THE EFFECT OF PROCESSING CONDITIONS ON THE PERFORMANCE OF HYBRID (SBS+PPA) MODIFIED BINDERS

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ABSTRACT

A study was conducted to characterize the performance of asphalt binders modified with a combination of SBS polymer and Polyphosphoric Acid (PPA). The first portion of this study investigated the impact of processing variables such as Blending Time and Temperature. The effect of PPA on cross link efficiency of SBS modified binder was also studied. High temperature performance was determined using the PG grading parameter (G/sinδ) as well as the parameters (Jnr and % recovery) from the newly developed MSCR test. It was found that in all cases the addition of PPA significantly improved the elastic response of the binder for a given non-recoverable compliance, as measured by the MSCR test. The G*/sinδ values were found to be less sensitive to processing variables than the MSCR parameters. Particularly notable was the finding that addition of PPA enhanced the efficiency of the cross-linker. Three Hybrid blends were selected for further studies on the effect of reduced polymer content on fatigue properties of hot-mix asphalt. In general it was found that under optimum processing conditions the addition of PPA increased the efficiency of SBS modification allowing us to produce modified binders with up to 1% lower polymer loadings without sacrificing fatigue performance. This paper summarizes the findings from this research on Hybrid (SBS+PPA) modified asphalt binders.*

Keywords: polyphosphoric acid, ppa, polymer, sbs, hybrid, mscr

The Effect of PPA on SBS Type, Content, and Crude Source in Modified Bitumen

INTRODUCTION

Polyphosphoric acid (PPA) is increasingly being used as a modifier for asphalt binders. One of its popular uses is to formulate '*hybrid*' binders in which Styrene-Butadiene-Styrene polymer is used in conjunction with PPA to obtain modified asphalt binders. These *hybrid* binders use less SBS without significant loss, and sometimes with significant gain, in performance as compared to similar performing SBS-only modified binders. Little was known about the effect of SBS type, content, and crude source of base binders used during formulation of *hybrid* binders on their performance properties. Base asphalt binders (PG 58-28) from two crude sources were used in conjunction with two types of SBS polymers to produce modified binders. The two SBS types used were SBS D1101 and the newly introduced SBS MD 0243, both from Kraton Polymers. Dr. Vonk of Kraton Polymers describes the new MD0243 SBS as follows, (1):

"A new class of Styrenic Block co-polymers with elevated vinyl content is available that offer significant improvements over standard SBS (e.g D1101). The molecules are shorter than standard SBS of equivalent molecular weight and thus provide better compatibility and lower blend viscosity. These polymers react more readily with bitumen components thus accelerating the compatibilization rate. Evidence that these reactions called grafting of bitumen and polymer molecules takes place has been generated using GPC separation technique with UV detection at the unusual wavelength of 450nm".

The MD0243 has relatively a higher di-block composition and lower viscosity, allowing its use at relatively higher concentration (>7%) in asphalts, whereas, the D1101 polymer is the classic linear SBS polymer that requires high shear mixing and is normally used at lower concentration levels (<4%), (K1). The PPA content was kept constant at 0.8%. The objective was to study the effect of PPA modification on the physical properties of the modified binders, including PG grading, PG Plus, and MSCR properties. The PG and PG Plus grading are part of the Superpave™ specifications long used for bitumen, primarily in the US (AASHTO M320). MSCR stands for Multiple Stress Creep Recovery and is a relatively new approach for bitumen grading. More specifically, this study evaluates the effect of PPA on the efficiency of the SBS type and content. This paper summarizes the effects of PPA modification on the performance related properties of *hybrid* asphalt binders.

BACKGROUND

Processing Conditions

In a previous study, it was shown that performance properties of *hybrid* asphalt binders (SBS-PPA) depend on processing conditions (formulation variables), (2). The most sensitive among them may be listed as blending time and temperature and base asphalt binder compatibility. For this study the blending time was selected to be 6 h at high shear (LR4 Silverson Mixer) and the blending temperature was set at 200°C. These are typical conditions used in laboratory evaluation, (2). In addition to PG grading test, properties measured using elastic recovery test and the new Multiple Stress Creep and Recovery Test (MSCR) were also considered in this research, [3,4,5].

