



University Transportation Research Center - Region 2

# Final Report

## Impact of Polymer Modification on Mechanical and Viscoelastic Properties

Performing Organization: Rowan University

October 2015



Sponsor:  
University Transportation Research Center - Region 2

## University Transportation Research Center - Region 2

The Region 2 University Transportation Research Center (UTRC) is one of ten original University Transportation Centers established in 1987 by the U.S. Congress. These Centers were established with the recognition that transportation plays a key role in the nation's economy and the quality of life of its citizens. University faculty members provide a critical link in resolving our national and regional transportation problems while training the professionals who address our transportation systems and their customers on a daily basis.

The UTRC was established in order to support research, education and the transfer of technology in the field of transportation. The theme of the Center is "Planning and Managing Regional Transportation Systems in a Changing World." Presently, under the direction of Dr. Camille Kamga, the UTRC represents USDOT Region II, including New York, New Jersey, Puerto Rico and the U.S. Virgin Islands. Functioning as a consortium of twelve major Universities throughout the region, UTRC is located at the CUNY Institute for Transportation Systems at The City College of New York, the lead institution of the consortium. The Center, through its consortium, an Agency-Industry Council and its Director and Staff, supports research, education, and technology transfer under its theme. UTRC's three main goals are:

### Research

The research program objectives are (1) to develop a theme based transportation research program that is responsive to the needs of regional transportation organizations and stakeholders, and (2) to conduct that program in cooperation with the partners. The program includes both studies that are identified with research partners of projects targeted to the theme, and targeted, short-term projects. The program develops competitive proposals, which are evaluated to insure the most responsive UTRC team conducts the work. The research program is responsive to the UTRC theme: "Planning and Managing Regional Transportation Systems in a Changing World." The complex transportation system of transit and infrastructure, and the rapidly changing environment impacts the nation's largest city and metropolitan area. The New York/New Jersey Metropolitan has over 19 million people, 600,000 businesses and 9 million workers. The Region's intermodal and multimodal systems must serve all customers and stakeholders within the region and globally. Under the current grant, the new research projects and the ongoing research projects concentrate the program efforts on the categories of Transportation Systems Performance and Information Infrastructure to provide needed services to the New Jersey Department of Transportation, New York City Department of Transportation, New York Metropolitan Transportation Council, New York State Department of Transportation, and the New York State Energy and Research Development Authority and others, all while enhancing the center's theme.

### Education and Workforce Development

The modern professional must combine the technical skills of engineering and planning with knowledge of economics, environmental science, management, finance, and law as well as negotiation skills, psychology and sociology. And, she/he must be computer literate, wired to the web, and knowledgeable about advances in information technology. UTRC's education and training efforts provide a multidisciplinary program of course work and experiential learning to train students and provide advanced training or retraining of practitioners to plan and manage regional transportation systems. UTRC must meet the need to educate the undergraduate and graduate student with a foundation of transportation fundamentals that allows for solving complex problems in a world much more dynamic than even a decade ago. Simultaneously, the demand for continuing education is growing – either because of professional license requirements or because the workplace demands it – and provides the opportunity to combine State of Practice education with tailored ways of delivering content.

### Technology Transfer

UTRC's Technology Transfer Program goes beyond what might be considered "traditional" technology transfer activities. Its main objectives are (1) to increase the awareness and level of information concerning transportation issues facing Region 2; (2) to improve the knowledge base and approach to problem solving of the region's transportation workforce, from those operating the systems to those at the most senior level of managing the system; and by doing so, to improve the overall professional capability of the transportation workforce; (3) to stimulate discussion and debate concerning the integration of new technologies into our culture, our work and our transportation systems; (4) to provide the more traditional but extremely important job of disseminating research and project reports, studies, analysis and use of tools to the education, research and practicing community both nationally and internationally; and (5) to provide unbiased information and testimony to decision-makers concerning regional transportation issues consistent with the UTRC theme.

### Project No(s):

UTRC/RF Grant No: 49198-24-26

**Project Date:** October 7, 2015

**Project Title:** Impact of Polymer Modification on Mechanical and Viscoelastic Properties

### Project's Website:

<http://www.utrc2.org/research/projects/impact-polymer-modification>

### Principal Investigator(s):

#### Dr. Yusuf A. Mehta

Professor, Department of Civil and Environmental Engineering  
Director, Center for research and Education in Advanced Transportation Engineering Systems (CREATEs)  
Rowan University  
Glassboro, NJ 08028  
Phone: (856) 256-5327  
Email: Mehta@rowan.edu

### Co-PI(s):

#### Ayman W. Ali, Ph.D.

Research Assistant Professor  
Department of Civil and Environmental Engineering  
Glassboro, NJ 08028  
Phone: (856) 256-5396  
E-mail: alia@rowan.edu

### Performing Organization:

Rowan University

### Sponsor:

- University Transportation Research Center (UTRC)

To request a hard copy of our final reports, please send us an email at [utrc@utrc2.org](mailto:utrc@utrc2.org)

### Mailing Address:

University Transportation Research Center  
The City College of New York  
Marshak Hall, Suite 910  
160 Convent Avenue  
New York, NY 10031  
Tel: 212-650-8051  
Fax: 212-650-8374  
Web: [www.utrc2.org](http://www.utrc2.org)

## Board of Directors

The UTRC Board of Directors consists of one or two members from each Consortium school (each school receives two votes regardless of the number of representatives on the board). The Center Director is an ex-officio member of the Board and The Center management team serves as staff to the Board.

### City University of New York

*Dr. Hongmian Gong - Geography*  
*Dr. Neville A. Parker - Civil Engineering*

### Clarkson University

*Dr. Kerop D. Janoyan - Civil Engineering*

### Columbia University

*Dr. Raimondo Betti - Civil Engineering*  
*Dr. Elliott Sclar - Urban and Regional Planning*

### Cornell University

*Dr. Huaizhu (Oliver) Gao - Civil Engineering*  
*Dr. Mark A. Turnquist - Civil Engineering*

### Hofstra University

*Dr. Jean-Paul Rodrigue - Global Studies and Geography*

### Manhattan College

*Dr. Anirban De - Civil & Environmental Engineering*  
*Dominic Esposito - Research Administration*

### New Jersey Institute of Technology

*Dr. Steven Chien - Civil Engineering*  
*Dr. Joyoung Lee - Civil & Environmental Engineering*

### New York Institute of Technology

*Dr. Nada Marie Anid - Engineering & Computing Sciences*  
*Dr. Marta Panero - Engineering & Computing Sciences*

### New York University

*Dr. Mitchell L. Moss - Urban Policy and Planning*  
*Dr. Rae Zimmerman - Planning and Public Administration*

### Polytechnic Institute of NYU

*Dr. John C. Falcocchio - Civil Engineering*  
*Dr. Kaan Ozbay - Civil Engineering*

### Rensselaer Polytechnic Institute

*Dr. José Holguín-Veras - Civil Engineering*  
*Dr. William "Al" Wallace - Systems Engineering*

### Rochester Institute of Technology

*Dr. J. Scott Hawker - Software Engineering*  
*Dr. James Winebrake - Science, Technology, & Society/Public Policy*

### Rowan University

*Dr. Yusuf Mehta - Civil Engineering*  
*Dr. Beena Sukumaran - Civil Engineering*

### Rutgers University

*Dr. Robert Noland - Planning and Public Policy*

### State University of New York

*Michael M. Fancher - Nanoscience*  
*Dr. Catherine T. Lawson - City & Regional Planning*  
*Dr. Adel W. Sadek - Transportation Systems Engineering*  
*Dr. Shmuel Yahalom - Economics*

### Stevens Institute of Technology

*Dr. Sophia Hassiotis - Civil Engineering*  
*Dr. Thomas H. Wakeman III - Civil Engineering*

### Syracuse University

*Dr. Riyad S. Aboutaha - Civil Engineering*  
*Dr. O. Sam Salem - Construction Engineering and Management*

### The College of New Jersey

*Dr. Thomas M. Brennan Jr. - Civil Engineering*

### University of Puerto Rico - Mayagüez

*Dr. Ismael Pagán-Trinidad - Civil Engineering*  
*Dr. Didier M. Valdés-Díaz - Civil Engineering*

## UTRC Consortium Universities

The following universities/colleges are members of the UTRC consortium.

