

Evaluation of the morphological and rheological impacts of cross-linking agents in polymer modified binders

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ABSTRACT

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. To complete this objective, two cross-linking agents (an aromatic oil and silicon oxide elemental sulfur) 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 master curves and the multiple stress creep recovery (MSCR) properties of these binders. The results show that with the increase in aromatic oil cross-linking agent dosage, there is a reduction in shear modulus results. In addition, the florescent microscope images show that there seems to be an improvement in the compatibility between the virgin asphalt and SBS in the presence of the aromatic oil extracts.

Keywords: Asphalt, Mechanical Properties, Polymers, Rheology

1. INTRODUCTION

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 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, the presented research studies did not 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.

2. STUDY OBJECTIVES

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

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

3. 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) were 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).

4. 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 two 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. It is noted that the blending temperature was selected based on typical values found in literature (Fernandes et al. 2008). Samples for FM testing were collected after 30, 60, and 90 minutes in order to 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	✓	✓	✓

5. 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.

5.1 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 (δ). 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-relaxation cycles. Two parameters were collected using this test: (1) Non-recoverable Creep Compliance (Jnr) 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.

5.2 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 below.

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	✓	✓

6. RESULTS AND DISCUSSION

The results of the rheological and morphological testing 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 Jnr values obtained for the material combinations prepared by adding different dosages of AEO were higher than the Jnr 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 Jnr values usually indicate higher rutting potential in asphalt mixtures. Figure 2b also shows that the percent recovery values for PMAs without AEO are higher than that for the PMA with AEO. This observation suggests that adding AEOs into PMA results in decreasing their "elasticity"; which might result in decreasing 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 Jnr 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 supports 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 does not.

