pavement temperature at a depth of 25 mm according to the LTPPBind 3.1 software. These testing parameters (temperature and applied stress) conform to the recommendations currently proposed in NCHRP Project 9-33, *A Mix Design Manual for Hot Mix Asphalt*. Testing was conducted until a permanent vertical strain of 5% or 10,000 cycles was obtained.

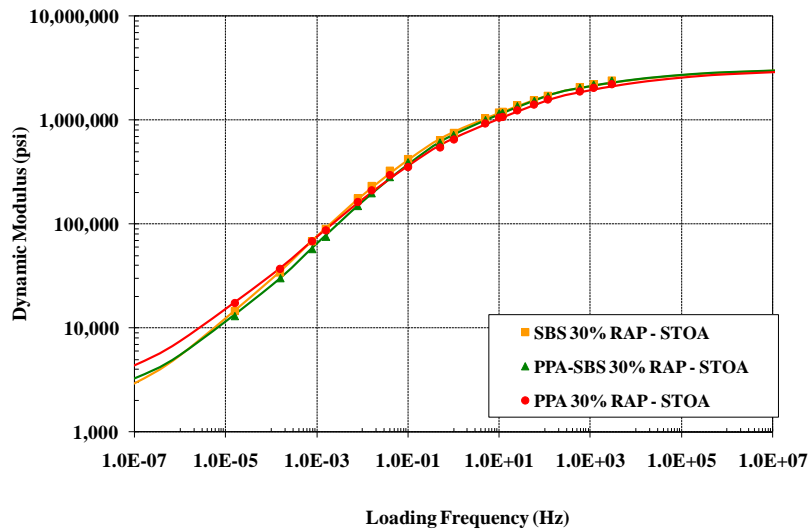
The test results for the AMPT repeated load tests are shown in Figure 6. The flow number results for the virgin mixes (0% RAP) indicate that all three modified binder mixtures performed equally as well. Based on current recommendations under the NCHRP 9-33 project, each of the mixtures should be able to withstand greater than 30 million ESAL's. Figure 6 also shows that as the RAP content increases, the Flow Number value also increases. However, the increases in Flow Number values for the different RAP materials at the same percentages were generally the same, with the greatest difference found at the 30% RAP content.



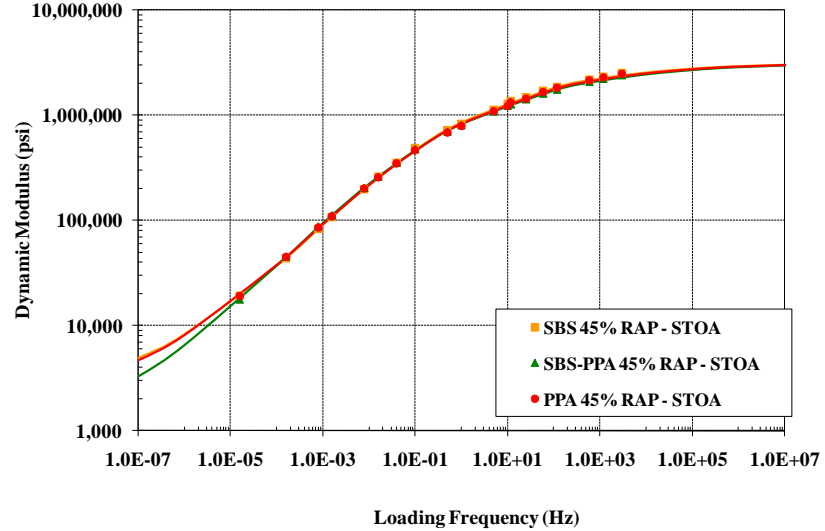
(a)



(b)