The MSCR Test

The MSCR test is a creep and recovery test that is conducted using a DSR and parallel plate geometry, (5). The test protocol requires a creep load of 1 second duration followed by recovery at zero load maintained for 9 seconds. The loading levels for this study were varied from 0.025 kPa to 25.6 kPa (0.025, 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 kPa) creep stress levels. All *hybrid* asphalt binder samples were aged in the RTFO oven prior to MSCR testing. Ten cycles of creep and recovery are applied at each stress level. A 1 mm gap is used in 25.0 mm parallel plate geometry to perform this test. The determination of the non-recoverable creep compliance Jnr and the % recovery are described in detail in the ASTM or AASHTO standards (see ref. 1 and 2). The MSCR test and related research has been previously described in detail elsewhere, [6, 7]. A key parameter of the MSCR test is the non-recoverable creep compliance, or J_{nr}. It is a measure of the strain build up that remains after the cycles of stress/relaxation are applied. J_{nr} can characterize the stress dependence of polymer modified as well as neat asphalt binders and is a relatively more discriminating specification parameter.

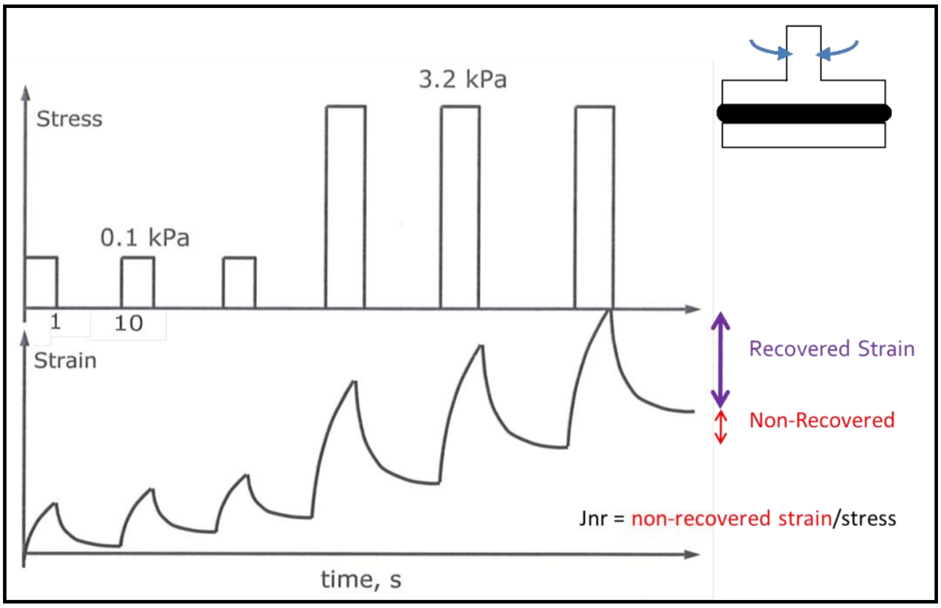

Figure 1: The Newly Developed MSCR Test Method Schematic.

LITERATURE REVIEW

The performance of PPA modified asphalt binders in general has been a subject of several recent studies. Arnold et al. found that the stiffening effect of the PPA modification is binder source dependent, (8). Bennert et al., have shown that lower SBS contents when used with PPA does not adversely affect the fatigue properties of the hot-mix asphalt, (9). In April 2009 a workshop on the use and performance of PPA in asphalt binders was held in Minneapolis MN, (10). The following finding emerged at the conclusion of the workshop:

> The new Table 3 PG binder specification (AASHTO M320 Table 3) is blind to modification and it works well as a purchase specification even when PPA is the modifier. However, to ensure that PPA does not react adversely with other ingredients that go in a hot mix asphalt (HMA or warm mix asphalt (WMA)), performance tests on the end product - which may be HMA or WMA - is essential.

The newly developed MSCR test is very sensitive to formulation of polymer modified binders in general. D'Angelo and Dongre have recently shown that performance of PPA and SBS modified binders may be highly dependent on formulation variables, (11). However, they only showed limited data directly concerning PPA+SBS *hybrid* binders. The suppliers of modified binders (with or without PPA) are reluctant to fully disclose the formulation details of their product. Therefore, the effect of various formulation related variables on the performance of modified asphalt binder with PPA is largely unknown.

