

CORRELATION OF POLYMER MODIFICATION TO MECHANICAL PROPERTIES OF BINDERS

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ABSTRACT

There is a need to identify a mechanical parameter measured from standardized test that is sensitive to polymer modification of binder. Presence of such parameters would enable an empirical evaluation of the impact of modification of the binder on mixture and eventually on pavement performance. Superpave specifications were primarily designed for neat binders. Researchers have determined that the tests specified in Superpave are not suitable for characterization of polymer modified binders. Asphalts modified with different polymers can behave very differently even when they have the same performance grade, as determined by the Superpave specifications. The objective of this study is to correlate the different quantities of polymer modification to mechanical properties of the binder. In this study, the amount of modification was measured in terms of absorbance as measured by Fourier Transform Infrared Spectrometer. The absorbance was correlated to non-recoverable creep compliance and $G^\sin(\delta)$ for different types of polymers and at different polymer concentration. The information about the chemical composition of different polymer modified binder and how a particular chemical component modifies or affects a particular mechanical property of the binder, can help the asphalt manufacturer in developing the most cost effective product to meet the specifications.*

Keywords: polymer, modified, binder, non-recoverable compliance

1. INTRODUCTION

1.1 Background

Currently, the Superpave Performance Grade (PG) binder specification, AASHTO M-320, is used throughout the United States to grade asphalt binders (*D'Angelo 2009*). This asphalt binder specification was derived as part of a Strategic Highway Research Program (SHRP) project and was based primarily on the study of neat asphalt binders with no polymer additives. The applicability of this specification to the polymer modified asphalt binders has long raised concerns from both industry and state highway agencies. The challenges with the Superpave high temperature specification parameter in Table 1 of AASHTO-M320, $G^*/\sin \delta$, to correctly grade the superior field performance of modified asphalt binders have been demonstrated by several researchers (*D'Angelo 2009*). Therefore, as a replacement for the existing high temperature binder test ($G^*/\sin \delta$), the FHWA and the Asphalt Binder Expert Task Group developed the multiple stress creep and recovery (MSCR) test. This test is used to characterize the asphalt binder high temperature properties at which the pavement performs in the field, referred to as the environmental use temperatures. As such, many state DOTs have implemented additional tests called Superpave PG Plus or SHRP Plus tests in an attempt to ensure that a modifier is included in the binder. The SHRP Plus tests do not relate to performance but only indicate the presence of a particular modifier in the binder.

At present, the state of New Jersey requires the use of styrene-butadiene or styrene-butadiene-styrene (SBS) formulations. In light of the polymer shortages circa 2008, the New Jersey Department of Transportation (NJ DOT) would like to broaden the options for use of polymers and rubbers in the binder. Before NJ DOT can allow the use of other modifiers, there is a need to first determine whether parameters such as non-recoverable creep compliance (J_{nr}) and the recoveries determined from MSCR and elastic recovery (ER) are sensitive to the polymer or rubber modification of the binder.

Table 1: Traffic Grading Based on J_{nr} Values

RTFO DSR			
J_{nr} (3.2 kPa)	T (°C)	Traffic	ESAL
≤ 4.0	64	Standard (S)	<10 million
≤ 2.0	64	Heavy (H)	10-30 million
≤ 1.0	64	Very Heavy (V)	>30 million
≤ 0.5	64	Extremely Heavy (E)	>30 million and standing traffic

1.2 Goal

The goal of the study is to gain a better understanding and to quantify the performance of different polymer modified binders under standard Superpave, PG Plus, and MSCR tests.

1.3 Significance Of Study

The study will assist in determining how a certain modification, such as ethylene terpolymer, styrene-Butadiene-styrene, or Polyphosphoric acid (PPA), is sensitive to parameters that were measured from these test methods. The results from the study will allow industry to progress in identifying appropriate test methods or parameters for characterizing polymer modified binders.

1.4 Research Approach

The research approach to achieve the stated goal consists of:

1. Conducting Superpave tests and determining the continuous grade of binder.
2. Conducting MSCR at PG grade temperature of the base binder, and ER test at 25°C

3. Conducting analysis to identify parameters that can be potentially considered for binder specifications.
4. A) Correlating recovery from MSCR with ER.
B) Correlating phase angle with recovery from MSCR and ER.