City University of New York (CUNY)  
Clarkson University (Clarkson)  
Columbia University (Columbia)  
Cornell University (Cornell)  
Hofstra University (Hofstra)  
Manhattan College  
New Jersey Institute of Technology (NJIT)  
New York Institute of Technology (NYIT)  
New York University (NYU)  
Polytechnic Institute of NYU (Poly)  
Rensselaer Polytechnic Institute (RPI)  
Rochester Institute of Technology (RIT)  
Rowan University (Rowan)  
Rutgers University (Rutgers)\*  
State University of New York (SUNY)  
Stevens Institute of Technology (Stevens)  
Syracuse University (SU)  
The College of New Jersey (TCNJ)  
University of Puerto Rico - Mayagüez (UPRM)

*\* Member under SAFETEA-LU Legislation*

## UTRC Key Staff

**Dr. Camille Kamga:** *Director, UTRC*  
*Assistant Professor of Civil Engineering, CCNY*

**Dr. Robert E. Paaswell:** *Director Emeritus of UTRC and Distinguished Professor of Civil Engineering, The City College of New York*

**Herbert Levinson:** *UTRC Icon Mentor, Transportation Consultant and Professor Emeritus of Transportation*

**Dr. Ellen Thorson:** *Senior Research Fellow*

**Penny Eickemeyer:** *Associate Director for Research, UTRC*

**Dr. Alison Conway:** *Associate Director for New Initiatives and Assistant Professor of Civil Engineering*

**Nadia Aslam:** *Assistant Director for Technology Transfer*

**Dr. Wei Hao:** *Post-doc/ Researcher*

**Nathalie Martinez:** *Research Associate/Budget Analyst*

**Tierra Fisher:** *Office Assistant*

## **Disclaimer**

The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the information presented herein. The contents do not necessarily reflect the official views or policies of the UTRC or the Federal Highway Administration. This report does not constitute a standard, specification or regulation. This document is disseminated under the sponsorship of the Department of Transportation, University Transportation Centers Program, in the interest of information exchange. The U.S. Government assumes no liability for the contents or use thereof.

1. Report No.	2. Government Accession No. UTRC	3. Recipient's Catalog No.	
4. Title and Subtitle <b>Impact of Polymer Modification on Mechanical and Viscoelastic Properties of Binders and Hot Mix Asphalt</b>		5. Report Date 07 October 2015	
		6. Performing Organization Code	
7. Author(s) Ali, Ayman & Mehta, Yusuf		8. Performing Organization Report No.	
9. Performing Organization Name and Address Rowan University 200 Mullica Hill Rd Glassboro NJ, 08028		10. Work Unit No.	
		11. Contract or Grant No. 49198-24-26	
12. Sponsoring Agency Name and Address University Transportation Research Center The City College of New York 160 Convent Avenue, New York, NY 10031		13. Type of Report and Period Covered	
		14. Sponsoring Agency Code	
15. Supplementary Notes			
<p>16. Abstract</p> <p>This study was initiated with the aim of evaluating the relative impact of different cross-linking agents on the rheological and morphological properties of polymer modified asphalt binders (PMAs). To complete this objective, two cross-linking agents (an aromatic oil and silicon oxide) were selected for evaluations. The cross-linking agents were then added to a styrene-butadiene-styrene (SBS) polymer modified binder (virgin PG 70-22) at different dosages. The selected cross-linking dosages were 2 and 4% by weight of virgin binder. The SBS, virgin binder, and cross-linking agents were mixed together for 90 minutes using a high shear mixer. The morphology of the modified binder was then tested using a florescent microscope and the rheological properties were evaluated using the dynamic shear rheometer (DSR) to determine the dynamic shear modulus values at different temperatures (i.e., 70°C and 76°C) and the multiple stress creep recovery (MSCR) properties of these binders. Based on the results obtained, it was found out that the addition of the Aromatic Oil agent might result in increasing the potential for rutting, decreasing the potential for low temperature cracking, and helps in improving the interlocking between the polymer modifier and the neat binder. It can also be concluded that the addition of the silicon oxide cross-linking agent to PMAs might have positive impact on rutting resistance without any adverse effects on low temperature cracking. Also, the addition of silicon oxide did not affect the morphology of PMAs. Furthermore, the collected results showed that the MSCR testing procedure is more capable at characterizing the properties of PMAs than can the traditional DSR test.</p>			
17. Key Words Binder, cross-linking, polymer modifier, DSR, MSCR		18. Distribution Statement	
19. Security Classif. (of this report)  Unclassified	20. Security Classif. (of this page)  Unclassified	21. No of Pages	22. Price

## TABLE OF CONTENTS

EXECUTIVE SUMMARY.....	4
BACKGROUND .....	5
OBJECTIVES.....	6
MATERIALS DESCRIPTION .....	6
POLYMER, BINDER, AND CROSS-LINKING AGENT BLENDING .....	7
Statistical Analysis .....	16
CONCLUSIONS.....	17
REFERENCES.....	18

## LIST OF FIGURES

Figure 1: Dynamic Shear Rheometer Binder Shear Modulus: (a) testing temperature of 70°C and (b) testing temperature of 76°C. ....	11
Figure 2: Multiple Stress Creep Recovery Testing Results: (a) Non-Recoverable Creep Compliance and (b) % Recovery. ....	12
Figure 3: Fluorescent Microscopy Images Obtained for the Different Binder, Polymer Modifier, and Cross-Linking Agents Combinations.....	14

## LIST OF TABLES

Table 1: Polymer and Cross-Linking Agents Dosages Used in this Study. ....	7
Table 2: Rheological and Morphological Testing Plan.....	8
Table 3: Statistical Analysis Results.....	17

## **EXECUTIVE SUMMARY**

This study was initiated with the aim of evaluating the relative impact of different cross-linking agents on the rheological and morphological properties of polymer modified asphalt binders (PMAs). To complete this objective, two cross-linking agents (an aromatic oil and silicon oxide) were selected for evaluations. The cross-linking agents were then added to a styrene-butadiene-styrene (SBS) polymer modified binder (virgin PG 70-22) at different dosages. The selected cross-linking dosages were 2 and 4% by weight of virgin binder. The SBS, virgin binder, and cross-linking agents were mixed together for 90 minutes using a high shear mixer. The morphology of the modified binder was then tested using a florescent microscope and the rheological properties were evaluated using the dynamic shear rheometer (DSR) to determine the dynamic shear modulus values at different temperatures (i.e., 70°C and 76°C) and the multiple stress creep recovery (MSCR) properties of these binders. Based on the results obtained, it was found out that the addition of the Aromatic Oil agent might result in increasing the potential for rutting, decreasing the potential for low temperature cracking, and helps in improving the interlocking between the polymer modifier and the neat binder. It can also be concluded that the addition of the silicon oxide cross-linking agent to PMAs might have positive impact on rutting resistance without any adverse effects on low temperature cracking. Also, the addition of silicon oxide did not affect the morphology of PMAs. Furthermore, the collected results showed that the MSCR testing procedure is more capable at characterizing the properties of PMAs than can the traditional DSR test.



## **BACKGROUND**

To accommodate the ever increasing traffic loading and the effects of the varying climatic conditions, state agencies and researchers alike recommend using polymer modified asphalt binders (PMA) when preparing hot mix asphalt (HMA) mixtures. This is because the addition of polymer modifiers into asphalt binders helps in significantly improving the mixtures' resistance to permanent deformation, cracking, and water-induced damage. The two most common polymers that can be added into asphalt binders are (1) Styrene-Butadiene-Rubber (SBR) and (2) Styrene-Butadiene-Styrene (SBS).