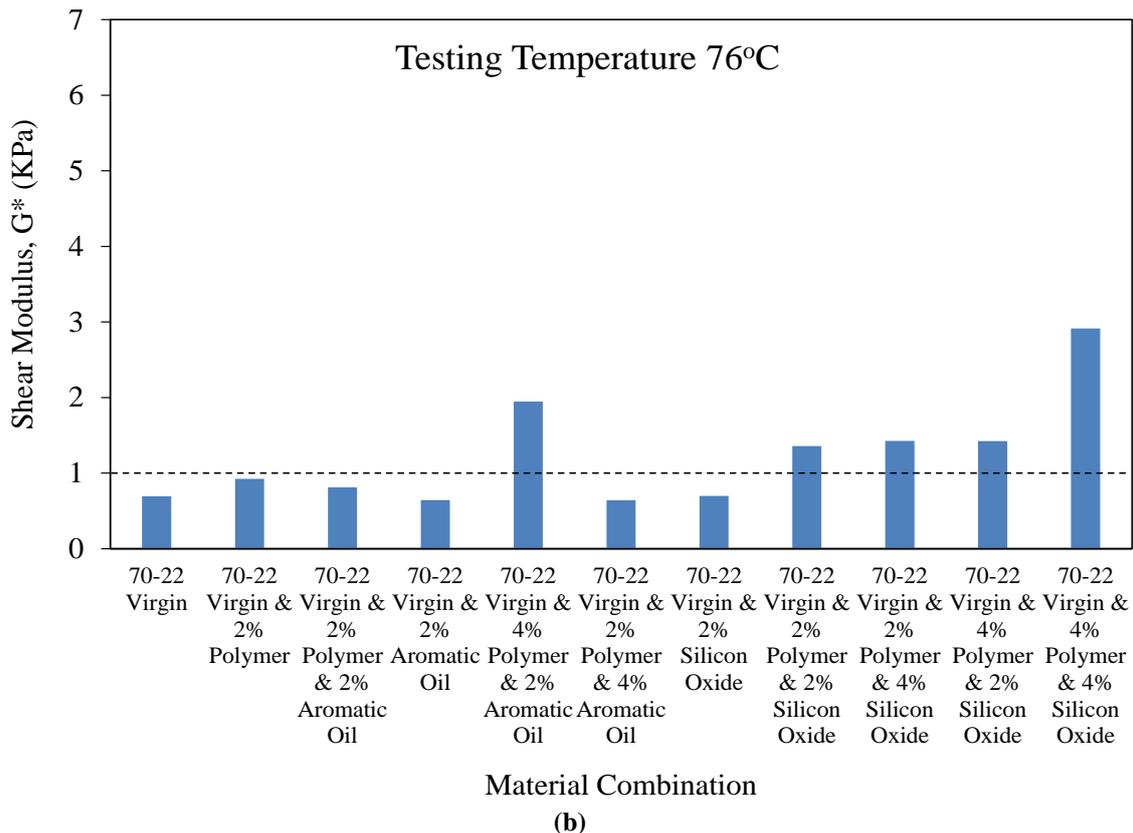
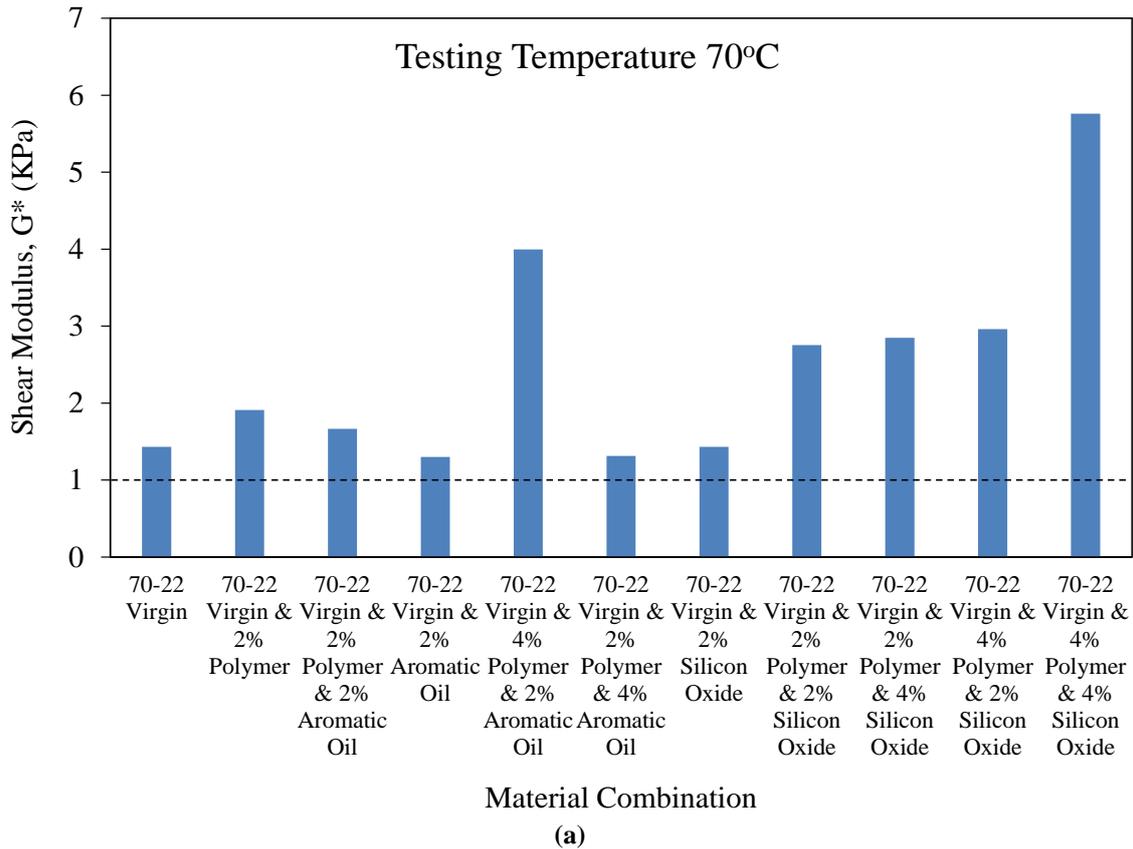


Figure 1: Dynamic Shear Rheometer Binder Shear Modulus: (a) testing temperature of 70°C and (b) testing temperature of 76°C.