2. LITERATURE REVIEW

The polymers used for bitumen modification are divided into two groups, namely elastomers and plastomers (Airey 2003). Approximately 75% of modified binders are classified as elastomers, 15% as plastomers, and 10% either rubber or miscellaneously modified (Airey 2003). Elastomers used in bitumen modification are SBS, natural rubber, reclaimed tire rubber/crumb rubber, polybutadiene, polyisoprene, isobutene isoprene copolymer, polychloroprene, and styrene butadiene rubber (SBR) (Airey 2003). In the elastomeric group, styrenic block copolymers like SBS have shown greatest potential when blended with bitumen. The polymers that are classified as plastomers or thermoplastics are ethyl-vinyl-acetate (EVA), polyvinyl chloride (PVC), ethylene propylene (EPDM), ethylene acrylate copolymer, and ethylene butyl acrylate (EBA) (Airey 2003).

SBS is mechanically dispersed in the molten asphalt under high shear for modification. The degree of SBS modification is a function of bitumen source, bitumen-polymer compatibility, crude source, polymer chemistry, and polymer concentration, with the higher polymer concentrations in high aromatic content bitumen producing a highly elastic network which increases the viscosity, complex modulus, and elastic response of the PMA (Polymer Modified Asphalt) especially at high service temperatures (Sengoz 2007).

Some SBS modification increases softening point and viscosity, which indicates increased stiffness of the PMA's. The high viscosity causes the mixing, laying and compaction of the mixture to be more difficult (Polacco 2006). Lu et al. (1998) observed that SBS polymers improved low-temperature properties of bitumen. The degree of improvement increased with SBS content and was influenced slightly by SBS structure.

According to Gonzalez et al. (2004), polyethylene and EVA are good modifiers to improve permanent deformation and thermal cracking. According to AASHTO T315, the temperature at which $G^*/\sin\delta = 1$ implies that this is the maximum temperature where the binder can have a good viscoelastic performance on the pavement. In their study, the maximum temperature, where $G^*/\sin\delta = 1$, was improved when copolymers of EVA were used as a modifier thus giving good results. The maximum temperature was even better, giving best results, with 3% of recycled EVA mixed with pure bitumen. A decrease in stiffness of binder at low temperatures is desirable as it avoids cracking but a high stiffness is beneficial at high temperatures to avoid viscous flow of the binder.

3. TESTING METHODS

Asphalt binders are required to meet current Superpave binder specifications (AASHTO M-320 2001). The Superpave Performance Grade (PG) system focuses on climatic effects, construction, aging (during construction and in-service), traffic speed, and traffic volume. The behavior of asphalt binders depends on temperature, time of loading, and aging and properties related to pavement performance are based on rheology. Tests used in PG specifications are Rotational Viscosity (RV) for construction (workability), Dynamic Shear Rheometer (DSR) for rutting and fatigue, and Bending Beam Rheometer (BBR) for thermal cracking.

Superpave Performance Grade (PG), AASHTO M-320, specifications used today to categorize asphalt binders are based on unmodified asphalt binders. AASHTO M-320 includes original DSR, RTFO DSR, PAV DSR, BBR, and RV. Since the introduction of polymer modifiers, Superpave PG grade has not been able to adequately characterize the performance of modified binders in the field. In response to this challenge, most states have employed Superpave Plus tests to ensure the presence of polymer modification. Superpave Plus tests may include Elastic Recovery (ER) ASTM D113-86, Force Ductility AASHTO T-300, and Multiple Stress Creep Recovery (MSCR), developed by FHWA. The NJ DOT currently uses ER.