The effect of formulation variables such as blending time, blending temperature, cross-linker content and PPA in modified asphalt binders has been reported elsewhere (5). What is still needed is to establish the effect of PPA modification on the SBS type and content. In other words, this study attempts to answer the question: "Can the efficiency of SBS be enhanced (reduction in SBS content without loss of performance properties) by addition of PPA to SBS modified binders?" The main objective of this study was to quantify the beneficial effects of PPA addition to SBS modified asphalt binders. In this study, the effect of SBS type, SBS content, and Crude source of the base asphalt were evaluated using performance related properties of *hybrid* asphalt binders.

OBJECTIVE

The objective of this study was to determine the effect of PPA modification on:

1. SBS type and content
2. Base binder crude source
3. Effect on physical properties
    a. Traditional tests versus MSCR test

METHODOLOGY

The methodology may be summarized as follows: PG 58-28 grade binders refined from three different crude sources were selected for this study. The PPA content was kept constant at 0.8% of the base binder. This content was selected because previous research has shown that this is the optimum PPA content that has shown optimum benefit for asphalt modification (6). Two SBS types were used to modify the base binder: 1) SBS D1101 and 2) SBS MD 0243, which were both supplied by Kraton Polymers. Two levels of polymer content were used: 1) 2.0% and 2) 3.0% of the base binder. The blends were made with and without cross-linking with elemental sulphur. The amount of cross-linker needed was determined by using 0.02 % Sulphur per percent of polymer used. The blending time was selected to be 6 h at high shear (LR4 Silverson Mixer) and the blending temperature was set at 200°C.

Traditional tests such as PG grading (AASHTO M320 Table 1), Elastic Recovery (UDOT Std. Test method), Separation using the DSR, and the newly developed MSCR test were conducted in this study (3,4,5). Table 1 presents the experiment design used for the blend optimization study. Hot-mix Fatigue testing was also done using the Bending Beam Fatigue Device (BBF).

Table 1: Experiment Design Used in the SBS Type and Content Study.

Base Binder PG 58-28 - Sources	**Paramount Petroleum, BP, and NuStar Energy**				
SBS (Kraton) Type	**MD243**		**D1101**		**none**
PPA Content, %	0.8	none	0.8	none	0.8
SBS Content, %	2	3	2	3	none
Cross-Linking, sulfur, %	none	none	0.04	0.06	none
MSCR, % recovery @ 3.2 kPa, 64°C	√	√	√	√	√
MSCR, J_{nr} at 3.2 kPA and 64°C, 1/kPa	√	√	√	√	√
Elastic Recovery @ 25 °C, %	√	√	√	√	√
PG Grade	√	√	√	√	√
Continuous Grade	√	√	√	√	√
Separation, % Diff Top & Bot G*/sinδ	none	none	√	√	none

RESULTS AND DISCUSSION

Effect of Crude Source

Tables 2, 3, and 4 show the results of PPA modification of PG 58-28 binders made from different crude sources. Table 2 shows the effect of PPA modification on PG 58-28 made from Alaska North Slope crude used by Paramount Petroleum. It is clear from the table that this binder is highly reactive to PPA. Let us first consider the traditional test properties. The ER values show significant improvement with addition of 0.8% PPA. The PG high temperature grade is also enhanced without significantly affecting the low temperature grade. The MSCR properties also show remarkable improvement for the systems with PPA, with *lower* J_{nr} and *higher* percent recovery values throughout. The percent separation is also lowered indicating a better dispersed D1101 SBS when PPA is present. In all cases the improvement is at a lower SBS level showing enhanced efficacy of the polymer in presence of PPA. Table 3 shows similar data for the PG 58-28 binder made from Whiting crude source (BP). In this case, however, the impact of PPA modification is more modest.

Table 4 shows data on PG 58-28 made from Bachaquero crude (NuStar – Venezuelan crude). Here once again the improvements due to PPA modification are significant. Separation results are also improved showing enhanced dispersion of the MD243 polymer in this case.