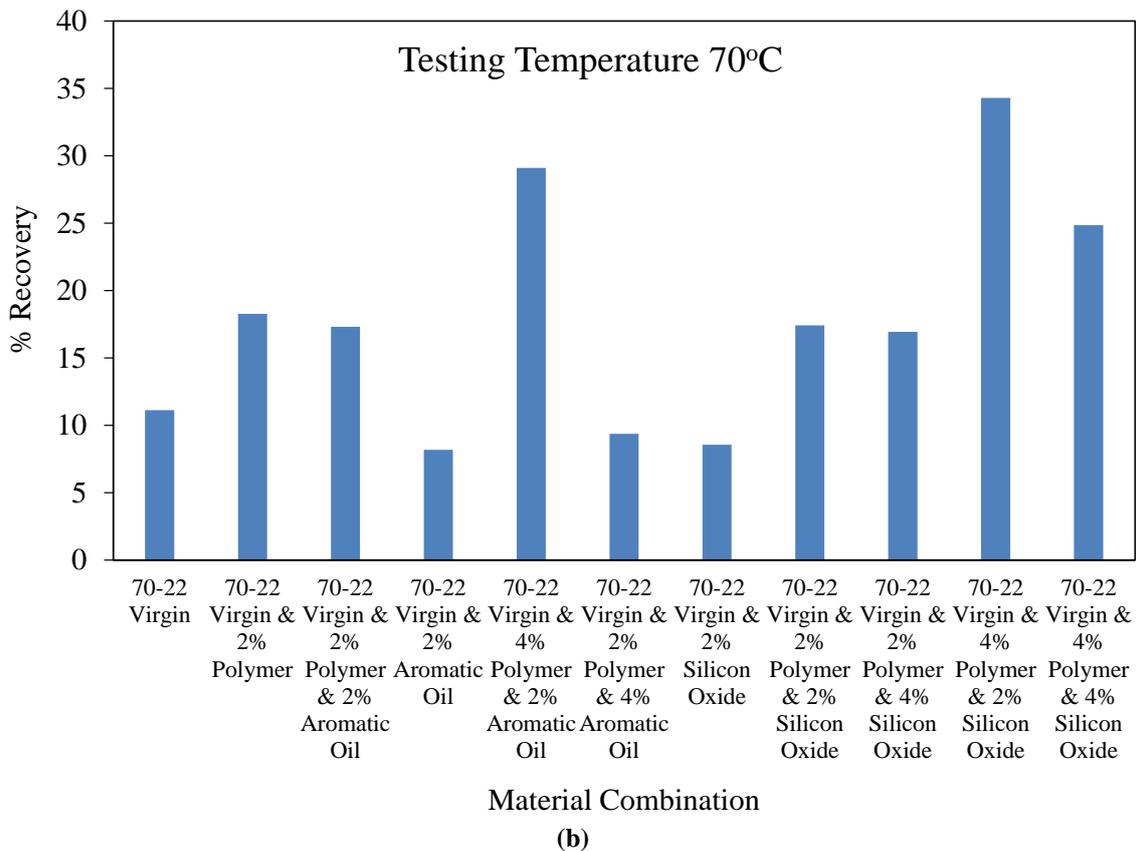
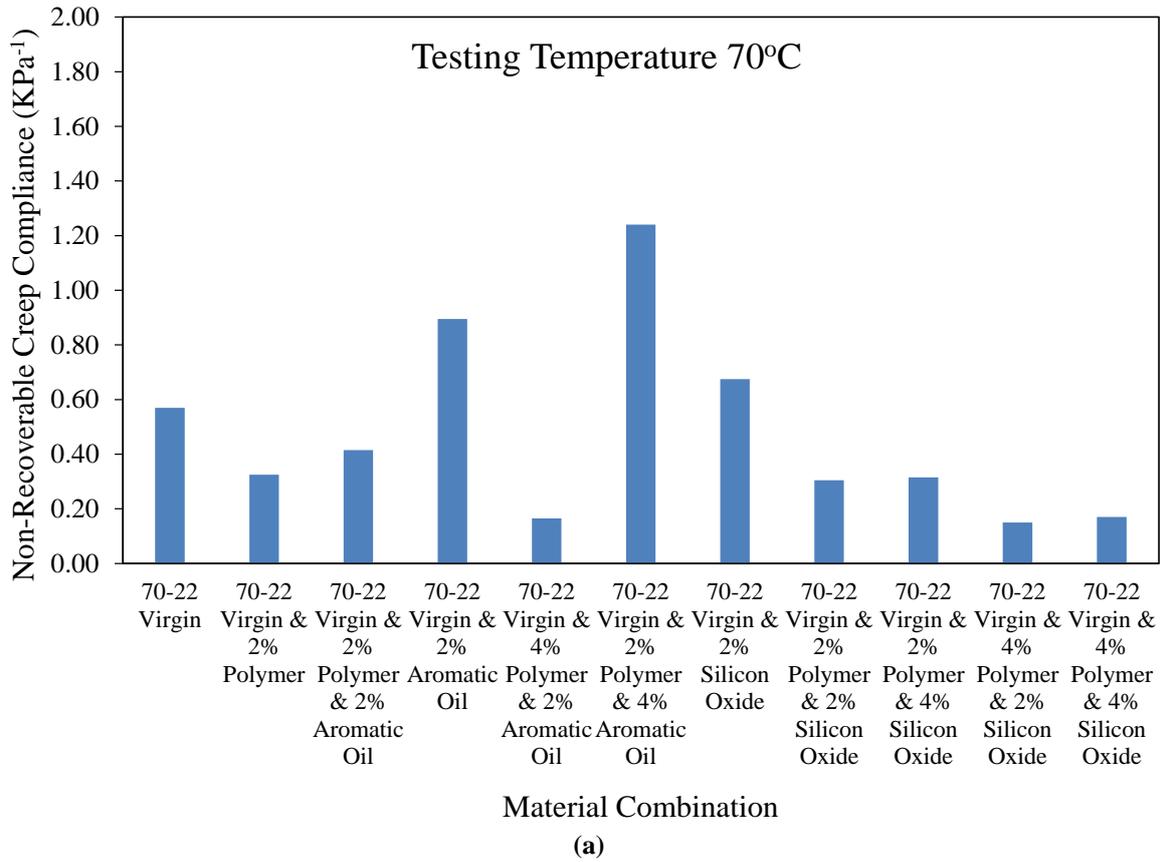