The blending of polymers with virgin asphalt binders changes the morphological and rheological properties of virgin asphalt binders. Several studies were conducted to evaluate these changes. For instance, Mitchel and Davis (1993) attempted to develop a simple quantitative fluorescence micro-photometric techniques for use in the measurement of asphalt quality and deterioration. As a part of this research a method was suggested to prepare samples for testing the fluorescence of asphalt binders and asphalt mixtures.

Soenen et al. (2005) conducted a study to evaluate the impact of thermal history on rheological and morphological properties of polymer modified and neat asphalt binders. For SBS modified binders, the researchers reported that binder pouring and cooling conditions have the largest influence on polymer-binder network formation. When the binder is heated to temperatures that are not sufficiently high to obtain phase miscibility, phase separation takes place. This has an important impact on the morphology of bitumen and polymer phases at service temperatures and on the low frequency rheological properties. Furthermore, the researchers reported that chemical cross-linking of the SBS prevents a large-scale phase separation between bitumen and polymer, which explains why the effects of pouring and cooling conditions are not seen in a binder that had a chemically cross-linked SBS.

Sengoz and Isikyakar (2008a) studied the effect of increasing the percentage of SBS polymer modifier (used 2, 3, 4, 5, and 6% by weight of asphalt) on virgin asphalt binder (base bitumen). It was reported that SBS usage resulted in hardening the base bitumen and making it less susceptible to high temperatures (Sengoz and Isikyakar, 2008a). The researchers also reported that the formation of a continuous interlocking phase between the binder and the polymer modifier depends on SBS content. In another study, Sengoz and Isikyakar (2008b) characterized the properties of SBS and ethylene vinyl acetate (EVA) modified asphalt binders. The researchers also evaluated the morphology of PMAs by assessing the state of dispersion of SBS and EVA polymer modifiers and the base bitumen phase using Fluorescent Microscopy (FM) images. The researchers reported that SBS is better than EVA for modifying their base bitumen. A continuous phase of interlocking was achieved after blending 5% or more of both polymer modifiers.

D'Angelo and Dongre (2009) conducted a study that utilized FM and Multiple Stress Creep Recovery (MSCR) to characterize the extent of dispersion of SBS polymer

modified asphalt binders. In this study, the researchers utilized MSCR test to optimize the blend between SBS and asphalt binders. In addition, the researchers studied the effect of blend time and temperature on the characteristics of the polymer modified asphalt binder. FM was also used to optimize blending between SBS and the base binders. D'Angelo and Dongre (2009) concluded that Blending time and temperature and cross-linking affect the properties of polymer-modified binders. The researchers recommended that optimization of blending between polymer modifiers and asphalt binders should be a standard practice to be followed by researchers doing PMA binder–related studies. This should be done with florescent microscopy and verification with MSCR testing.

Oliver et al. (2012) in Australia attempted to clarify how the properties of SBS modified asphalt binders depend on morphology and identify the main factors that control morphology. The researchers utilized the FM to quantify compatibility between SBS and base bitumen. They also looked at the effect of isothermal storage and how does the morphology change as the storage temperature change and how long the can containing the polymer modified binder be subjected to that temperature.

The studies presented above provide clear evidence that blending polymers with virgin asphalt binders substantially improves the rheological properties (at high temperatures) of the resulting blend (or PMA) and changes the morphology of virgin asphalt binders. However, these studies have only focused on assessing the blend of polymers with binders. They had limited consideration to chemical cross-linking agents that might improve the interlocking of virgin asphalt binders and added polymers. In addition, limited to no research was conducted to comprehensively evaluate the impact of chemical cross-linking agents on the morphological and rheological properties of PMAs as well as the overall performance of asphalt mixtures. Therefore, it is of essence to conduct such research and further advance our knowledge of PMAs produced using chemically cross-linked polymers.

## **OBJECTIVES**

The study presented in this paper was initiated to accomplish the following objectives:

1. Evaluate the ability of different chemical cross-linking agents to improve the interlocking of virgin asphalt binders and polymers;
2. Investigate the impact of various chemical cross-linking agents on the rheological properties of PMAs;
3. Examine the influence of cross-linking agents on the morphological properties of PMAs using a Fluorescent Microscope; and,
4. Correlate the rheological and morphological properties of PMAs to performance.

## **MATERIALS DESCRIPTION**

The materials selected for this study included one asphalt binder (neat PG 70-22) and one polymer modifier (Kraton SBS). The polymer modified asphalt binder produced using

these materials (i.e, the neat PG 70-22 and SBS) was further modified by blending a chemical cross-linking agent. Two cross-linking agents were selected for the purposes of this study. These agents included: (1) Petroleum Aromatic Extracts Oil (AEO) and (2) Silicon Oxide Nanopowder (SON).

### **POLYMER, BINDER, AND CROSS-LINKING AGENT BLENDING**

The SBS polymer modifier, the neat PG 70-22, and each of the selected cross-linking agents were blended using a high shear mixer. The blending process for making one blend started by first mixing one cross-linking agent with the neat PG 70-22. It should be noted that each of the three cross-linking agents were ground to fine powder before mixing with the neat binder. The SBS polymer modifier was then gradually added to the blend of binder and cross-linking agent. The dosages of SBS and each of the cross-linking agents are provided in Table 1. The materials were blended at a temperature of 190°C (374°F) for a period of 120 minutes. Samples for FM testing were collected after 30, 60, and 90 minutes in order evaluate the morphological properties of the overall blend. Dynamic Shear Rheometer (DSR) samples were also collected at the end of the 120 minutes mixing time.

Table 1: Polymer and Cross-Linking Agents Dosages Used in this Study.

Cross-Linking Dosages	SBS Polymer Dosage, %			
	0	2	4	
Dose of Aromatic Oil, %	0	✓	✓	✓
	2	✓	✓	✓
	4	✓	✓	✓
Dose of Silicon Oxide Nanopowder, %	0	✓	✓	✓
	2	✓	✓	✓
	4	✓	✓	✓

### **TESTING PLAN**

The testing plan prepared for this study involved conducting rheological testing and morphological testing. The rheological testing included using the DSR to obtain binder grading. The rheological testing also included using the DSR to conduct the Multiple Creep Stress Recovery (MSCR) test. The morphological testing included using a fluorescent microscope for capturing images of the polymer structure within the neat asphalt binder and how is the morphology influenced by adding the various cross-linking agents. The following subsections provide a detailed discussion of each of the tests utilized in this study.

#### **Rheological Testing (DSR and MSCR)**

As mentioned above, the DSR was used to determine the binder grade of each of the cross-linked PMAs prepared according to the blending procedure discussed previously. This test was conducted according to AASHTO T 315 “Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)” standards. In order to complete this test, two sets of samples were prepared. The first set of samples were tested under the “original” setting without subjecting the PMA blend to any aging procedures while the second set of samples was first aged using the Rolling Thin Film Oven (according to AASHTO T 240 “Effect of Heat and Air on a Moving Film of Asphalt” standards) and then tested using DSR. In addition, DSR testing was conducted at high temperatures (i.e., 70 and 76). The parameters collected through DSR testing include Shear Modulus ( $G^*$ ) and Phase Angle ( $\delta$ ). These parameters can be used to determine the Superpave  $G^*/\sin(\delta)$  and  $G^*\sin(\delta)$  values. Superpave values are then compared to those found in AASHTO M 320 standards for determining the binder grade. Two replicates were prepared when conducted DSR testing.

In addition to DSR testing, the MSCR test was also conducted. The MSCR test utilizes the DSR equipment to also grade asphalt binders. This test was used because it accounts for the shortcomings of the current binder grading method (AASHTO M 320) that poorly characterizes rutting or PMAs. It was conducted according to AASHTO T 350 “Multiple Stress Creep Recovery (MSCR) Test of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)”. The MSCR procedure involves testing a binder sample using the DSR by applying 10 load-relax cycles. Two parameters were collected using this test: (1) Non-recoverable Creep Compliance ( $J_{nr}$ ) and (2) Percent Average Recovery. Using these two parameters, asphalt binders (including PMAs) can be graded to withstand different traffic levels (i.e., standard, heavy, very heavy, and extremely heavy). Table 2 below shows the rheological testing matrix implemented for this study.