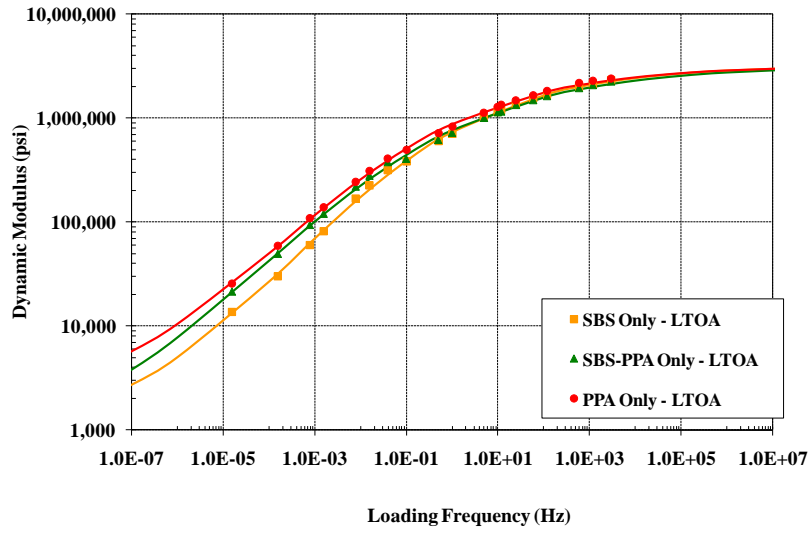
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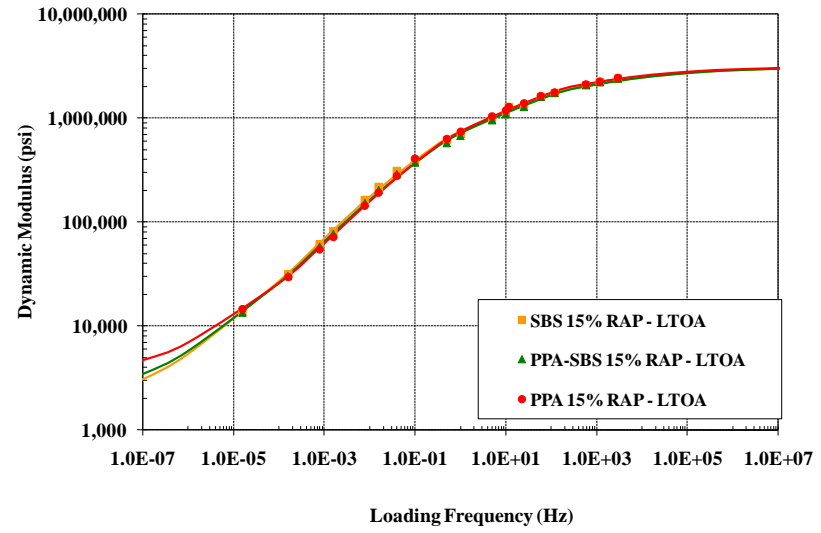
(d)