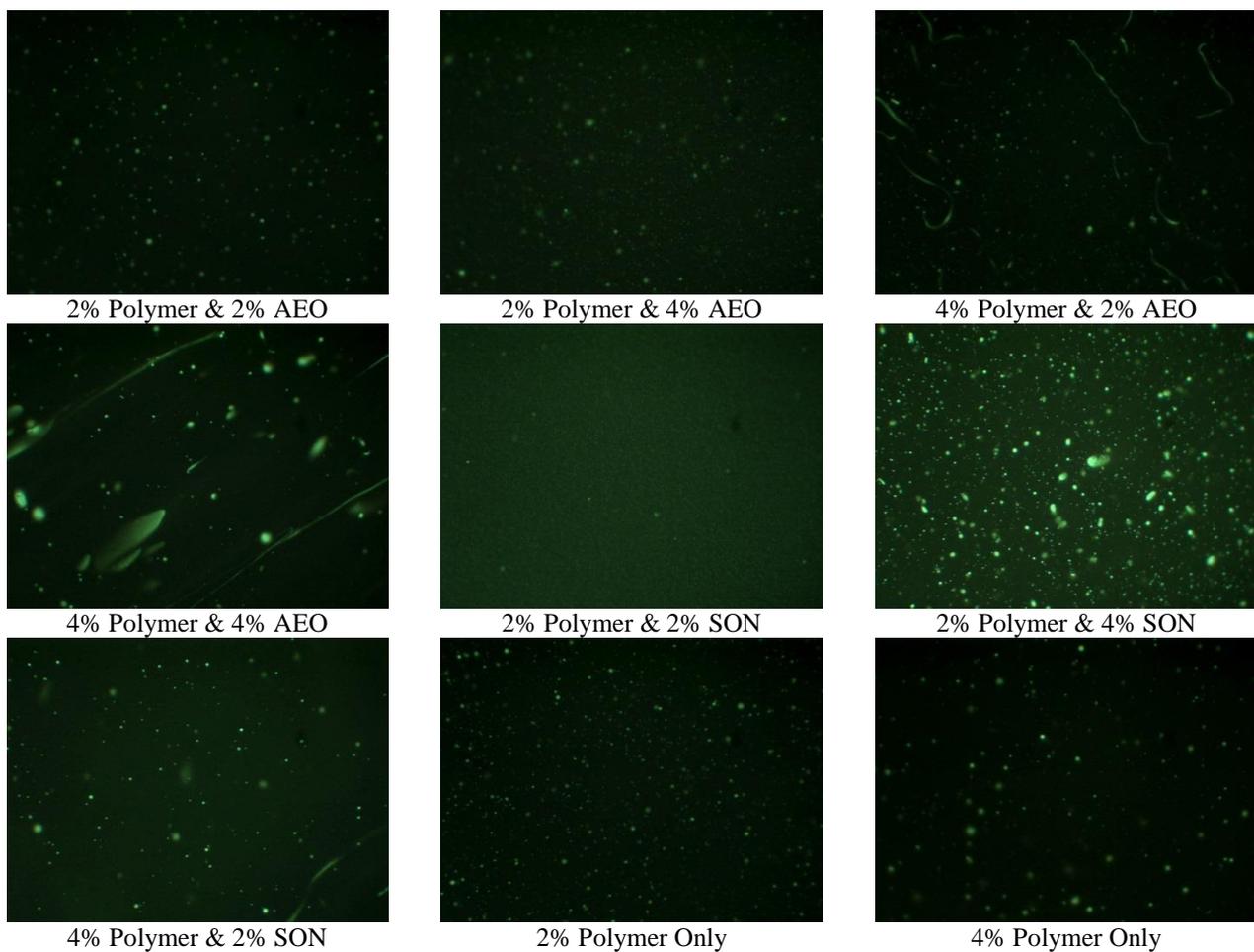