3.1 Multiple Stress Creep Recovery

MSCR may potentially be able to provide a solution to address issues with the ER test and the DSR test for rutting analysis. DSR uses the AASHTO M-320 specification $G^*/\sin(\delta)$ to correlate rutting resistance. AASHTO M-320 is based on homogeneous, isotropic binders that include particles less than 0.25 mm in diameter that perform in the linear viscoelastic region. This is problematic because rutting is a plastic (nonlinear) deformation of pavement material. The parameters of MSCR are % recovery and non-recoverable creep compliance (J_{nr}). J_{nr} is equal to the non-recoverable shear strain divided by the applied shear stress. The MSCR test uses RTFO-aged binders run on the DSR machine. The test is performed by applying a shear stress of 0.1 kPa for one second and releasing the load (recovery) for nine seconds over 10 cycles, followed by the same procedure using a shear stress of 3.2 kPa (Figure 1). The cyclic loading at different stress levels describes properties of the binder in the nonlinear region.

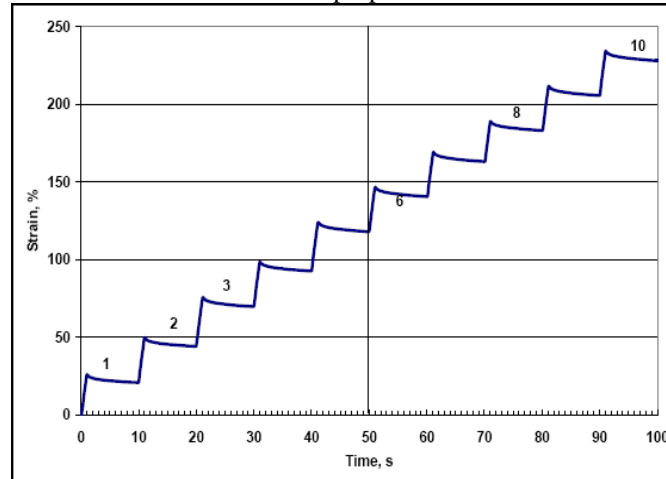


Figure 1: Typical MSCR Test Plot (AASHTO TP70, 2001)

3.2 MSCR Traffic Grading

After completing MSCR testing of numerous binders, each binder could then be classified for traffic grading. Using the RDSR results at 64°C, various binders were labeled as PG 64X. The X would be replaced by an E, V, H, or S, which symbolizes traffic levels of extremely heavy, very heavy, heavy or standard traffic respectively. In order to meet the criteria for the different traffic grades, Table 1 was generated and presents the J_{nr} that corresponds to the level of traffic loading.

3.3 Elastic Recovery

Elastic Recovery is performed using a brass mold to form an asphalt binder briquette that is submerged in a 25°C water bath and connected to an elongation device. The ER procedure includes elongating specimens to 20 cm, cutting at the midpoint of the binder specimen, and observing the percent recovery obtained.

4. MIXING STUDY

A polymer mixing study was initiated to better understand the relationship between polymer type and concentration to the various PG Plus specifications. The sensitivity of these tests (MSCR, Elastic Recovery, Force Ductility, and DSR phase angle) to polymer type and concentration could be understood if we could control these parameters. The authors adopted a procedure provided by Refinery 1 Energy for blending SBS. The author acknowledges that this particular mixing procedure is not universal and may be different depending on polymer type. The procedure used for creating the mixes is detailed below:

1. Heat a quart of the chosen base binder to 190°C,
2. Begin high shear mixer and maintain 2500-3500 rpm,
3. Begin slowly adding the polymer (no more than 5g/min) after 20 minutes,

4. Continue mixing for two hours Once all the polymer is added and maintain the temperature at 190°C at a speed near 3000 rpm, and
5. Run an original DSR, if this is the only modifier being added, to find the grade of the binder.

If PPA is also being added, follow steps 6 through 8

6. Add PPA and continue mixing for 30 minutes, maintaining the temperature at 190°C and a speed around 3000 rpm,
7. Run an original DSR, then cover the can loosely and place in an oven at 163°C overnight, and
8. Test the sample using original DSR at the target temperature grade. If this is more than 3% different than the first DSR results, put sample back in the oven and continue testing at 30 minutes intervals until there is a difference of less than 3%.