**Figure 3: Master Stiffness Curves for Short-Term Aged Conditions**

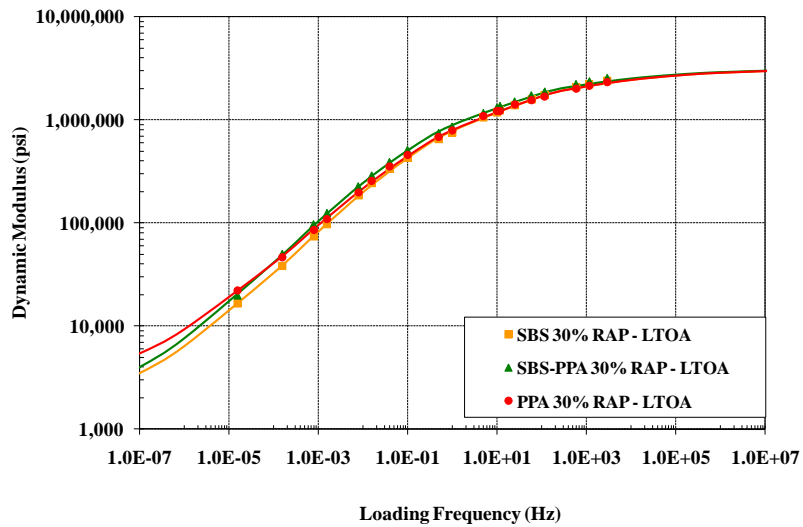




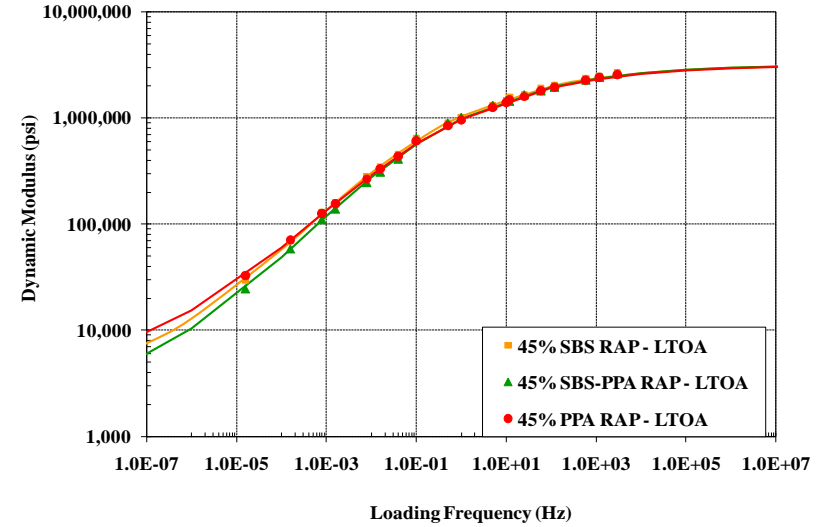
(a)



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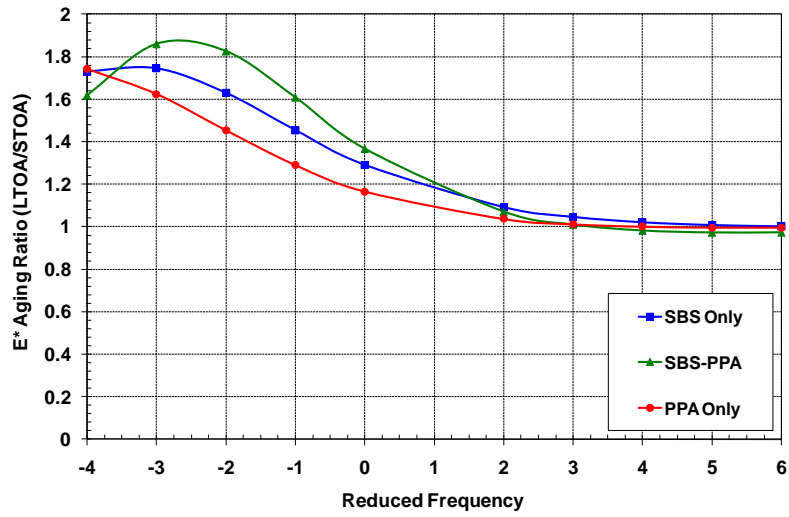


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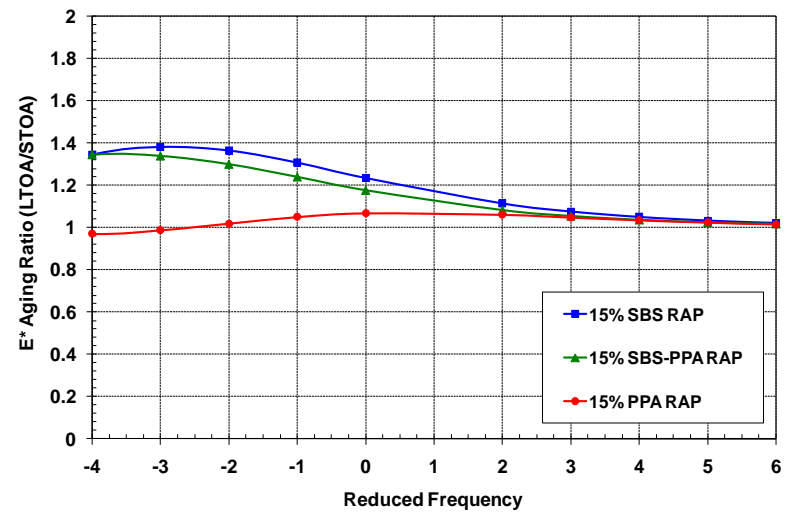