Table 2: Rheological and Morphological Testing Plan

Test Conducted or Sampling Time (minutes)		SBS Polymer Modifier	
		Silicon Oxide Nanopowder	Aromatic Oil
Rheological Testing	DSR	✓	✓
	MSCR	✓	✓
Morphological Testing (Fluorescent Microscopy)	30	✓	✓
	60	✓	✓
	90	✓	✓

### Morphological Testing (Fluorescent Microscopy)

In order to evaluate the morphological properties of PMAs, a fluorescent microscope (FM) was utilized. Using this device, blended binder samples were illuminated with a light of a specific wavelength. This light is typically absorbed by the polymer fluorophores in the binder sample causing them to emit light of longer wavelengths (i.e., the emitted light would have a different color than the absorbed light). A spectral emission filter was used to separate the emitted fluorescence from the illumination light. Images of the polymer fluorophores representing its dispersion within the virgin asphalt binder were captured using a camera embedded into the FM. These images were used to characterize the blending degree between the virgin asphalt binder and the chemically cross-linked polymer (SBS). It is hypothesized that the higher is the dispersion of the polymer within the virgin asphalt binder the higher is the degree of blending.

The morphological testing of cross-linked PMAs also involved evaluating the effect of blending time on the blending degree between the virgin asphalt and the cross-linked polymer. In order to complete this objective, binder samples were collected during the blending process at various periods of time. Specifically, the samples were collected after 30, 60, and 90 minutes of blending. These samples were also tested in the FM and polymer dispersion images were captured. The complete morphological testing matrix is shown in Table 2 above.

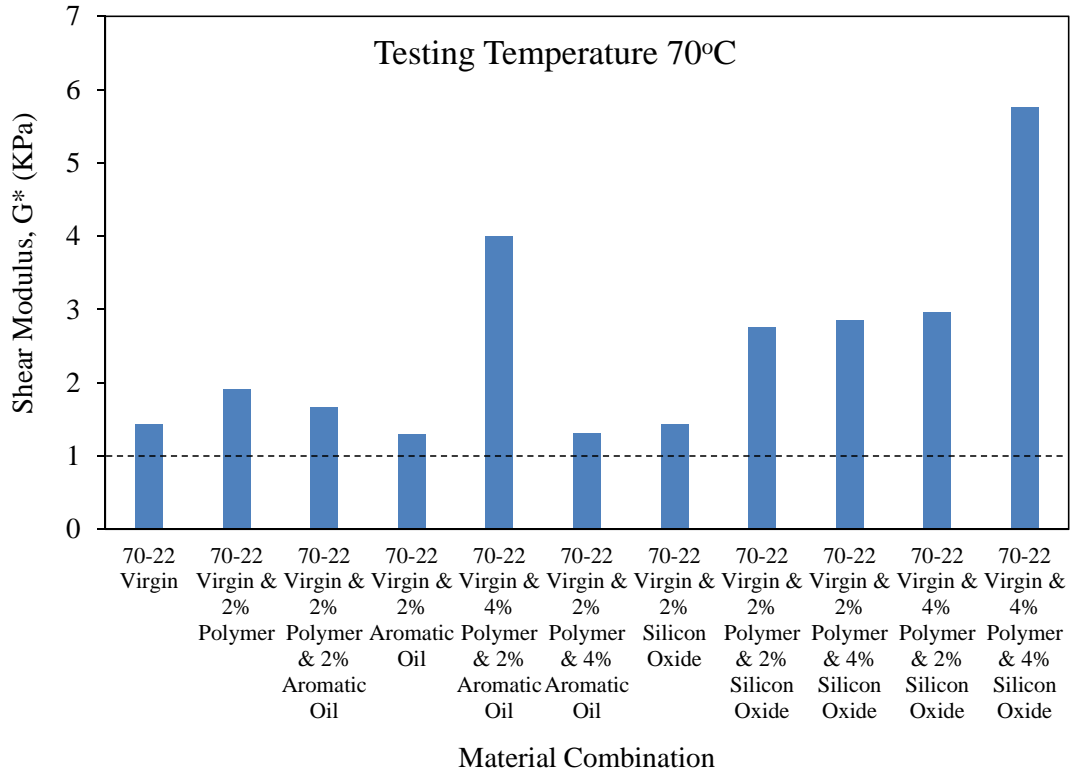
## **RESULTS AND DISCUSSION**

The results of the rheological and morphological testing results are presented in Figures 1 through 3. Figure 1 presents the shear modulus results obtained for all material combinations tested at 70 and 76°C. As can be seen from this figure, the shear modulus obtained for all material combinations tested at 76°C were lower than those tested at 70°C. This is expected because of the temperature dependency of the binders'. Figure 1 also shows that adding an AEO to a polymer modified binder results in reducing the shear modulus values regardless of the testing temperature. This is believed to be due to the behavior of AEO when added into binders (i.e., the matrix, or Maltenes, in which the Asphaltenes are dispersed in is increased due to the addition of AEO). This observation indicates that AEO might help in incorporating more polymers within binders; thus, could serve as a good "cross-linking" agent. Furthermore, Figure 1 shows that the addition of the SON cross-linking agent results in increasing (by about 1 KPa for 70°C and 0.5 KPa for 76°C) the shear modulus values of the binders tested. However, the shear modulus values obtained for material combinations prepared using different dosages of polymer and SON were relatively similar (i.e., within 0.1 KPa). These observations indicate that the SON has a stiffening effect when added to PMAs. Based on these observations, it might be concluded that the addition of AEO results in increasing the potential for permanent deformation (rutting) while reducing the potential for low temperature cracking. It can also be concluded that the impact of SON cross-linking agent results in decreasing

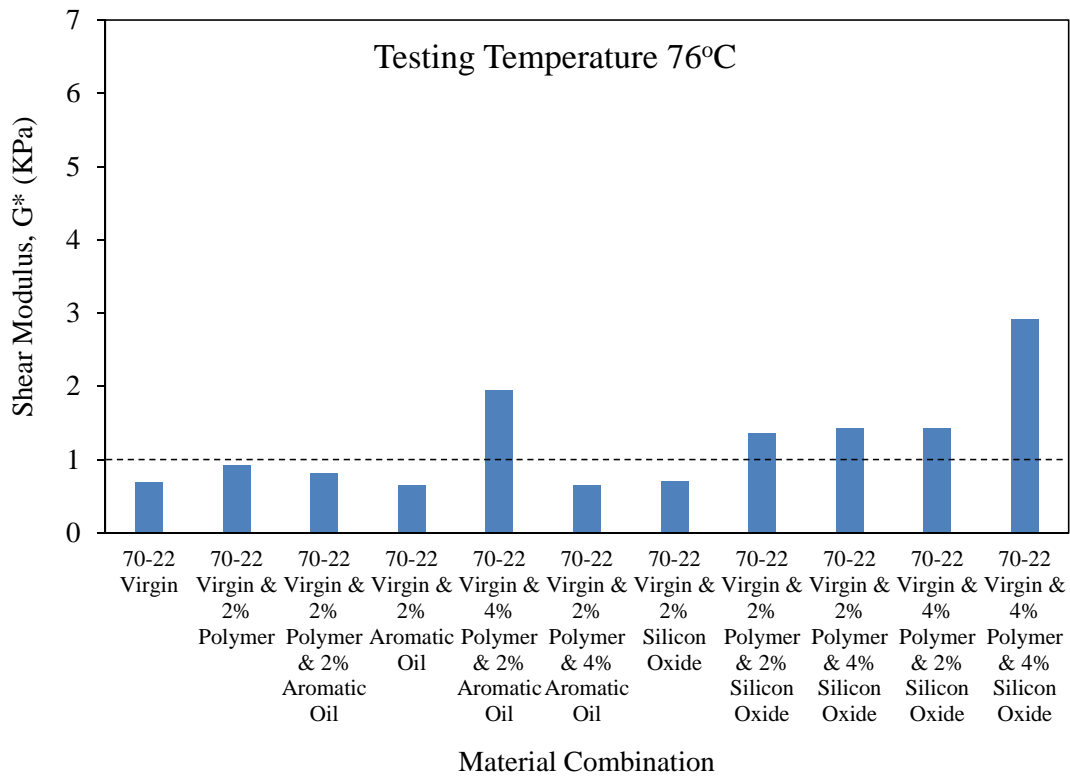
the rutting potential of PMA mixtures while increasing the susceptibility of mixtures prepared using PMAs and SON to low temperature cracking.