Figure 2: Multiple Stress Creep Recovery Testing Results: (a) Non-Recoverable Creep Compliance and (b) % Recovery.

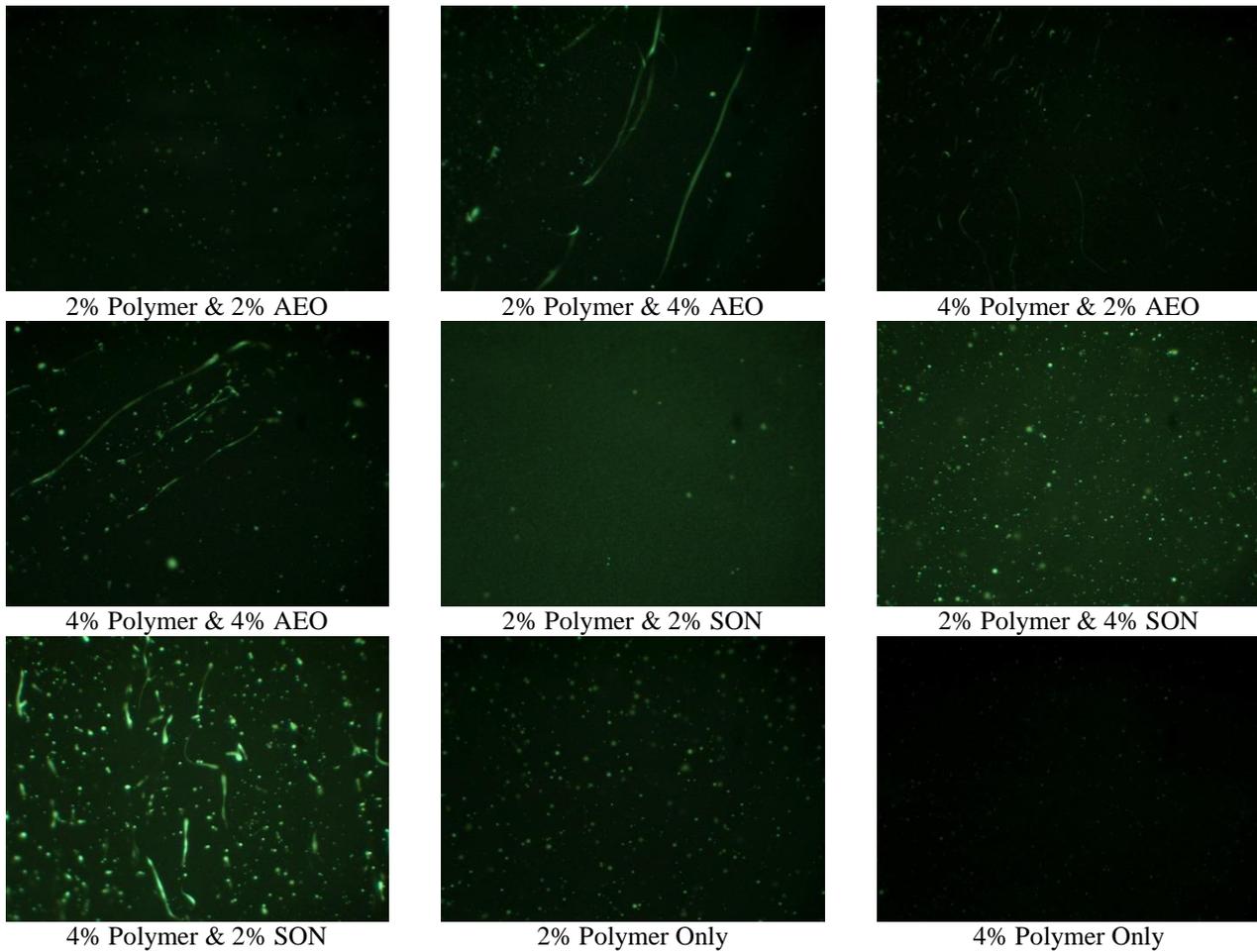
By comparing the images presented in Figure 3 for the binder combinations containing various dosages of AEO to the binder combinations only containing the polymer modifier, it can be seen that the concentration of the polymer modifier

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.