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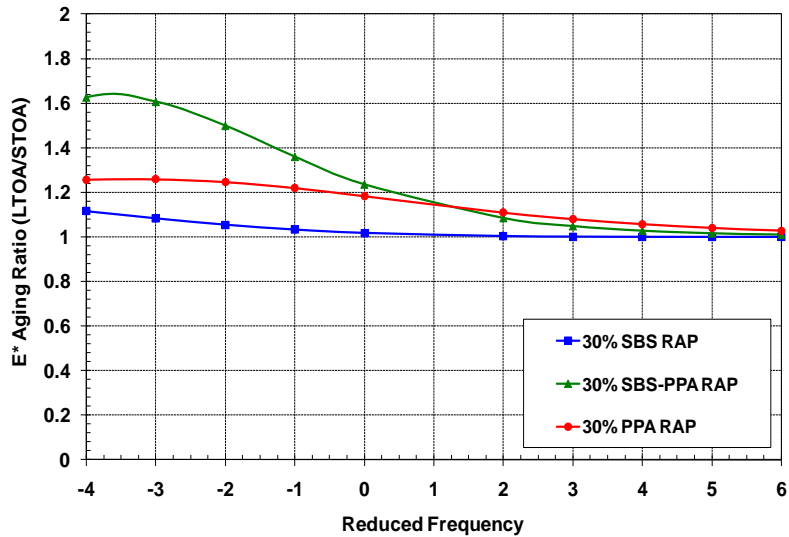
**Figure 4: Dynamic Modulus Master Curves for Long-Term Aged Conditions**



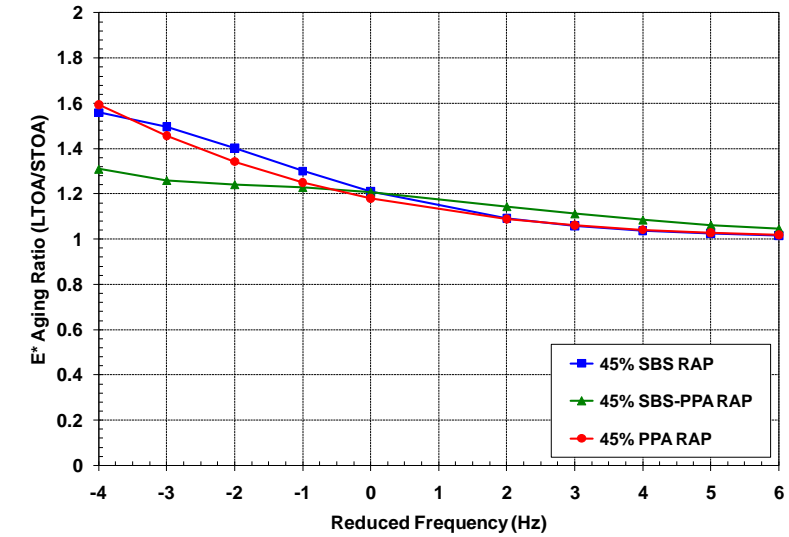
(a)