Figure 2 shows the MSCR testing results obtained for all material combinations that were prepared in this study. As shown in Figure 2a, the  $J_{nr}$  values obtained for the material combinations prepared by adding different dosages of AEO were higher than the  $J_{nr}$  value obtained for the PMA without AEO. Similar to the results presented in Figure 1, this observation indicates that the addition of AEO into PMAs results in lowering the stiffness of the binder; thus, increasing the potential for rutting. This is the case because higher  $J_{nr}$  values usually indicate higher rutting potential in asphalt mixtures. Figure 2b also shows that the percent recovery values for PMAs with AEO are higher than that for the PMA without AEO. This observation suggests that adding AEOs into PMA results in increasing their “elasticity”; which might help in increasing the resistance of asphalt mixtures prepared using PMAs and AEOs to low temperature cracking. In the case of SON cross-linking agent, Figure 2a shows that the  $J_{nr}$  values for binders prepared using different dosages of SON and polymer modifier were lower than the material combination prepared using only polymer modifier. This again suggests that the SON might have a stiffening effect when added to PMAs. However, Figure 2b shows that percent recovery for the 2% polymer combinations with SON are relatively similar (i.e., within 1%) to that obtained for the 2% polymer combination without SON. This might indicate that although the addition of SON has a stiffening effect on the resulting PMA, SON does not adversely affect the low temperature performance asphalt mixtures prepared using SON and a polymer modifier. This observation also support the current belief among researchers that the MSCR test is more capable of characterizing PMAs than traditional SuperPave DSR test. In an overall sense and based on the MSCR results presented, it can be concluded that the addition of AEO cross-linking agent results in increasing the susceptibility of asphalt mixtures to rutting and increases the resistance of these mixtures to low temperature cracking. It can also be concluded that the addition of SON cross-linking agent results in increasing the resistance of asphalt mixtures to rutting while not adversely affecting the cracking resistance of these mixtures.

Figure 3 presents the morphological images of the different binders prepared using the various dosages of the polymer modifier and the two cross-linking agents. Figure 3a presents the images obtained after 30 minutes of mixing, Figure 3b shows the images obtained after 60 minutes of mixing, and Figure 3c presents the images obtained after 90 minutes of mixing. It is noted that only the combinations that contain the polymer modifier were tested using fluorescent microscopy (FM). This is the case because only the polymer modifier is the element that has fluorescence while other component do not.

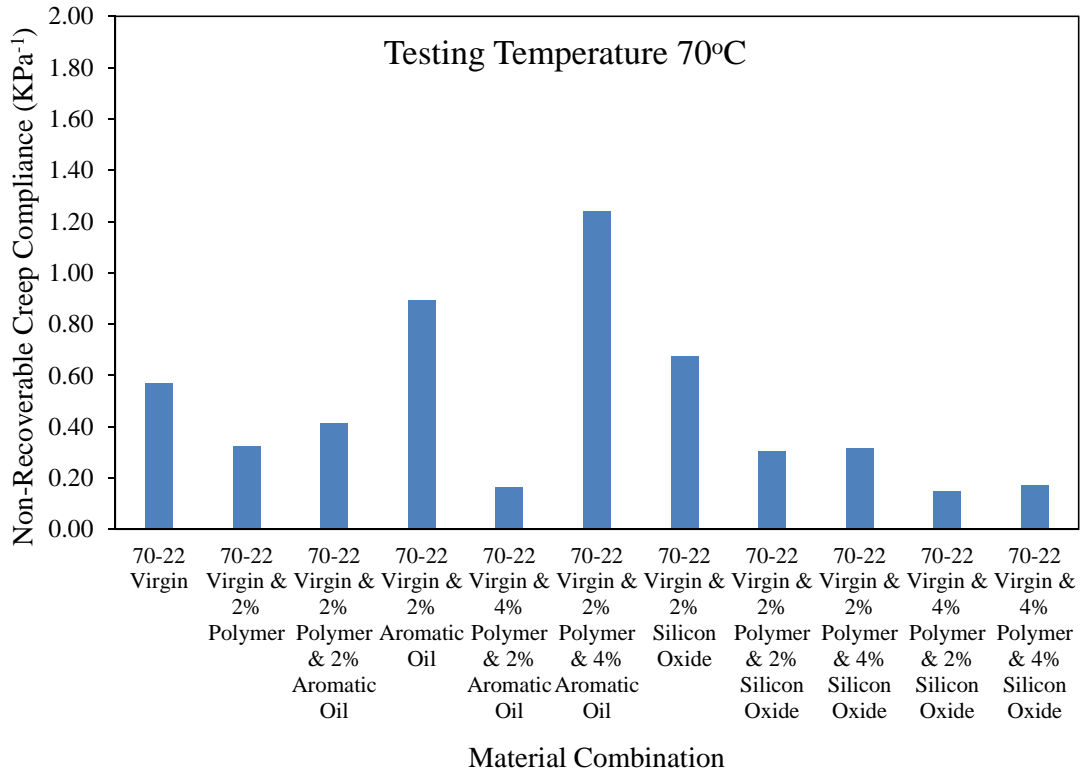


(a)

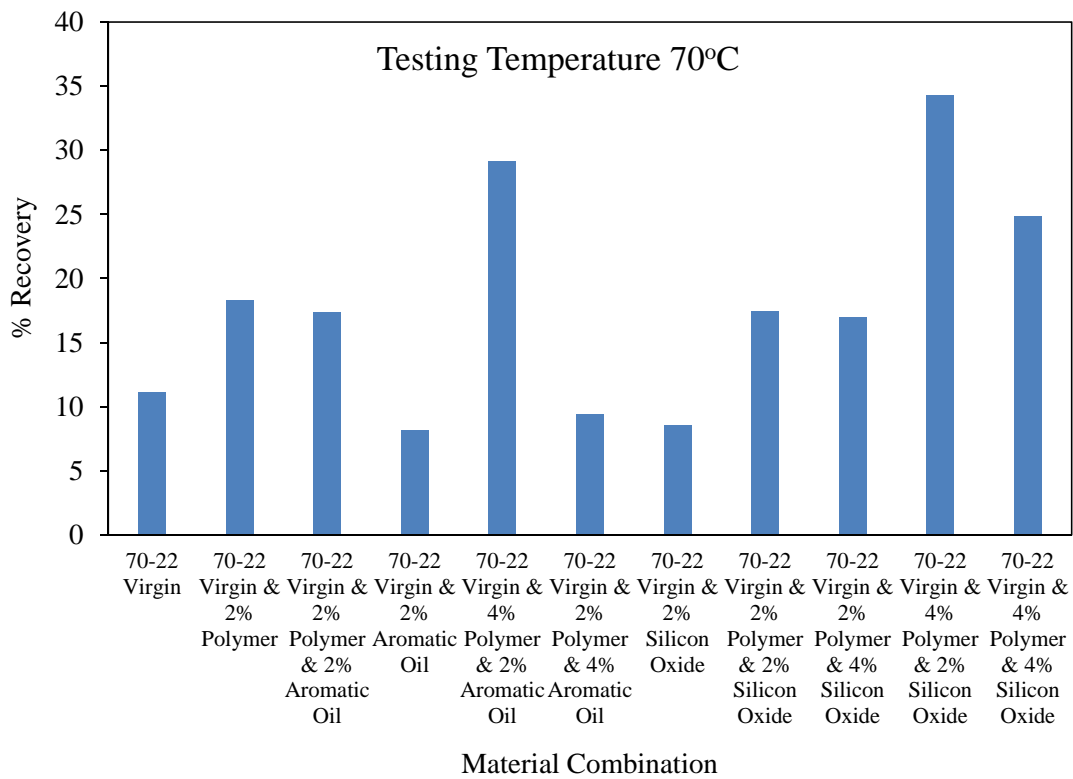


(b)

Figure 1: Dynamic Shear Rheometer Binder Shear Modulus: (a) testing temperature of 70°C and (b) testing temperature of 76°C.



