Laboratory Evaluation of Sustainable PMA Binder Containing Styrene-Isoprene-Styrene (SIS) and Thermoplastic Polyurethane

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Abstract: In this study, thermoplastic polyurethane (TPU) and styrene-isoprene-styrene (SIS) were utilized to enhance asphalt binder properties. Superpave asphalt binder tests and multiple stress creep recovery (MSCR) were conducted to evaluate the physical and rheological performance (viscosity, rutting, and cracking properties) of the asphalt binders before and after short-term aging and after the long-term aging process. The results showed that (i) TPU has a positive effect on workability, including the mixing and compaction processes, which was evident from the reduced binder viscosity; (ii) asphalt binders with TPU and SIS showed better rutting resistance compared to the SIS binders without TPU; (iii) the cracking resistance of asphalt binders was found to be improved significantly with the addition of TPU; and (iv) TPU has the potential to be considered as a sustainable polymer modifier for producing bearable asphalt binders by improving rutting and crack resistance without increasing the melting temperature of the asphalt binders.

Keywords: TPU; SIS; viscosity; rutting; cracking

1. Introduction

Day by day, severe traffic conditions, such as more traffic volume and loads based on industry developments, are becoming critical to asphalt pavements. Global warming is also one of the factors which accelerates asphalt pavement deterioration. As such, traffic volume, traffic load, and weather conditions are factors that have a significant influence on the defects of asphalt pavements [1,2]. Due to limited budget and time, achieving a more extended service period of asphalt pavements is one of the transportation industry’s primary goals. It can significantly reduce maintenance cost and time. In general, three types of failure mode are considered: rutting, fatigue cracking, and thermal cracking. Even though all kinds of deficiencies are critical to the pavement service life, cracking has more impact on reducing pavement service life, eventually leading to a severe failure mode of the asphalt pavement [3]. There are two types of cracking: (i) fatigue and (ii) thermal cracking. In general, fatigue cracking occurs due to repetitive traffic loads at an intermediate temperature, and thermal cracking is due to a rapid temperature change and cycle. As a result, it is necessary to develop a sustainable asphalt binder which is highly resistant to cracking under intermediate temperatures.

Several kinds of polymer additives have been utilized to produce durable asphalt binders. Thermoplastic polyurethane (TPU) is a type of polymer with rigid and flexible properties based on a molecule that contains hard and soft segments [4]. TPU has been widely used in many fields, mainly in foam plastics, elastomers, and adhesives [5–7]. TPU can improve the flexibility as well as the strength of a modified asphalt system as a polymer modifier [8,9]. Its compatibility can also be enhanced through
the reaction of the functional group of TPU with the fundamental asphalt component to improve the rheological properties considering rutting and cracking performances [10–12]. There are few research works that have been conducted on TPU-modified asphalt binders.

Styrene-isoprene-styrene (SIS) is relatively new and is considered a potential additive to overcome the challenge of pavement problems [13,14]. The molecular chain of isoprene increases the complex modulus of SIS at high temperatures. It has better toughness and compatibility with other materials due to the branched methyl of the isoprene group [15,16]. SIS dispersion in asphalt binders is relatively homogeneous, though it requires specific temperature control and mixing times. The molecular structure of an asphalt binder can be modified by completely dispersed polymers [17]. Even though SIS addition is beneficial to produce a more robust binder, it increases binder viscosity. Furthermore, it has problems such as high fuel consumption and poor workability due to the high melting temperature. In addition, the percentage increase in polymer additives does not significantly improve cracking properties compared to rutting properties. Thus, there is a need to increase the content to have better cracking resistance and, at the same time, maintain binders with less viscosity.

The purpose of this study is to evaluate the performance characteristics of sustainable polymer-modified asphalt (PMA) binders containing TPU and SIS. The rolling thin film oven (RTFO) and pressure aging vessel (PAV) procedures were applied to produce artificially aged binder samples. A series of Superpave binder tests were carried out to investigate the PMA binders in three aging states (original, short aging, and long aging). Additionally, the multiple stress creep recovery (MSCR) test was used to assess the deformation properties of SIS-modified binders with TPU more effectively. Figure 1 shows the research procedure.