Table 2: **Effect of PPA Modification on Paramount PG 58-28 Binder.**

Base Binder PG 58-28	**Paramount**				
SBS (Kraton) Type	**MD243**		**D1101**		**none**
PPA Content, %	0.8	none	0.8	none	0.8
SBS Content, %	2	3	2	3	none
Cross-Linking, sulfur, %	none	none	0.04	0.06	none
MSCR, % recovery @ 3.2 kPa, 64°C	74.6	45.7	64.0	39.0	4.2
MSCR, J_{nr} at 3.2 kPA and 64°C, 1/kPa	0.07	0.43	0.18	0.93	2.17
Elastic Recovery @ 25 °C, %	68.5	75.5	71.3	81.6	7
PG Grade	70-28	70-22	76-28	70-28	64-28
Continuous Grade	72.8-28.8	71.8-27.3	81.3-29.4	71.2-28.1	69.2-29.44
Separation, % Diff Top & Bot G*/sinδ			1.3	5.2	

Table 3: Effect of PPA Modification on BP PG 58-28 Binder.

Base Binder - PG 58-28	**BP**				
SBS (Kraton) Type	**MD243**		**D1101**		**none**
PPA Content, %	0.8	none	0.8	none	0.8
SBS Content, %	2	3	2	3	none
Cross-Linking, sulfur, %	none	none	0.04	0.06	none
MSCR, % recovery @ 3.2 kPa, 64°C	51.0	41.2	48.7	32.0	0.4
MSCR, J_{nr} at 3.2 kPA and 64°C, 1/kPa	0.33	0.51	0.63	1.32	4.47
Elastic Recovery @ 25 °C, %	73.0	77.5	76.3	82.5	1
PG Grade	70-28	70-28	70-28	64-22	64-28
Continuous Grade	71.7-29.3	70.9-28.0	73.4 - 29.17	69.8-27.9	64.1-30.38
Separation, % Diff Top & Bot G*/sinδ		0.00	0.9	3.3	0.5

Table 4: Effect of PPA Modification on NuStar Energy PG 58-28 Binder.

Base Binder - PG 58-28	**Nustar**				
SBS (Kraton) Type	**MD243**		**D1101**		**none**
PPA Content, %	0.8	none	0.8	none	0.8
SBS Content, %	2	3	2	3	none
Cross-Linking, sulfur, %	none	none	0.04	0.06	none
MSCR, % recovery @ 3.2 kPa, 64°C	58.0	29.0	63.3	16.0	2.1
MSCR, J_{nr} at 3.2 kPA and 64°C, 1/kPa	0.21	0.95	0.20	1.75	3.34
Elastic Recovery @ 25 °C, %	65	68.8	83.5	63.8	4
PG Grade	76-28	70-28	76-28	70-28	64-28
Continuous Grade	79.2-30.83	72.8-29.98	77.0-31.9	71.2-31.49	67.2-30.86
Separation, % Diff Top & Bot G*/sinδ	2	5.6			

The efficacy of PPA modification is clearly evident in Figures 2 to 4. The effect of PPA on the cross-linking efficiency is also borne out by this data analysis using the new proposed specification. Note that when PPA is not present all blends fail to exceed the proposed MSCR specification curve (see Table 5) which would indicate failing the PG 64H-XX grade for these blends. The cross-linked blends at both blend temperatures just clear the curve and hence may be classified as PG 64H-XX. The blends made with 0.5% PPA, on the other hand, would exceed PG 64V-XX. This gives formulators another option when making a polymer modified asphalt trial blend to meet a certain specification.

Figures 2 to 4 also suggest that one may be able to reduce polymer content to obtain certain grades for any given traffic level (also see Table 5). Figures 2 to 4 show the MSCR data obtained on these reduced polymer blends plotted with the proposed new MSCR specification. It was found that it is possible to reduce the polymer content by as much as 0.66% and still be able to meet or exceed the properties of the polymer modified asphalt binder that was formulated without using PPA. Note that the gains obtained using PPA have two sources. One is the stiffness increase obtained as a result of addition of 0.5% PPA while the other is the increased efficiency of polymer network creation that PPA addition seems to impart to a SBS modified asphalt binder.

Table 5: The Proposed New High Temperature PG Grade Designations for a PG 64-XX Grade.