5. EXPERIMENTAL DESIGN

The experimental design, Table 2, consists of a number of Superpave, PG Plus, and MSCR tests. The X's indicate the number of replicates completed for each test. The material tested in the laboratory consisted of unmodified base binders (Refinery 1 PG 64-22, Refinery 4 (R4) 937 PG 64-22, and Refinery 1 70-22). Modified binders were mixed in-house and obtained from refineries such as Refinery 1 (R1), Refinery 2 (R2), and Refinery 3 (R3), as well as some from unknown sources. Those from unknown sources are labeled with their PG grade and a characteristic name. Binders of the same PG grade from the same refinery but different tanks were tested separately.

Table 2: Binder Tests & Sources (X: Number of Replicates)

Binder	Source	AASHTO M-320	ER	MSCR
R1 64-22	Refinery 1	XX	XX	
R1 70-22	Refinery 1	XX	XX	XX
Kraton R1 BD	Refinery 1	XX	XX	XX
R1 76-22	Refinery 1	XX	XX	XX
R1 76-22 Tank 1007	Refinery 1	XX	XX	XX
R2 76-22	Refinery 2	XX	XX	XX
R3 76-28	Refinery 3	XX	XX	XX
R1 82-22	Refinery 1	XX	XX	
R1 82-22 Tank 73	Refinery 1	XX	XX	XX
R1 Stavola	Refinery 1	XX	XX	XX
CRM v=2900	NJDOT	XX	XX	
CRM v=3200	NJDOT	XX	XX	XX
R4 937, 1.5% K	In-House	XX	XX	XX
R1 64-22, 1.5% E, 0.8% PPA	In-House	XX	XX	XX
R1 64-22, 1.5% E	In-House	XX	XX	
R1 64-22, 2.5% E	In-House	XX	XX	XX
R1 64-22, 5% E	In-House	XX		XX
R1 64, 1% K	In-House	XX		XX

R1 64, 1.5% K	In-House	XX	XX	
R1 64, 2% K	In-House	XX		
R1 64, 3% K	In-House	XX	XX	XX
R1 64, 4.5% K	In-House	XX	XX	XX
R1 64, 5% K	In-House	XX	XX	XX
R1 64, 7% K	In-House	XX	XX	XX

Three binders modified with rubbers were included in this group: the crumb rubber with viscosity of 2900 Pa-s, the crumb rubber with viscosity of 3200 Pa-s, and the Refinery 1 Stavola. Two bridgedecks were also included: the Refinery 1 bridgedeck using SBS polymer as a modifier, and the R3 76-28. The twelve binders that make up the end of the table were all mixed in-house as part of a mixing study. Only one of these mixes was created from Refinery 4 937, the rest began as Refinery 1 PG 64-22. The three polymer modifiers used were SBS D1101 (SBS), ethylene terpolymer (RET), and PPA (polyphosphoric acid).

The binders were evaluated at the test temperature of the base binder grade that they were modified from. All experiments followed a controlled single mixing methodology. All of the in-house modified binders were made by adding polymers to PG 64-22. However, in the cases of modified binders that were obtained directly from the refineries, the Performance Grades of base binders were not known.

6. RESULTS

6.1 Multiple Stress Creep Recovery

In order for binders to be considered for research purposes, they must have two acceptable test replicates. A total of 26 binders were included in this document, 12 of which were mixed in-house. The experimental plan is tabulated in Table 3 along with the traffic grade for the binders tested.

Table 3 Modified Performance Grading of Binder Based on AASHTO MP19

Binder	J_{nr} (1/kPa) (3.2 kPa)	PG 64-YY
R1 70-22	0.05	Extreme (E)
Kraton R1 BD	0.01	Extreme (E)
R1 76-22	0.18	Extreme (E)
R1 76-22 TANK 1007	0.53	Very Heavy (V)
R2 76-22	0.11	Extreme (E)
R3 76-28	0.07	Extreme (E)
76-28 Rt 295	0.23	Extreme (E)
R1 82-22 Tank 73	0.13	Extreme (E)
R1 Stavola	0.13	Extreme (E)
CRM $v=3200$	0.09	Extreme (E)
R4 937, K	3.31	Standard (S)
R1 64-22, 1.5% E, 0.8% PPA	0.34	Extreme (E)