Figure 1. Flow chart of experimental design procedures.
2. Experimental Design

2.1. Materials

PG 64-22 was used as a base binder for this study. Table 1 exhibits the base binder properties. Thermoplastic polyurethane (TPU) is a polyester-based material with excellent wear resistance, low-temperature properties, and high hardiness as an elastomer with perfect thermoplastic properties. In this study, TPU at 5% of the binder’s weight was fixed and blended with the PG 64-22 base asphalt binder. Table 2 shows the characteristics of the TPU used in the study.

| Aging States       | Test Properties          | Test Result |
|--------------------|--------------------------|-------------|
| Unaged binder      | Viscosity @ 135 °C (Pa-s) | 0.531       |
|                    | G*/sin δ @ 64 °C (kPa)    | 1.415       |
| RTFO aged residual | G*/sin δ @ 64 °C (kPa)    | 2.531       |
| RTFO+PAV aged residual | Stiffness @ -12 °C (MPa) | 287         |
|                    | m-value @ -12 °C         | 0.307       |

| Properties          | Test Method       | Units   | Typical Value  |
|---------------------|-------------------|---------|----------------|
| Density             | ASTM D792         | lb/in³  | 0.0426         |
| Hardness, Shore A   | ASTM D2240        | -       | 67             |
| Tensile strength    | ASTM D412         | psi     | 2900           |
| Elongation at break | ASTM D412         | %       | 700            |
| 100% modulus        | ASTM D412         | psi     | 435 @ Strain 100% |
| 300% modulus        | ASTM D412         | psi     | 725 @ Strain 300% |
| Tear strength       | ASTM D624         | pli     | 371            |
| Abrasion            | DIN Abrasion Loss; DIN 53516 | -     | 40             |
| Glass Transition Temp, Tg | DSC               | °C      | 42.0           |

Many plants and animals produce isoprene (C₅H₈), which is the main component of SIS. Therefore, SIS addition is expected to improve the aging resistance, mixing stability, and elasticity of their asphalt binder because isoprene is the main component of natural rubber. Cohesion, tensile strength, and low-temperature flexibility can also be strengthened with SIS. SIS at 0, 5, 10, and 15% of the binder’s weight was added and then blended with the base binder and the 5% TPU-modified binder. The characteristics and images of the SIS used in the study are shown in Table 3 and Figure 2.

![Figure 2. Styrene-isoprene-styrene (SIS).](image-url)
Table 3. Properties of SIS.

| Properties               | Test Method       | Units      | Typical Value |
|--------------------------|-------------------|------------|---------------|
| Styrene                  | TSRC/DEXO Method  | wt%        | 15            |
| Diblock content          | TSRC/DEXO Method  | wt%        | 18            |
| Melt flow rate (200 °C/5 kg) | ASTM D1238     | g/10 min   | 11            |
| Solution viscosity       | ASTM D2196        | cps        | 1240          |
| Ash                      | ASTM D5630        | wt%        | 0.3           |
| Tensile strength         | TSRC/DEXO Method  | MPa        | 25            |
| 300% modulus             | TSRC/DEXO Method  | MPa        | 1.1           |
| Elongation               | TSRC/DEXO Method  | %          | 1250          |
| Hardness                 | ASTM D2240        | Shore A    | 33            |
| Bulk density             | ASTM D1895        | g/cm³      | 0.55 (4113A)  |
| Specific gravity         | ASTM D792         | -          | 0.92          |

The binder was modified by adding 5% TPU to the control PG 64-22 binder. SIS contents of 5, 10, and 15% of the weight of the basic PG 64-22 asphalt binder and 5% TPU-modified binder were used to produce the SIS+TPU binder. The modified binder was mixed using a wet process. The 5% TPU-modified binder was made with an open blade mixer, and then 0, 5, 10, and 15% of SIS was added and blended. Both additives, TPU and SIS, were mixed for 30 and 60 min at 700 rpm, respectively, at 177 °C.