New PG Grade Designation	MSCR Jnr Parameter Value	Design Traffic Level
PG 64S-XX	Less than or Equal to 4.0	Standard (S)
PG 64H-XX	Less than or Equal to 2.0	Heavy (H)
PG 64V-XX	Less than or Equal to 1.0	Very Heavy (VH)

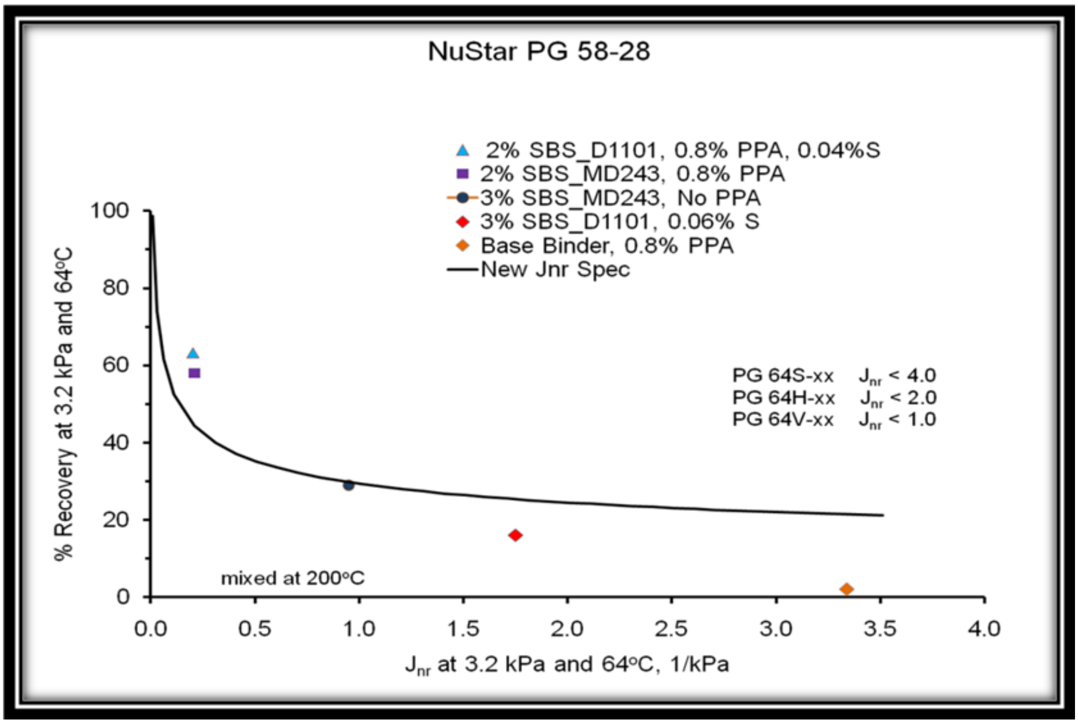

Figure 2: Effect of Polymer Content reduction on the Newly Proposed MSCR based High Temperature PG Grade for the Bachaquero Crude Source (NuStar).