R1 64-22, 1.5% E	1.18	Heavy (H)
R1 64-22, 2.5% E	1.16	Heavy (H)
R1 64-22, 5% E	0.63	Very Heavy (V)
R1 64, 1.5% K	1.49	Heavy (H)
R1 64, 3% K	0.75	Very Heavy (V)
R1 64, 4.5% K	0.33	Extreme (E)
R1 64, 5% K	0.63	Very Heavy (V)
R1 64, 7% K	0.29	Extreme (E)
76-22 3/10/10	0.35	Extreme (E)

6.2 Non-Recoverable Compliance, Elastic Recovery, and Percent Recovery Data

Figure 3 shows the non-recoverable compliance for similar performance grades of binder. At a performance grade of 70°C, all binders had a J_{nr} between 1.00 and 1.50. Similarly, for binders with a Performance Grade of 82°C, the binders fell between a J_{nr} of 0.00 and 0.50. From this, it is evident that binders are characterized relatively equally using J_{nr} results and Performance Grade. J_{nr} also decreased as the performance grade of a binder was increased.

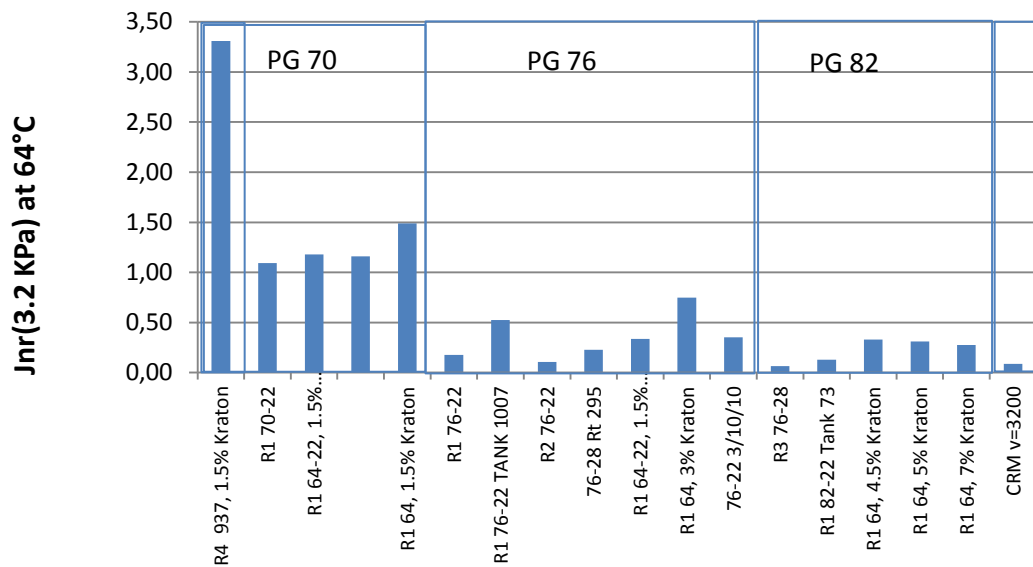


Figure 2: J_{nr} (3.2 kPa) at 64°C

Figure 4 shows the Elastic Recovery results and the data indicates that as the Performance Grade increased, the Elastic Recovery generally increased. However, at higher Performance Grades, binder properties did not vary regardless of the base binder or polymer percentage.