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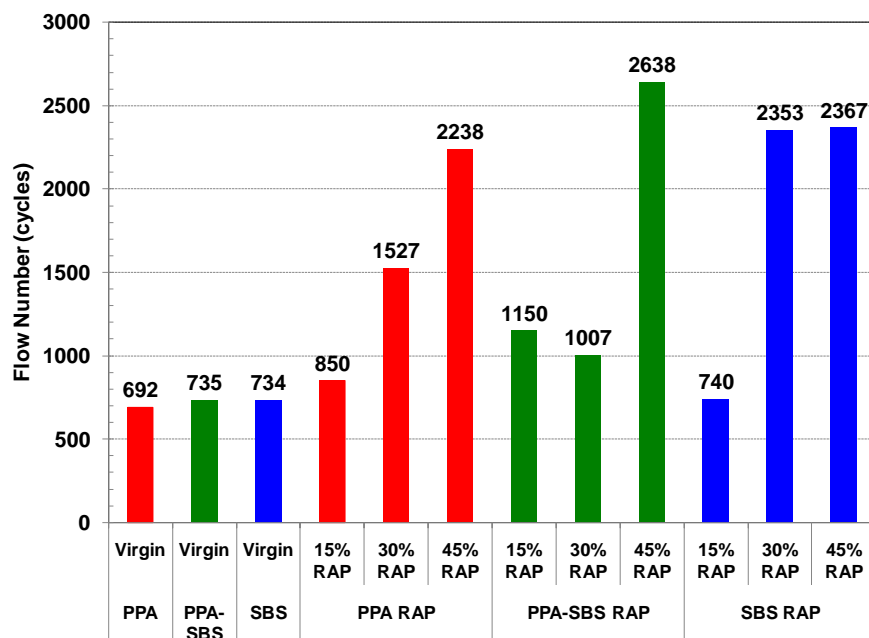


(c)



(d)

Figure 5: E\* Aging Ratio Results



**Figure 6: Repeated Load (Flow Number) Test Results**

#### 4.3 Flexural Beam Fatigue (AASHTO T321)

Fatigue testing was conducted using the Flexural Beam Fatigue test procedure outline in AASHTO T321, *Determining the Fatigue Life of Compacted Hot-Mix Asphalt (HMA) Subjected to Repeated Flexural Bending*. Testing was conducted on duplicate specimens at the following applied tensile strain levels; 450, 600, and 900 micro-strains. Samples used for the Flexural Beam Fatigue test were compacted using a vibratory compactor designed to compact brick samples of 400 mm in length, 150 mm in width, and 100 mm in height. After the compaction and aging was complete, the samples were trimmed to within the recommended dimensions and tolerances specified under AASHTO T321. The test conditions utilized were those recommended by AASHTO T321 and were as follows:

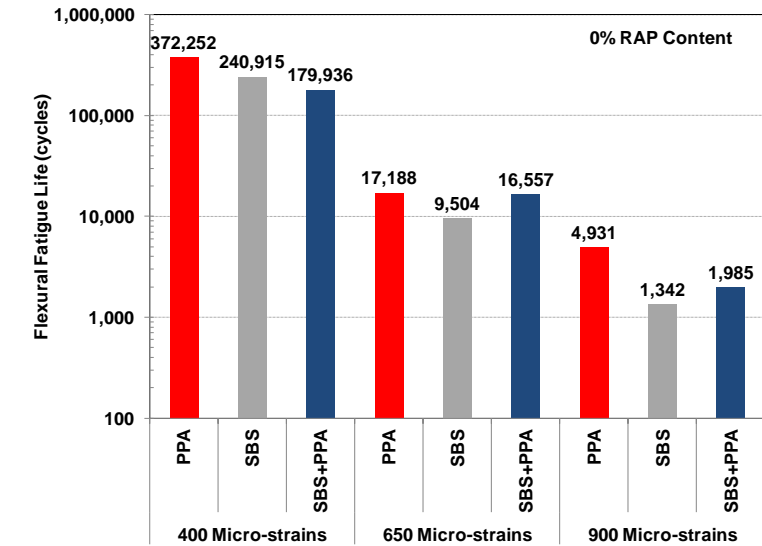
- Test temperature = 15°C;
- Haversine waveform;
- Strain-controlled mode of loading; and
- Loading frequency = 10 Hz;

The test results for the beam fatigue testing are shown in Figure 7. The PPA modified binder with no RAP exhibit the highest fatigue resistance. The test results also indicated that the flexural fatigue results improved until 30% RAP and then decreased for the 45% RAP content mixtures. The strain range experiences by a pavement (18) is typically below or at 400 microstrain up to 35-40C. For 400 microstrains, the PPA modified binder has the highest fatigue resistance up to 30% of RAP content.