2.2. Superpave Binder Tests

The Superpave binder test evaluated the properties of the samples in three stages of aging: immediately after sample preparation (before aging), after mixing and laying (short-term aging), and after aging during use (long-term aging). In this study, binder tests, including the kinematic viscosity test (AASHTO T 316), the dynamic shear rheometer (DSR) test (AASHTO T 315), and the bending beam rheometer (BBR) test (AASHTO T 313), were performed, and the average of the test values of three identical samples was reported as a result. A 10.5-g binder sample was measured for viscosity properties in the viscosity test using a Brookfield rotational viscometer at 135 °C. In the DSR test, the binders were tested at a frequency of 10 radians per second, equal to about 1.59 Hz. Each asphalt binder was used to determine $G'\sin \delta$ in the original state (unaged state) and in the short aging state. $G'\sin \delta$, which indicates the fatigue cracking resistance of the long-term aged binder (RTFO+PAV residual samples), was measured at 25 °C. The BBR test was completed using an asphalt beam (125 × 6.35 × 12.7 mm) at −18 °C [18], and the creep stiffness (S) of the binder was measured at 60 s of loading time. A constant load of 100 g was applied to the beam sample supported at both ends, and the displacement at the center point was continuously quantified. Long-term aged PMA binder samples were utilized to conduct the BBR test.

2.3. Multiple Stress Creep Recovery (MSCR) Test

The MSCR test was carried out using the same DSR equipment used to measure the plastic deformation characteristic value $G'\sin \delta$ of the binder. The test was carried out at 76 °C, according to AASHTO T 350-14. In addition, all binders were tested under short-term aging conditions, and the samples were tested in creep recovery mode at two stress levels of 0.1 and 3.2 kPa. Non-resilient creep compliance ($J_{nr}$) and recovery rate (%rec) were obtained through MSCR test analysis. As shown in Figure 3, the binder has a creep loading and unloading cycle of 1 and 9 s, respectively, at the stress levels of 0.1 and 3.2 kPa, and a load of 10 cycles is given at each stress level. The MSCR test results were used to calculate the non-recoverable creep compliance ($J_{nr}$) and recovery rate (%rec) to quantify the asphalt binders’ plastic deformation susceptibility. The non-recovery creep compliance ($J_{nr}$), determined by dividing the unrecovered shear strain by the shear stress, is used to evaluate an asphalt binder’s plastic deformation potential.
2.4. Statistical Analysis Method

Statistical analysis was performed using a Statistical Analysis System (SAS) program to perform an analysis of variance (ANOVA) and a Fisher’s Least Significant Difference (LSD) comparison with a $\alpha = 0.05$. First, the ANOVA was performed to determine if there were any significant differences between the sample means. In this study’s analysis, the significance level was 0.95, indicating a 95% probability that each result is true. LSD was calculated using ANOVA to see if there was a difference between the sample means. It is necessary to define the LSD to find out the observed difference between the two sample means, which can be used to declare the corresponding population means difference. Once the LSD was calculated, the means of the samples of all pairs were compared. The population means were reported to be statistically different if the difference between the two sample means was more significant than or equal to the LSD [19].

3. Results and Discussions

3.1. Rotational Viscosity

The viscosity of the binder represents the ability to be pumped in the plant. It is an essential factor in determining the workability of the process of compacting after coating the aggregate at a high-temperature mixture and laying it on the site [20]. Figure 4 shows the experimental value of the viscosity measured at 135 $^{\circ}$C. By comparing the base binder without the addition of SIS, it was found that the addition of 5% TPU did not significantly increase the viscosity. However, after the addition of SIS, it showed a noticeable increase in viscosity, and from the content of 10%, it was found to exceed the maximum value of 3000 cP suggested by Superpave. This means that the addition of high content of SIS negatively affects the workability for mixing and compaction in the plant and at the construction site. On the other hand, the SIS-modified binders containing 5% TPU showed a slightly lower viscosity value, despite the absolute modifier content being higher than that of the binder without TPU. In particular, with SIS 15%, the SIS-modified binder without TPU could not be measured at 135 $^{\circ}$C. In contrast, in the modified binder containing 5% TPU, the viscosity could be measured and data could be obtained. These results suggest that even though TPU is a polymer modifier, it has an insignificant effect on increasing the viscosity of the asphalt binder compared to the existing polymer additive, or rather has the potential of lowering the viscosity of other modified asphalt binders.
The statistical significance of viscosity, along with the additional percentage of SIS with the presence or absence of TPU, was investigated. The results are shown in Table 4. The data demonstrate that the addition of SIS has a significant effect on the increase in viscosity values. Most of the statistical results showed a significant difference in viscosity with the increase in SIS content. Furthermore, it was found that the addition of TPU did not show a significant difference in increasing viscosity. In comparison with SIS 0% and 10%, there was no significant difference due to the addition of TPU. However, at 5% and 15%, it is shown that the addition of TPU had a statistically considerable effect on the binder viscosity.