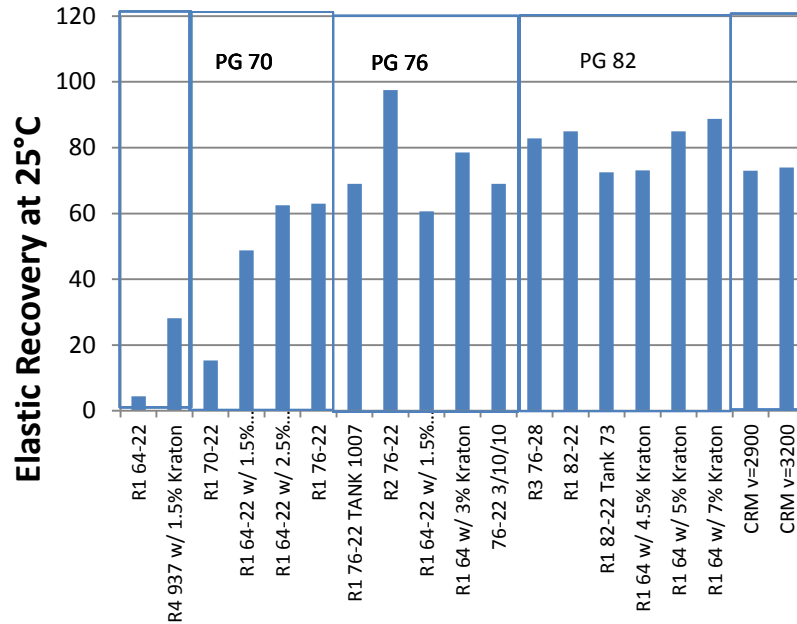


Figure 3: Elastic Recovery at 25°C

7. ANALYSIS

7.1 Effect of Polymer Modification

The addition of a polymer, at different percentages, had an effect on the Elastic Recovery of the binder. As seen with R1 64-22, with the addition of Kraton polymer from zero to 3%, there was a steady increase in Elastic Recovery as shown in Figure 8.

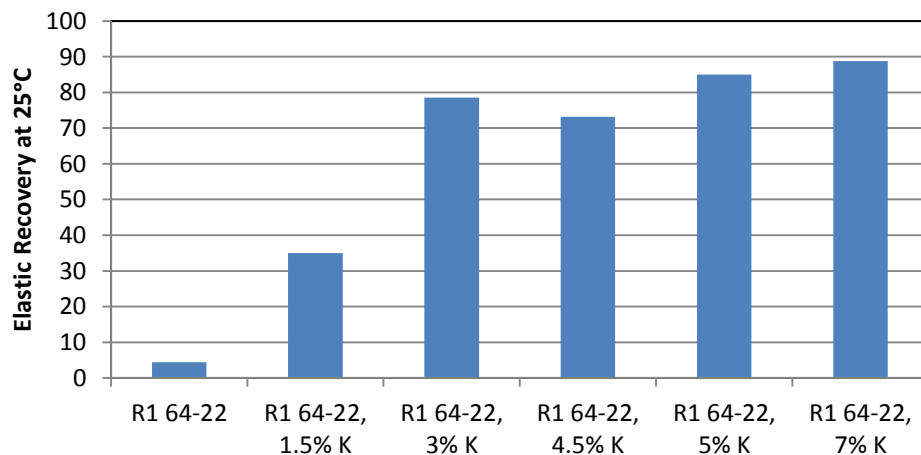


Figure 4: Elastic Recovery at 25°C for Kraton Modified Binders

However, once the polymer level reached 3% Kraton, the Elastic Recovery remained relatively constant all the way to 7% Kraton. There was actually a drop in Elastic Recovery from 3% to 4.5% Kraton. Finally, it seems that ER does not adequately characterize the effects of the addition of PPA. The R1 64-22 with 1.5% Elvaloy increased in Elastic Recovery as the polymer percentage increased to 2.5% as shown in Figure 9.

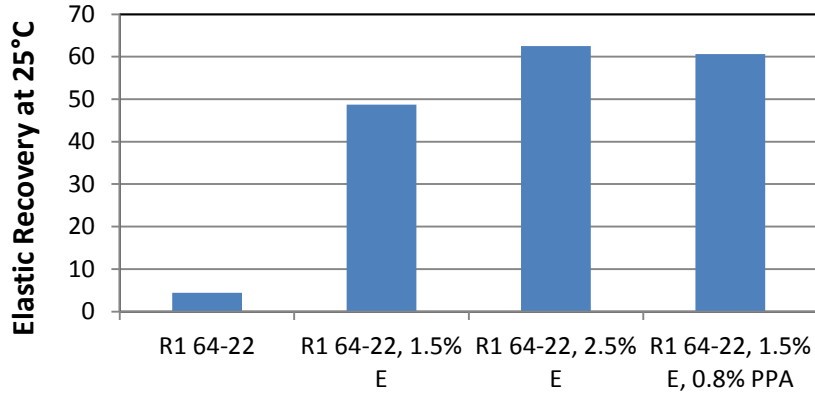


Figure 5: Elastic Recovery at 25°C for Elvaloy and PPA Modified Binders

Once the 0.8% PPA was added to the 1.5% Elvaloy, the Performance Grade increased, however the Elastic Recovery decreased in comparison to the R1 64-22 with 2.5% Elvaloy. The percent recovery showed a much greater variation within a Performance Grade when compared to the Elastic Recovery. As Figure 10 shows, the percent recovery did not consistently increase as the Performance Grade increased; however, there was a large variation of percent recovery within a Performance Grade.