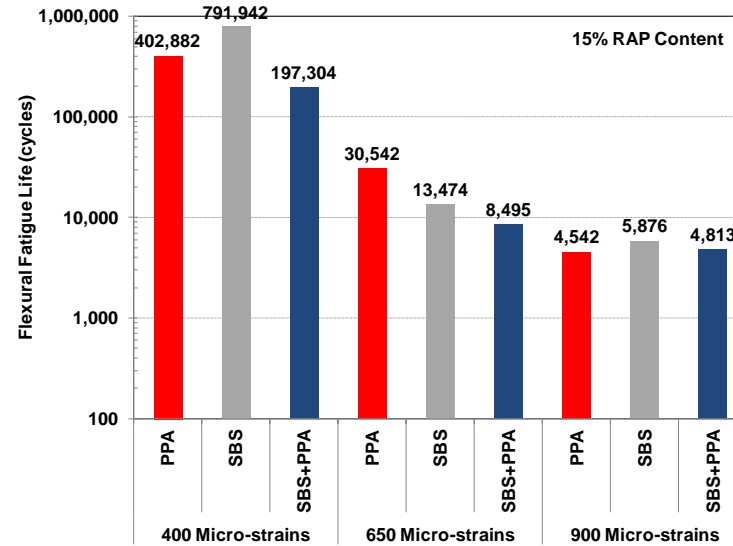
#### 4.4 Potential for Moisture Induced Damage (AASHTO T283)

Moisture damage potential was assessed using the Tensile Strength Ratio (TSR) methodology as outlined in AASHTO T283, *Resistance of Compacted Hot Mix Asphalt (HMA) to Moisture-Induced Damage*. Specimens were compacted between 6.5 and 7.5% air voids and conditioned in accordance to Section 10 of AASHTO T283. The TSR test results are shown in Table 3.

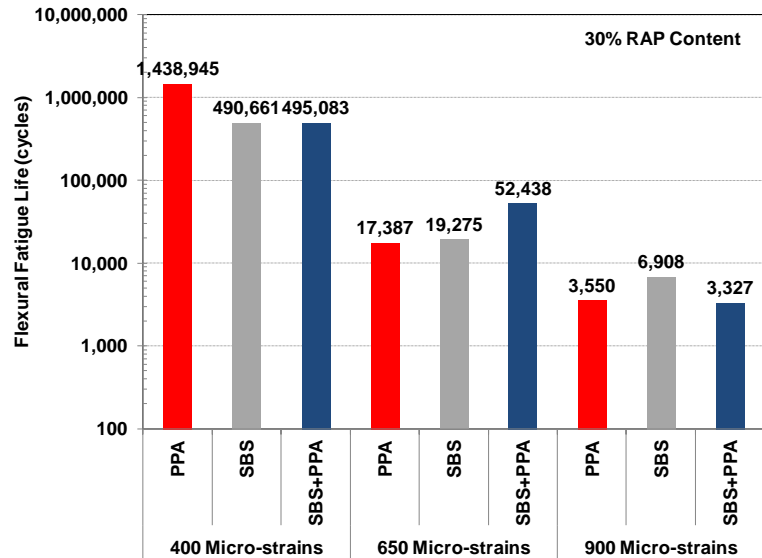
In comparing to the virgin mixes, when the bitumen binder was modified with PPA, the TSR value was over 100%, indicating the material was resistant to moisture damage even after the environmental conditioning took place. On average, the addition of the laboratory manufactured RAP generally increased in the dry and wet tensile strength 75% over the virgin SBS modified mixture, which was used as the base mixture blended with the laboratory manufactured RAP. In all cases, except for the 15% PPA RAP, the TSR values were above the 80% generally recommended by state agencies.