### Table 4. Statistical analysis results of the viscosity at 135 °C as a function of the addition of TPU and SIS content (α = 0.05).

| Viscosity | Control | TPU5% |
|-----------|---------|-------|
|           | SIS Content |       |
|           | 0% | 5% | 10% | 15% | 0% | 5% | 10% | 15% |
| Control   | -  | S  | S  | S  | N  | S  | S  | S  |
| SIS content | 5% | -  | S  | S  | S  | S  | S  | S  |
|           | 10% | -  | S  | S  | S  | N  | S  | |
|           | 15% | -  | S  | S  | S  | S  | S  | |
| TPU5%     | 0%  | -  | S  | S  | S  | -  | -  | -  |
|           | 5%  | -  | S  | S  | -  | -  | -  | -  |
|           | 10% | -  | S  | -  | -  | -  | -  | -  |
|           | 15% | -  | -  | -  | -  | -  | -  | -  |

N: non-significant; S: significant.

### 3.2. Rutting Property

The DSR test shows that the higher the $G^*/\sin \delta$ value, the less sensitive the binder is to permanent deformation, called rutting, at higher pavement temperatures. Figure 5 shows the $G^*/\sin \delta$ values of the binder before and after the RTFO aging process measured at 76 °C. The addition of SIS showed a clearly increasing $G^*/\sin \delta$ value with an increase in the content at both aging conditions, which means that the addition of SIS has a positive influence on the binder’s plastic deformation resistance. It is also considered that the addition of 5% TPU does not significantly improve rutting resistance compared to the unmodified PG 64-22 control binder. However, the TPU-with-SIS-modified asphalt binders exhibited higher $G^*/\sin \delta$ values compared to the SIS binders without TPU at both aging conditions.
thus demonstrating the positive effect of TPU on the rutting resistance of the polymer-modified asphalt binder. Furthermore, in the case of the 5% SIS-modified binder containing 5% TPU, the $G^*/\sin \delta$ value measured at 76 °C was 5 kPa or higher both before and after short term aging, which is considered to be a level that can sufficiently satisfy the high-temperature grade of 82.

![Figure 5. $G^*/\sin \delta$ values of the asphalt binder containing 5% TPU and SIS at 76 °C.](image)

The statistical analysis results of $G^*/\sin \delta$ values are shown in Table 5. Generally, the data show that the added SIS significantly affects the $G^*/\sin \delta$ values within each aging level. Furthermore, it was found that the difference in TPU in SIS-modified binders, except for the comparison of the base binder and TPU 5%, was significant at both aging states. According to the SIS content, the $G^*/\sin \delta$ values were found to have statistically significant differences in both aging states, indicating that the effect of the SIS content was statistically evident on the plastic deformation characteristics.

**Table 5. Statistical analysis results of the $G^*/\sin \delta$ values as a function of the addition of TPU and SIS content ($\alpha = 0.05$).**

|                  | Control          | TPU5%            |
|------------------|------------------|------------------|
|                  | SIS content      | SIS Content      |
|                  | 0%   5% 10% 15%  | 0%   5% 10% 15%  |
| **Control**      |                  |                  |
| 0%               | - S S S N S S S S |
| 5%               | - S S S S S S S S |
| 10%              | - S S S S S S S S |
| 15%              | - S S S S S S S S |
| **SIS content**  |                  |                  |
| 0%               | - S S S S S S S S |
| 5%               | - S S S S S S S S |
| 10%              | - S S S S S S S S |
| 15%              | - S S S S S S S S |
| **TPU5%**        |                  |                  |
| 0%               | - S S S S S S S S |
| 5%               | - S S S S S S S S |
| 10%              | - S S S S S S S S |
| 15%              | - S S S S S S S S |