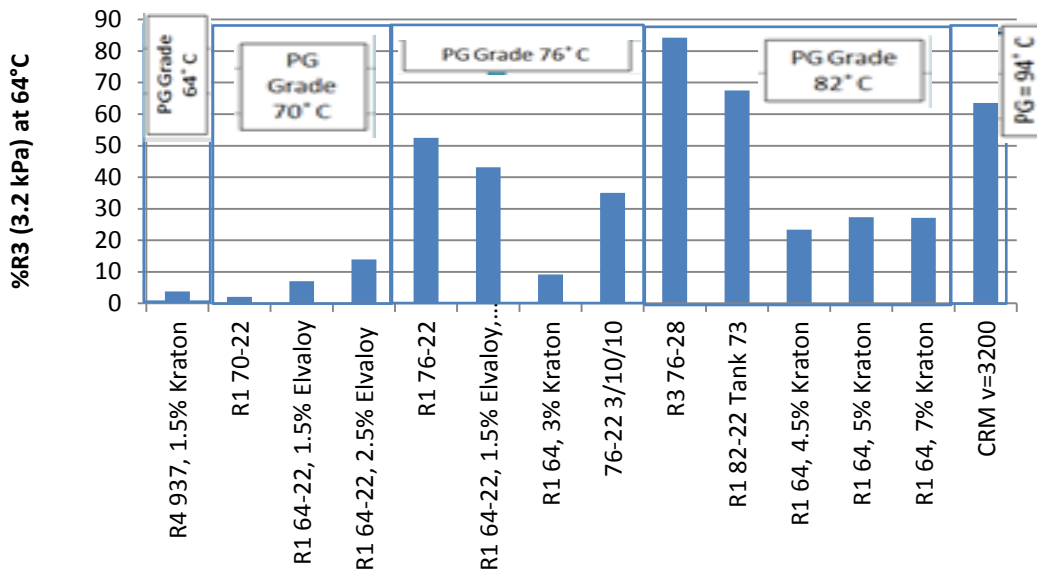


Figure 6: Percent Recovery from MSCR at 64°C

The addition of the 0.8% PPA to the R1 64-22 with 1.5% Elvaloy is better characterized when examining %Re measured from MSCR. As Figure 11 indicates, the percent recovery increased in this circumstance compared to the R1 64-22 with only 1.5 and 2.5% Elvaloy.