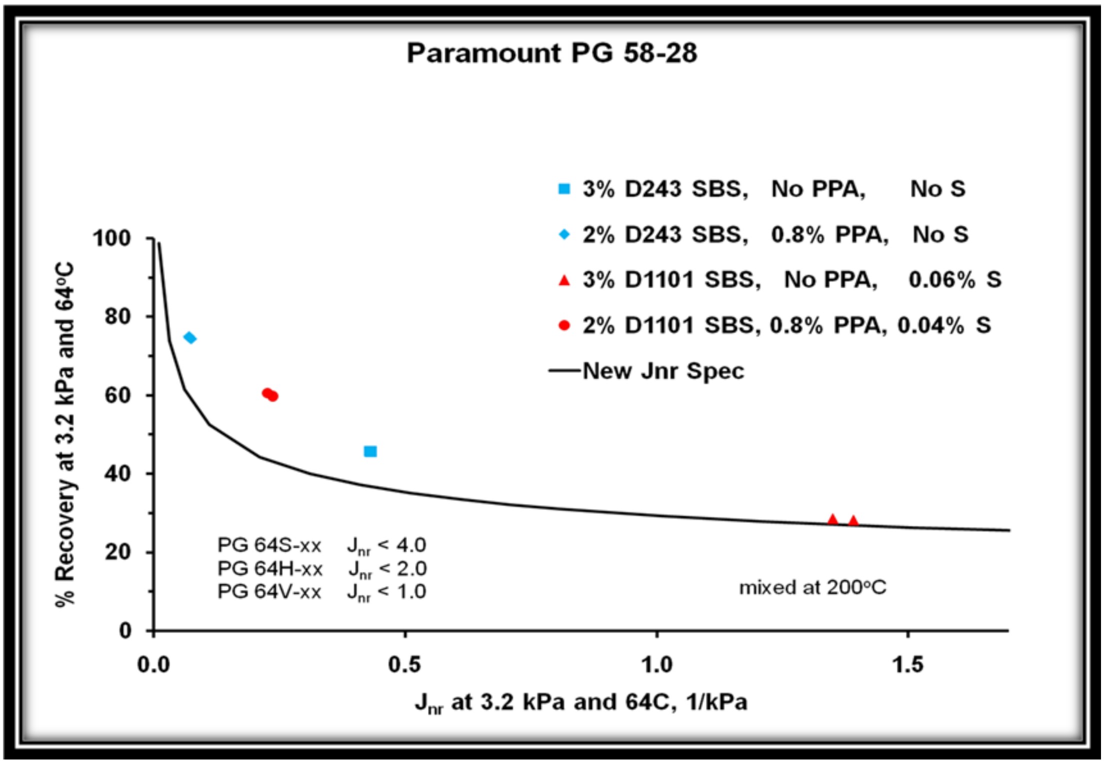

Figure 3: Effect of Polymer Content reduction on the Newly Proposed MSCR based High Temperature PG Grade for the Alaska North Slope Crude Source (Paramount).

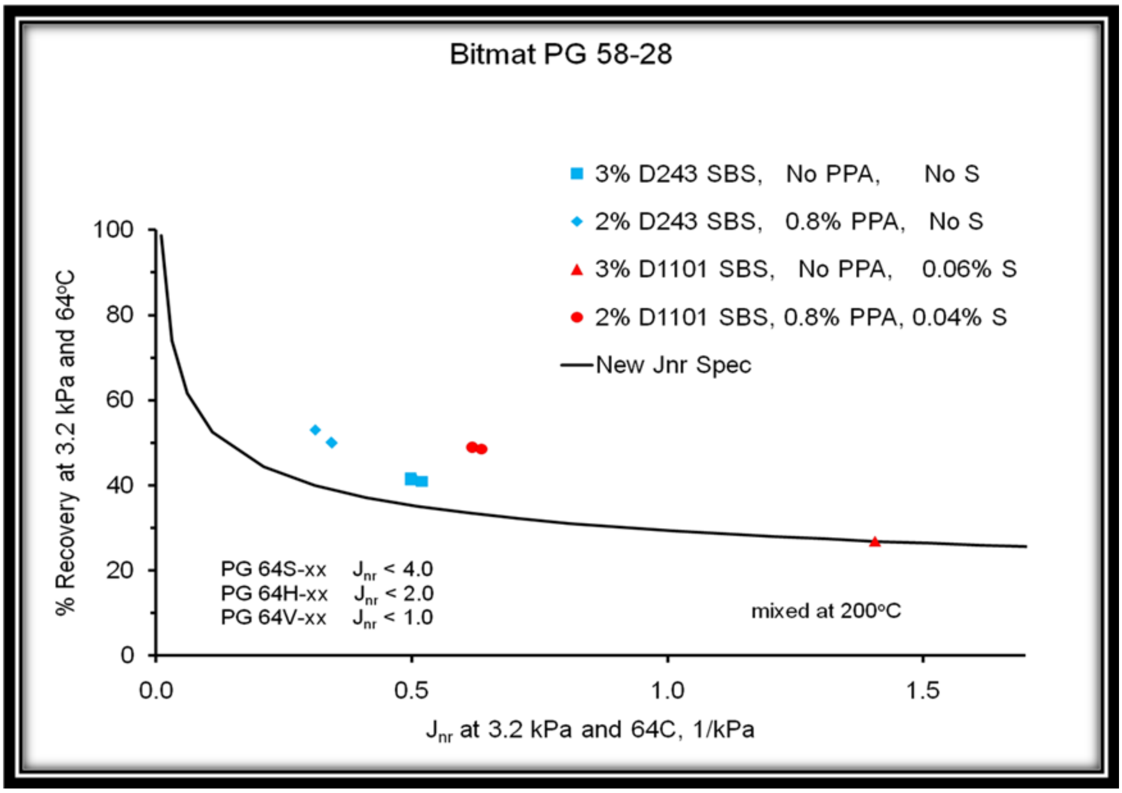

Figure 4: Effect of Polymer Content reduction on the Newly Proposed MSCR based High Temperature PG Grade for the Whiting Crude Source (BP).