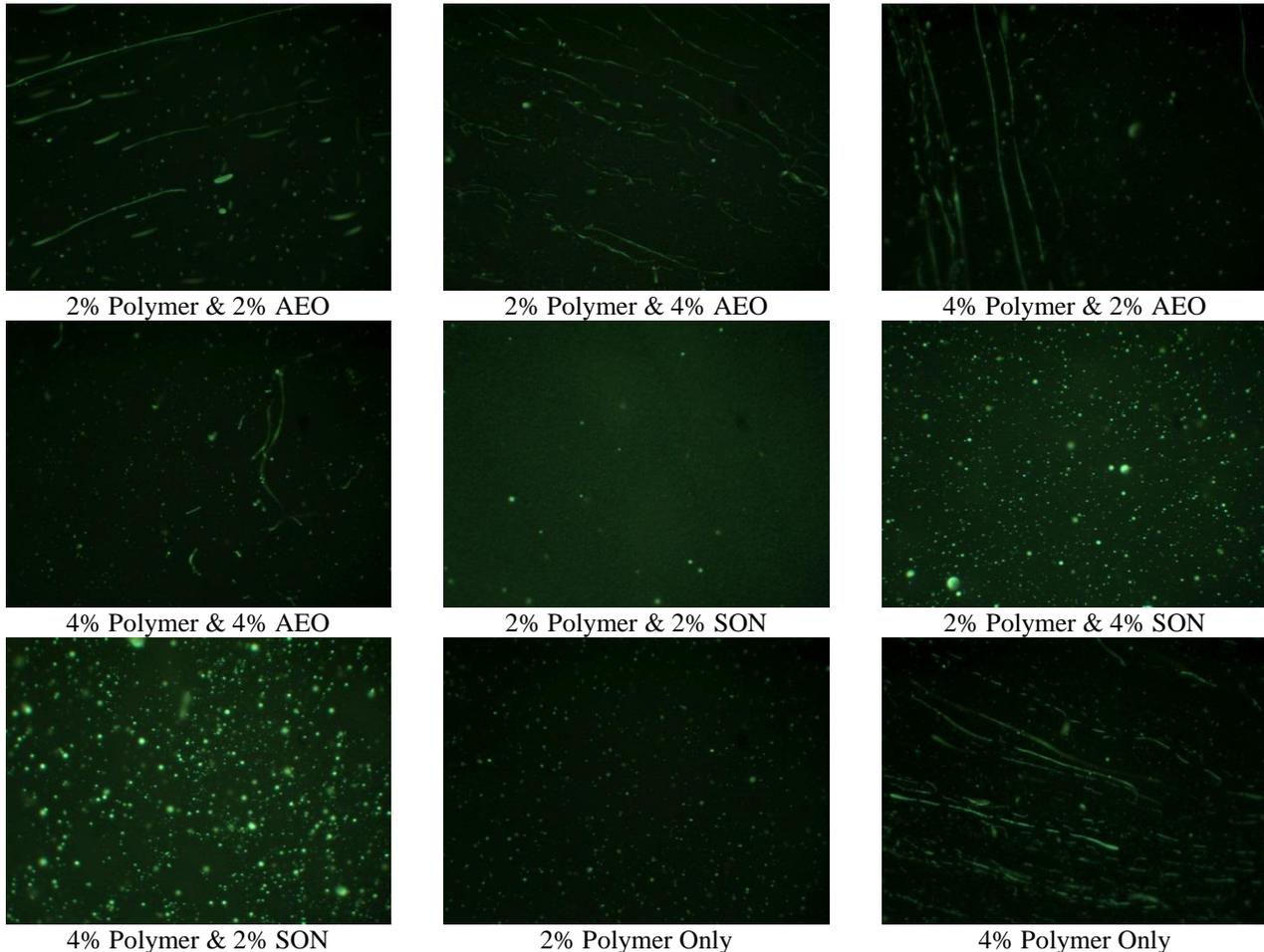


(b) Images Obtained After 60 Minutes of Mixing

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

7. 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).



(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.).

Table 3: Statistical Analysis Results.

Statistical Results for SON				
Statistical Factor	DSR		Jnr	
	F-Value	α	F-Value	α
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
Statistical Results for Aromatic Oil				
Statistical Factor	DSR		Jnr	
	F-Value	α	F-Value	α
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

8. 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.

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