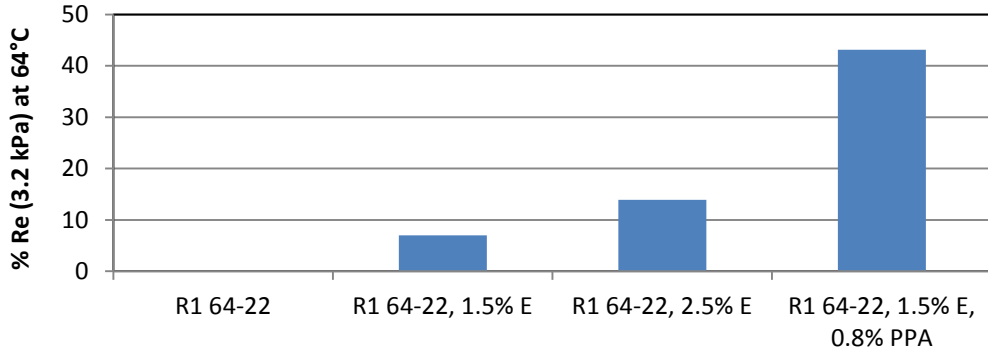


Figure7: Percent Recovery at 64°C for Elvaloy and PPA Modified Binders

The percent recovery from MSCR increased with the addition of the 0.8% PPA, which is consistent with the trend of increase in the Performance Grade of the binders. The trend is accurate when examining R1 64-22 with various percentages of Kraton. As the percentage is increased from 0 to 3%, the Performance Grade jumps two temperature levels and the percent recovery increases. The Performance Grade once again increased from 3 to 4.5% Kraton, but only by one temperature level. At the high Performance Grade of 82°C, the polymer did not elevate to another temperature level, as shown with the increase of 4.5 to 7% Kraton. With the same binders, percent recovery remained relatively constant after it was increased from the 3% modification as shown in Figure 12.

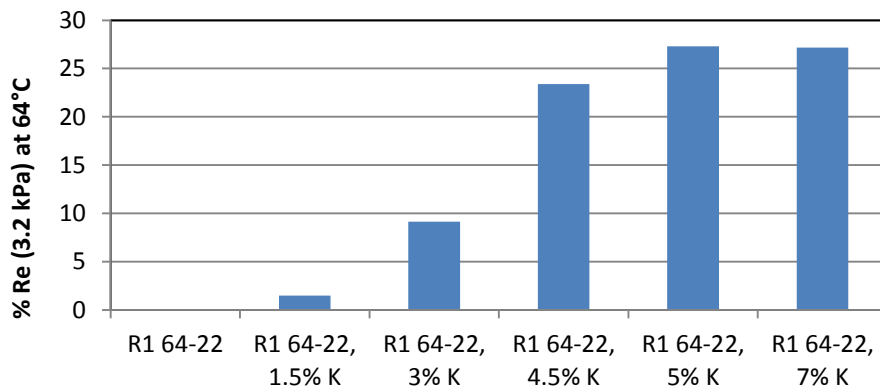


Figure 8: Percent Recovery at 64°C for Kraton Modified Binders

The data imply that at a certain concentration of polymer, there appears to be a plateau in both Performance Grade and effect of additional polymer. The base binders of Refinery 1 and R2 also yielded dramatically different %Re at the Performance Grade of 76°C. The recovery for the R1 76-22 was much less than the recovery of R2 76-22; this was also apparent when examining ER results. A notable difference between the Elastic Recovery results and percent recovery results is the variation within a Performance Grade. As previously mentioned, ER was relatively constant in each Performance Grade. However, percent recovery from MSCR showed significant differences within each Performance Grade.

8. SUMMARY OF FINDINGS

The summary of findings based on the study conducted to date follows:

1. MSCR parameters were more sensitive than Elastic Recovery. MSCR revealed J_{nr} and percent recovery differences within Performance Grades.
2. Binders that passed the Elastic Recovery criterion of 60% for NJ DOT did not necessarily show that elastic response is generated primarily from elastomers.
3. Phase angle at 64°C decreased with decreasing J_{nr} .

4. The binders that exhibited forty percent recovery or greater appeared to be above the MSCR recovery curve. The same binders also passed the phase angle criterion of 75°C that exists in much of the southeastern U.S.
5. Binders that have low percent recovery at the 64°C temperature, appear to also have decreasing recoveries in relation to an increasing J_{nr} .
6. Binders appeared to be stiffer {high $G^*/\sin(\delta)$ } at low strains, but a similar effect was not observed in J_{nr} .

9. CONCLUSIONS

The conclusions based on the summary of findings are as follows:

1. The percent recovery from MSCR appears to be more sensitive to binder modification, such as PPA, than the elastic recovery at 25°C.
2. The continuous high temperature grade and phase angle are not sensitive to the non-recoverable creep compliance.
3. Polymer modified binders of similar grades are performing differently in MSCR tests. This is largely attributed to Superpave being performed at lower strains.
4. The influence of polymer modification on binder properties was dependent on the properties of the base binder.
5. The percent recovery parameter from MSCR appears to rank consistently with the phase angle. It also appeared to be consistent with the MSCR curve.
6. The percent recovery from MSCR along with non-recoverable compliance has the potential of being used as specification for polymer modified binders.

10. ACKNOWLEDGEMENTS

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