We were also concerned about any detrimental effect of polymer reduction on fatigue properties for the formulations with reduced polymer content. To determine this, a strain control fatigue study was undertaken using Bending Beam Fatigue (BBF) test (AASHTO T 321), (12). Three blends were selected and modified as shown in Table 6. The term "Dump & Stir" used in Table 6 refers to PMBs made by simply dumping the polymer and stirring it without any optimization. Hot-mixes were made from these blends and tested using the BBF device after long term oven aging (LTOA). Figure 5 shows the results of the Fatigue study.

It was found that there is no significant change in fatigue resistance due to a reduction in polymer content from 4.0 to 3.0% as shown in Figure 5. This finding is corroborated by earlier finding by Bennert et al., where they found that two PG 76-22 asphalt binders one made using PPA and reduced polymer and another just using polymer did not show significant degradation in fatigue resistance as measured by BBF device (see ref. 9).

Table 6: Experiment Design to Study the Effect of Reduced Polymer Content on the Fatigue Resistance of Hot-Mix Asphalt.

Blend ID	Polymer Content (SBS), %	Blend Temperature °C	Blend Time h	Base Asphalt	PPA Level %	Cross-Linking
Blend 1 – Dump & Stir	4.00	188	2	NuStar PG 58-28	0.5	Yes (0.06% Elemental Sulfur)
Blend 2 – Optimized	3.00	200	6			
Blend 3 – No Cross-Link	2.33	200	6			No

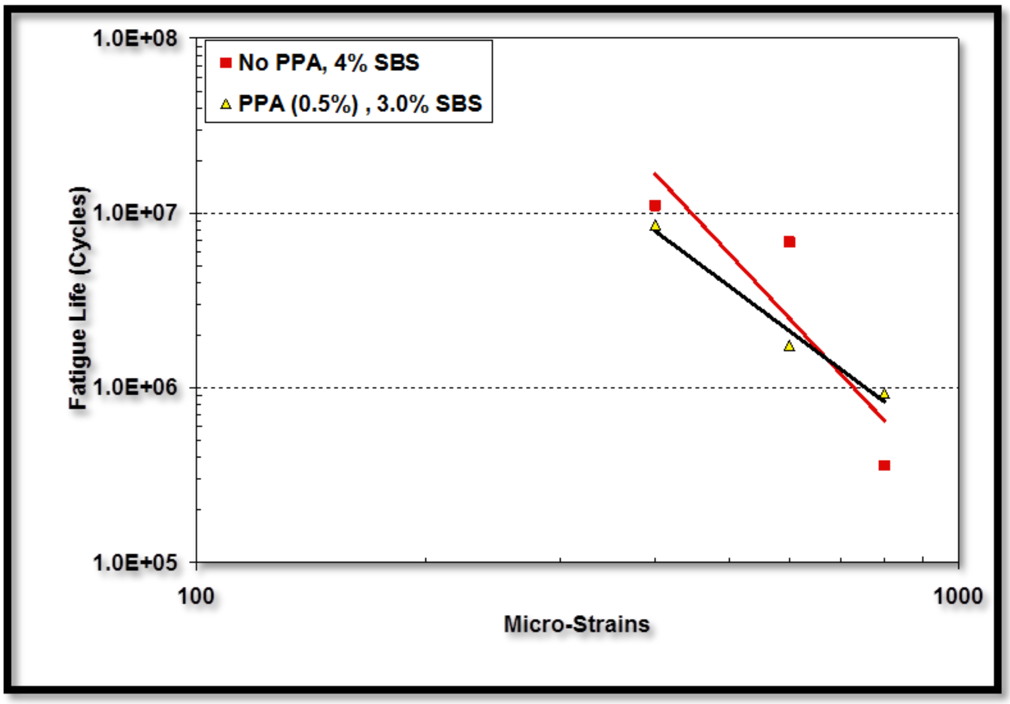

Figure 5: Effect of Polymer Content Reduction on the Fatigue Resistance of Hot-Mix Asphalt.