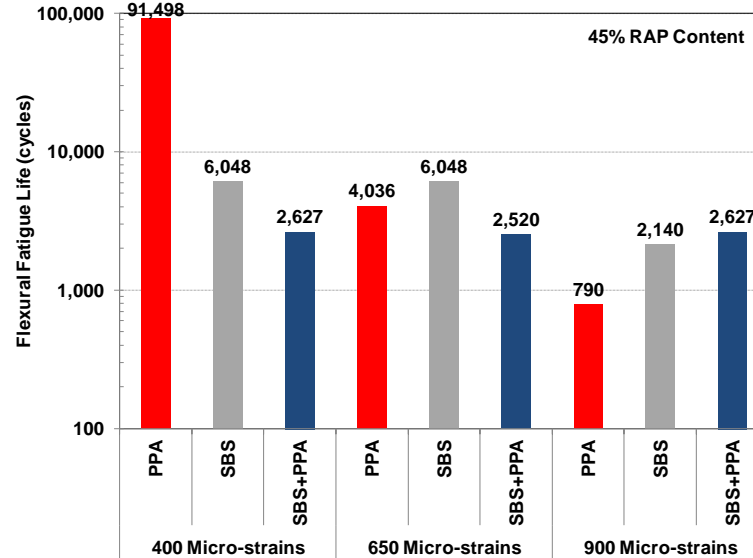
(a)



(b)



(c)



(d)

Figure 7: Flexural Beam Fatigue Result

**Table 3: Tensile Strength Ratio (TSR) Results**

Specimen Type	RAP Content	Average Air Voids (%)	Indirect Tensile Strength		Average TSR (%)
			Dry	Conditioned	
SBS Modified	Virgin	6.8	209.4	193.5	92.4%
SBS Modified RAP	15% RAP	6.5	290.1	241.0	83.0%
	30% RAP	6.6	280.2	281.0	100.3%
	45% RAP	6.5	278.2	261.3	93.9%
SBS-PPA Modified	Virgin	6.5	200.5	191.6	95.5%
SBS-PPA Modified RAP	15% RAP	6.6	253.3	258.5	102.1%
	30% RAP	6.6	289.8	262.7	90.6%
	45% RAP	6.6	270.9	237.3	87.6%
PPA Modified	Virgin	6.6	162.9	164.7	101.1%
PPA Modified RAP	15% RAP	6.5	260.0	187.9	72.3%
	30% RAP	6.6	279.6	255.4	91.3%
	45% RAP	6.7	330.4	347.8	105.3%

## 5. SUMMARY AND CONCLUSIONS

A research effort was undertaken to evaluate how bitumen binder modification, with and without Polyphosphoric Acid, influenced the performance properties of RAP mixtures. The RAP was produced in the laboratory using three different modified binders, each produced to achieve a PG76-22, while using an identical job mix formula. The research results showed that:

- The laboratory procedure used in the study generated RAP that had PG grades representative of typical RAP found in New Jersey.
- Larger differences between the dynamic modulus master curves were found for the short-term oven aged (STOA) when compared to the long term oven aged (LTOA) specimens. This would indicate that the as the bitumen mixtures age, they generally converge to have similar stiffness properties when the bitumen binder grade and mixture volumetrics are similar. This may also be the case with higher RAP contents. For the STOA mixtures, the 45% RAP specimens achieved similar modulus values while at lower RAP percentages, the dynamic modulus of the mixtures were not as similar. The Aging Ratio values also indicated that the mixtures with RAP did not age to the degree of the virgin mixes.
- As the RAP content increased, the modulus values of the mixtures increased. However, the magnitude of the increased modulus was greater at the higher test temperatures than the lower temperatures.
- The flow number values measured from the repeated load tests were generally consistent and comparable when comparing the virgin and RAP at identical RAP contents.
- The flexural beam fatigue results indicated that as the RAP content increased to 30%, the general fatigue resistance increased as well at the lower microstrain levels (i.e. – 400 microstrains). Meanwhile, the flexural fatigue results were similar at the higher strain levels. The PPA modified bitumen exhibiting the highest fatigue resistance at this strain level. The fatigue results drastically dropped for all strain levels when using 45% RAP.
- Tensile Strength Ratio (TSR) values for the virgin and RAP mixes were all found to be acceptable with respect to a majority of state agency specifications (> 80%). However, there was one specimen in the testing, 15% PPA RAP, was considered an outlier in the study.
- The test results provided indicate that both SBS and PPA bitumen binder, even at a high content of 2.25%wt, modifications provide similar bitumen mixture performance in both the virgin mixes, as well as the mixtures containing RAP.
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