(a)

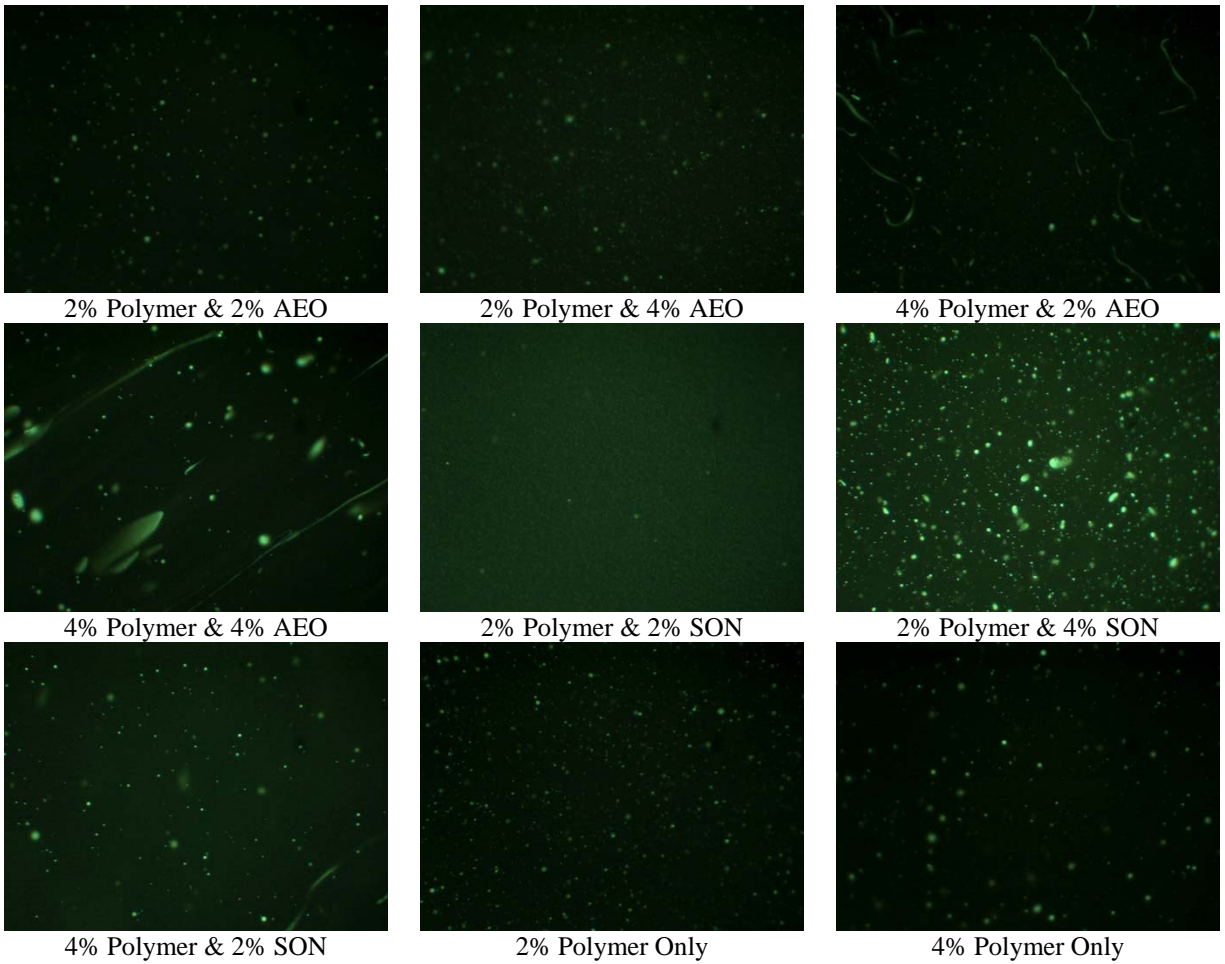


(b)

Figure 2: Multiple Stress Creep Recovery Testing Results: (a) Non-Recoverable Creep Compliance and (b) % Recovery.