Elastic Recovery versus MSCR

The Elastic Recovery (ER) test method was primarily designed to indicate the absence or presence of elastomeric polymers such as SBS. The higher the cross-linking in a polymer modified binder (PMB) the better the ER value. However, the ER value is not as sensitive to the formulation variables as is the new and more fundamental MSCR test. Figure 6 shows the comparison between the ER % recovery value and the MSCR %recovery value at 3.2 kPa stress level. Both tests were performed on RTFO aged materials. Note that the lack of correlation is across the three crude sources tested.

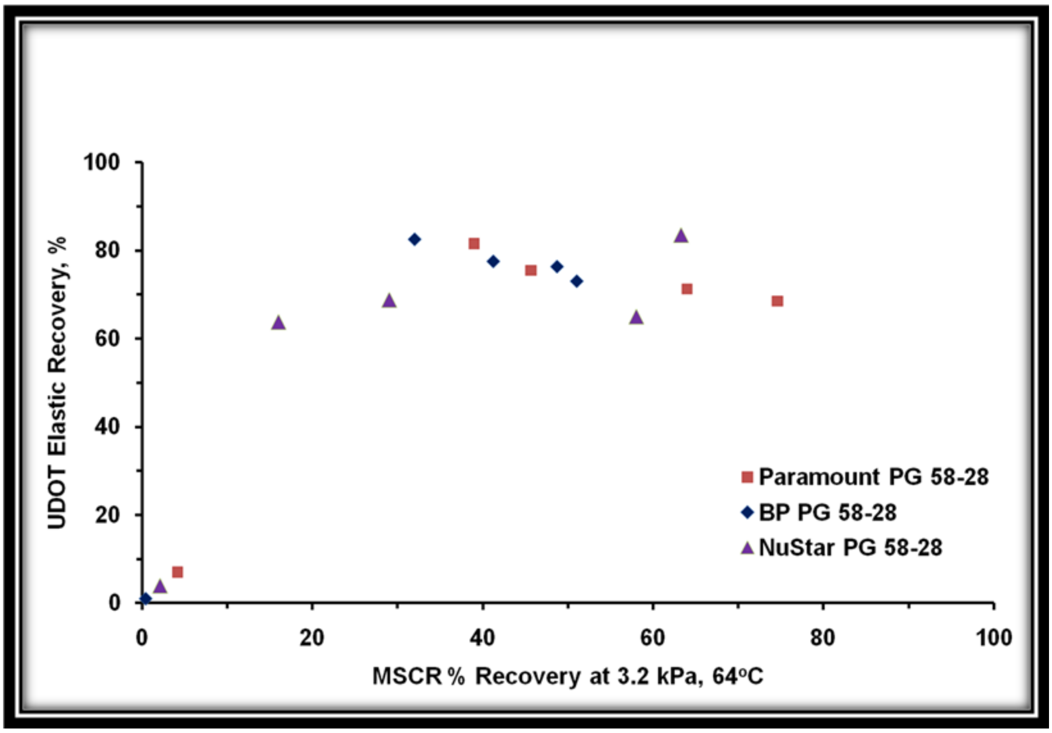

Figure 6: Relationship Between ER Value and MSCR %Recovery Value.

CONCLUSIONS

The following conclusions may be drawn from this study:

1. Effect on AASHTO Table 3 related properties.
2. PPA by itself reduces strain which implies improved high-temperature performance (MSCR Test).
3. PPA in combination with a low level of SBS results in improved strain recovery (MSCR Test).
4. MSCR test data shows that PPA + Polymer (*hybrid* Binders) is better than either alone.
5. Current PG grading parameters and ER values are not highly sensitive to the improved performance related properties of *hybrid* Binders.
6. MSCR parameters are highly sensitive and discriminate between well formulated (optimized and normal 'dump and stir' PMA binders.

Use of PPA also allows the formulator to:

1. Reduce polymer level thereby reducing overall costs of producing *hybrid* binder without significantly affecting, and frequently improving, performance.
2. Reduce blending time and temperature thereby reducing energy costs.

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