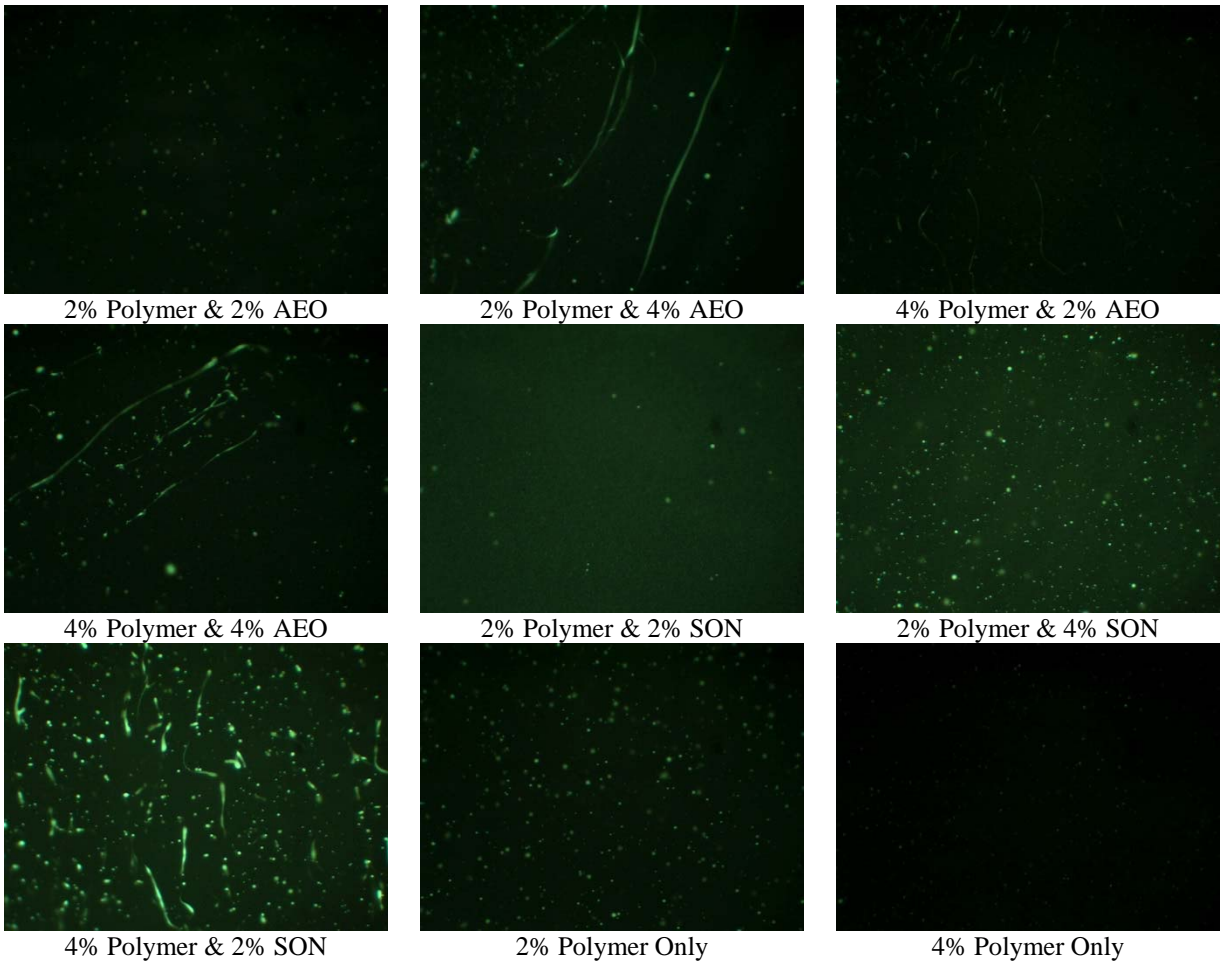


By comparing the images presented in Figure 3 for the binder combinations containing various dosages of AEO to the binder combinations only containing the polymer modifier, it can be seen that the concentration of the polymer modifier within the binder for the combinations containing AEO is lower than that for the combinations with only polymer modifier. This was the case for samples collected after 30 minutes of mixing. After allowing the combinations to mix further (i.e., 60 and 90 minutes) it can be seen that the polymer modifier, in the combinations containing AEO, started to form a “string” like structure while for the polymer modifier only combinations the polymer showed a structure that can be described as a “star field”. These observations might generally indicate that the addition of AEO cross-linking agent to the PMA might help in improving the interlocking between the asphalt binder and the polymer modifier. For the case of the SON cross-linking agent, the images presented in Figure 3 and obtained after 30 minutes of mixing show that the polymer modifier distribution within the binder for the binder combinations containing SON is either lower (at 2% SON) or higher (at 4% SON) than that for combinations prepared without SON. The structure at this stage (after 30 minutes of mixing) can be considered as a “star field”. In addition, the images presented in Figure 3 and obtained after 60 and 90 minutes of mixing show that the distribution of the polymer modifier can still be described as “star field”. This is similar to the binder combination containing only the polymer modifier. The observations made from the SON image generally indicate that adding this particular cross-linking agent might not significantly affect the morphology of PMAs. These observations also suggest that utilizing a higher dosage of the SON cross-linking agent might help in slightly improving the interlocking of the polymer modifier and the binder. This is believed to be the case because the combinations containing 4% SON had higher polymer modifier than those containing 2% SON for all images obtained. Therefore, based on all these observations it can be concluded that the addition of AEO cross-linking agents to PMAs helps in improving the interlocking between the polymer modifier and the neat binder. The addition of AEO can also help in reducing the amount of time needed blend PMAs. Based on the observations, it can also be concluded that the addition of the SON cross-linking agent to PMAs does not necessarily improve the interlocking of the polymer modifier and the neat binder. The addition of SON also does not help in reducing the blending time needed for blending PMAs.



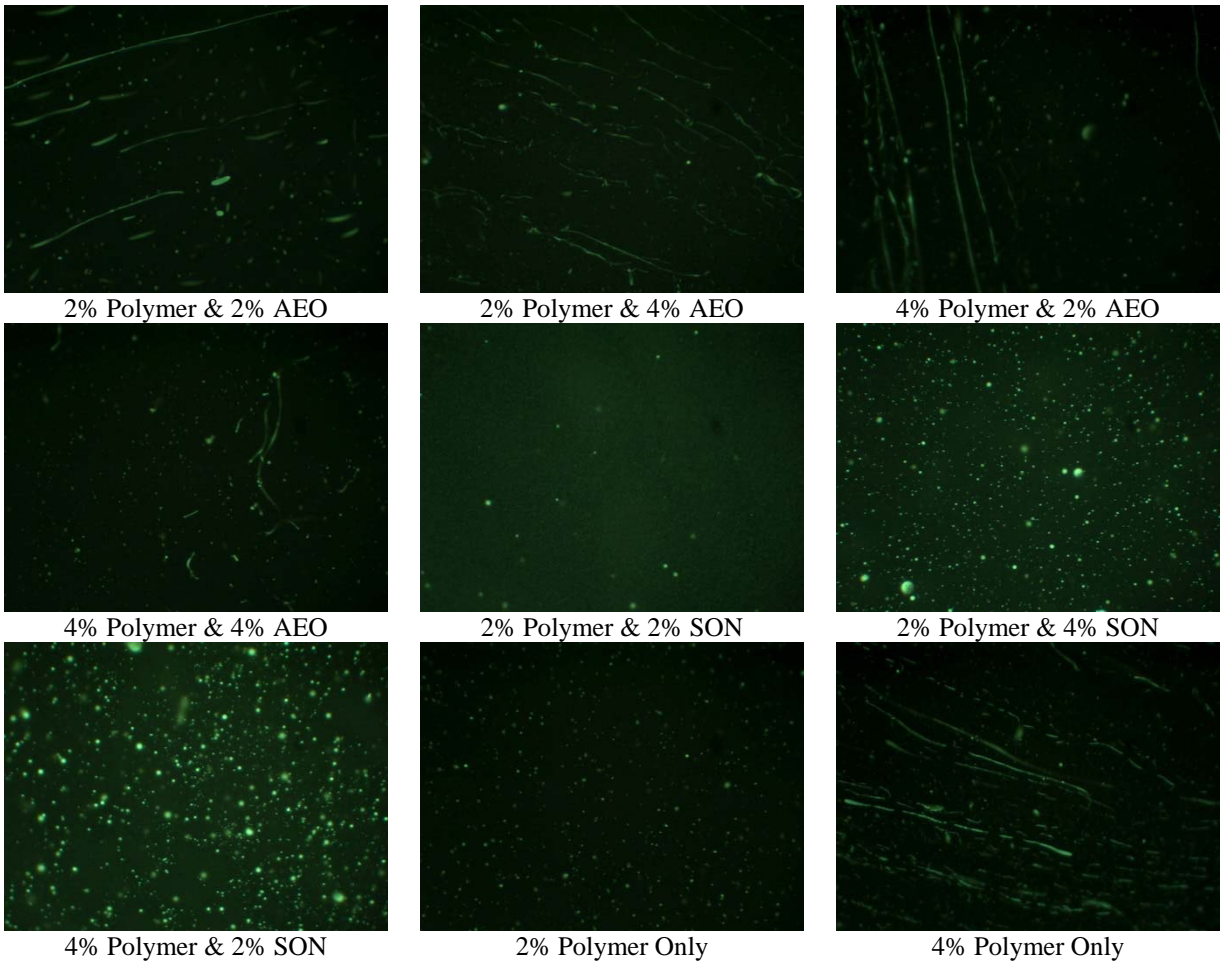
**(a) Images Obtained after 30 Minutes of Mixing**

Figure 3: Fluorescent Microscopy Images Obtained for the Different Binder, Polymer Modifier, and Cross-Linking Agents Combinations.



**(b) Images Obtained After 60 Minutes of Mixing**

Figure 3: Fluorescent Microscopy Images Obtained for the Different Binder, Polymer Modifier, and Cross-Linking Agents Combinations (Cont.).



**(c) Images Obtained after 90 Minutes of Mixing**

Figure 3: Fluorescent Microscopy Images Obtained for the Different Binder, Polymer Modifier, and Cross-Linking Agents Combinations (Cont.).

### Statistical Analysis

A multi-factor Analysis of Variance (MANOVA) was also conducted to evaluate the statistical significance of the polymer modifier dosage, cross-linking agents' dosages, and interactions between these factors on the results obtained from the DSR and MSCR tests. Table 3 presents the MANOVA results for both the SON and Aromatic Oil cross-linking agent combinations. As can be seen from Table 3, the impact of the polymer modifier dosage, SON dosage, and interaction between the two factors was significant on the DSR results. However, only the SON dosage factor was found to be significant on the results of Jnr results. These results support the observation that MSCR testing is better at characterizing the polymer modified asphalt binders. The results in Table 3 also show the same observations (i.e., all factors significantly impact DSR results but only cross-linking agent dosage significantly influences MSCR results).

Table 3: Statistical Analysis Results.

<b>Statistical Results for SON</b>				
<b>Statistical Factor</b>	DSR		Jnr	
	F-Value	$\alpha$	F-Value	$\alpha$
Polymer Dosage	406.721	0.000	0.110	0.897
SON Dosage	876.272	0.000	6.098	0.025
Polymer * SON	458.815	0.000	0.472	0.640
<b>Statistical Results for Aromatic Oil</b>				
<b>Statistical Factor</b>	DSR		Jnr	
	F-Value	$\alpha$	F-Value	$\alpha$
Polymer Dosage	2340.676	0.000	0.845	0.465
Aromatic Oil Dosage	2724.349	0.000	44.916	0.000
Polymer * Aromatic Oil	1761.932	0.000	1.775	0.229

## CONCLUSIONS

Based on the rheological and morphological testing results obtained in this study, the following conclusions can be drawn:

- The addition of AEO results in increasing the potential for permanent deformation (rutting) while reducing the potential for low temperature cracking. This is mainly attributed to the reducing in the DSR shear modulus values with the addition of AEO to PMAs.
- The impact of SON cross-linking agent results in decreasing the rutting potential of PMA mixtures while increasing the susceptibility of mixtures prepared using PMAs and SON to low temperature cracking. This is because the addition of SON to PMAs resulted in an increase in the DSR obtained shear modulus values.
- The addition of AEO cross-linking agent results in increasing the susceptibility of asphalt mixtures to rutting and increases the resistance of these mixtures to low temperature cracking. This is mainly because the Jnr and the percent recovery values obtained using the MSCR test were either higher (in the case of Jnr) or slightly lower (in the case of elastic recovery) for the combinations containing AEO.
- Similarly, the addition of SON cross-linking agent results in increasing the resistance of asphalt mixtures to rutting while not adversely affecting the cracking resistance of these mixtures. This is because the Jnr values for combinations containing SON were lower to those prepared with only the polymer modifier while the percent recovery values were found to be higher. It can also be concluded, based on these observations, that the MSCR test is better at characterizing the properties of PMAs than does the traditional DSR.
- The addition of AEO cross-linking agents to PMAs helps in improving the interlocking between the polymer modifier and the neat binder. The addition of AEO can also help in reducing the amount of time needed blend PMAs. This is mainly because of the

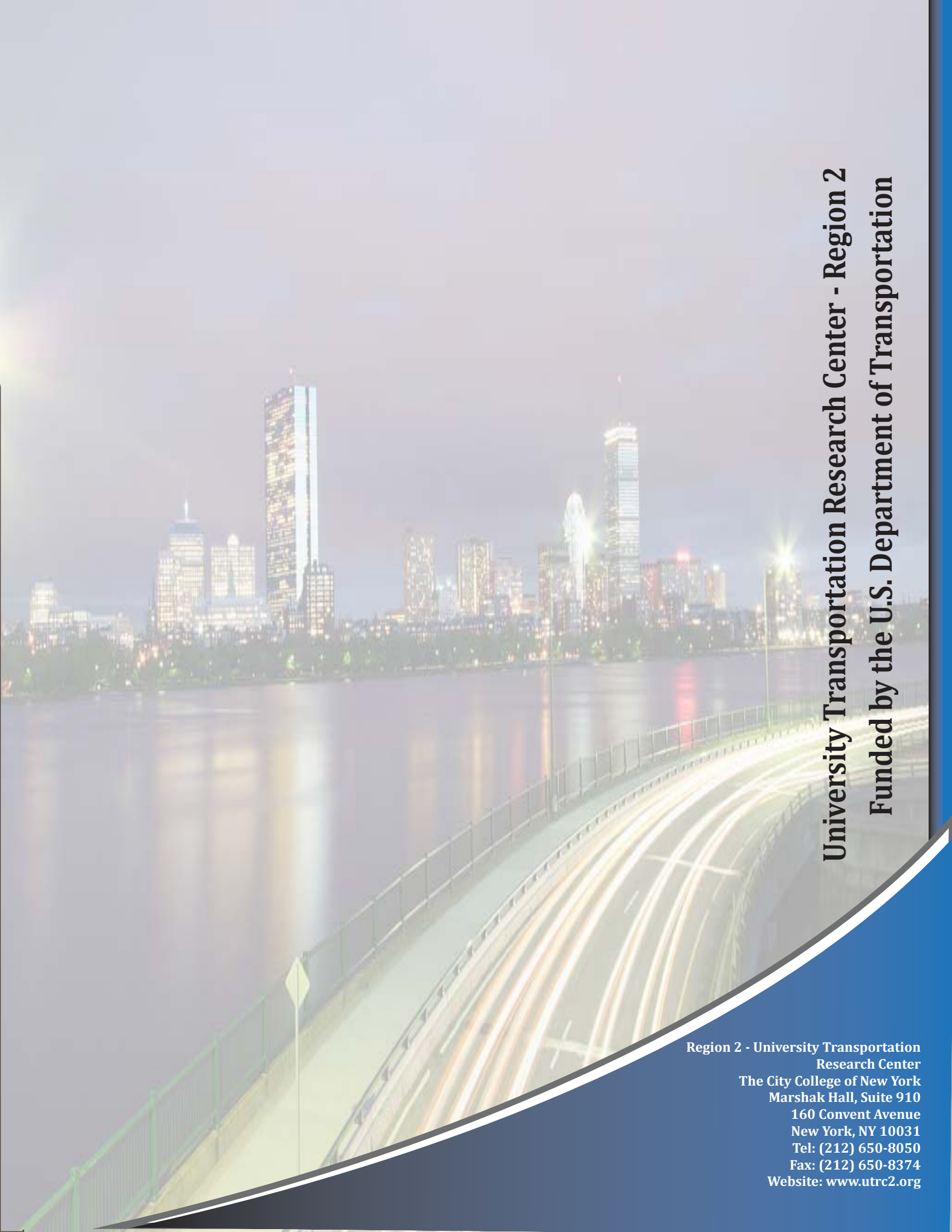
“string” like structure observed for the polymer modifier within the neat binder in combinations containing AEO.

- The addition of the SON cross-linking agent to PMAs does not necessarily improve the interlocking of the polymer modifier and the neat binder. The addition of SON also does not help in reducing the blending time needed for blending PMAs. This is mainly because the FM images obtained for the combinations containing SON showed a relatively similar distribution of polymer modifier within the binder to those combinations prepared using only the polymer modifier.

## REFERENCES

- [1] Fluorometric Characterization of Asphalts, G. Mitchel and A. Davis, Strategic Highway Research Program (SHRP) Rport No. SHRP-A-649, (1993).
- [2] Influence of thermal history on rheological properties of various bitumen, H. Soenen; J. De Visscher; A. Vanelstraete; and P. Redelius, *Rheologica Acta* pp. 45(5):729-739, (2005).
- [3] Analysis of styrene-butadiene-styrene polymer modified bitumen using fluorescent microscopy and conventional test methods, B. Sengoz and G. Isikyakar, *Journal of Hazardous Materials* 150 pp. 424–432, (2008a).
- [4] Evaluation of the properties and microstructure of SBS and EVA polymer modified bitumen, B. Sengoz and G. Isikyakar, *Journal of Construction and Building Materials* 22 pp. 1897–1905, (2008b).
- [5] Practical Use of Multiple Stress Creep and Recovery Test Characterization of Styrene–Butadiene–Styrene Dispersion and Other Additives in Polymer-Modified Asphalt Binders, J. D’Angelo and R. Dongré, *Transportation Research Record: Journal of the Transportation Research Board* No. 2126 pp. 73–82, (2009).
- [6] The Effect of Styrene Butadiene Styrene (SBS) Morphology on Field Performance and Test Results: An Initial Study, J. Oliver; K. Y. Khoo; and K. Waldron, *Austrroads Technical Report Publication* No. AP–T197-12, (2012).



A long-exposure photograph of a city skyline at night, reflected in a body of water. In the foreground, a bridge or highway is visible with light trails from moving vehicles. The sky is dark, and the city lights are bright and colorful.

**University Transportation Research Center - Region 2**  
**Funded by the U.S. Department of Transportation**

**Region 2 - University Transportation  
Research Center**  
**The City College of New York**  
**Marshak Hall, Suite 910**  
**160 Convent Avenue**  
**New York, NY 10031**  
**Tel: (212) 650-8050**  
**Fax: (212) 650-8374**  
**Website: [www.utrc2.org](http://www.utrc2.org)**