N: non-significant; S: significant.
3.3. Multiple Stress Creep Recovery (MSCR) Test

An MSCR test was performed according to AASHTO TP 70 with a short-term aged binder for further evaluation of rutting characteristics. The MSCR test method is a technical improvement to better show the high-temperature performance characteristics related to plastic deformation compared to the current performance grade (PG) specification [21]. Non-recoverable creep compliance ($J_{nr}$) after deformation indicates the susceptibility to plastic deformation of the polymer-modified binder. Besides, %rec shows the delayed elasticity development of the asphalt binder, and high elasticity delay means that the binder has a significant elastic component at the test temperature.

As shown in Figure 6a, the addition of SIS reduced the $J_{nr}$ value in the PMA binder. On the other hand, it was observed that the addition of TPU slightly increased the $J_{nr}$ value. The %rec of the binders is also presented in Figure 6b. The 15% SIS binder showed approximately 50% recovery, whereas the same content of SIS-modified binder containing 5% TPU reduced the recovery rate by 12%. This result is contrary to the fact that the addition of TPU was positive in increasing the $G^*/\sin \delta$ values and raising the high-temperature grade. The reason for the reduced elasticity of the polymer binder at a high temperature is the effect of lowering the viscosity. Furthermore, this result verified the reasoning of why it is important to measure not only the $G^*/\sin \delta$ values but also the $J_{nr}$ and %rec of PMA binders.

The statistical significance of $J_{nr}$ and %rec measured with a short-term aged binder by the addition of TPU and SIS contents was analyzed. Table 6 shows the statistical results. First, it was found that in both $J_{nr}$ and %rec, the effect of improving plastic deformation due to elasticity according to the content of SIS was statistically significant. On the other hand, the impact of increasing the $J_{nr}$ value by the addition of TPU was found to be statistically effective in all binders except for SIS15%.

![Figure 6. Cont.](image-url)
Figure 6. Variations in creep compliance and percent recovery of the PMA binder with 5% TPU and SIS at 76 °C; (a) $J_{nr}$ and (b) %rec, respectively.

Table 6. Statistical analysis results of the multiple stress creep recovery (MSCR) as a function of the addition of TPU and SIS content ($\alpha = 0.05$).

| SIS content | Control | TPU5% |
|-------------|---------|-------|
|              | SIS     |       |
| 0%          | - S     | S     |
| 5%          | - S     | S     |
| 10%         | - S     | S     |
| 15%         | - S     | S     |

%rec

| SIS content | Control | TPU5% |
|-------------|---------|-------|
|              | SIS     |       |
| 0%          | - S     | S     |
| 5%          | - S     | S     |
| 10%         | - S     | S     |
| 15%         | - S     | S     |

N: non-significant; S: significant.

3.4. Fatigue Cracking Property

According to the Superpave binder specification, the product of the complex shear modulus $G^*$ and the phase angle sine ($\delta$) is applied to control the fatigue of the asphalt pavement. Lower $G^*\sin \delta$
values are considered desirable in terms of fatigue crack-resistance. DSR was used to measure the $G^\ast \sin \delta$ value (RTFO+PAV aging) at 25 °C. The results are shown in Figure 7. The PG 64-22 binder showed the highest $G^\ast \sin \delta$ value among all binders. However, with 5% TPU, the $G^\ast \sin \delta$ value of the base binder reduced by 10%. This trend was also observed in the SIS-modified binder. All SIS-modified binders with 5% TPU showed lower $G^\ast \sin \delta$ values compared to those of general SIS PMA binders, indicating that the addition of TPU plays a vital role in improving the fatigue cracking resistance. Meanwhile, the addition of SIS content was observed to have decreased the $G^\ast \sin \delta$ values with the increased content, and at 15% SIS, the result was significantly reduced, which is less than 1000 kPa. The blending of SIS and TPU at the same time could be considered as an effective solution to reduce the deterioration of pavements due to fatigue cracking.

Figure 7. $G^\ast \sin \delta$ values of the polymer-modified asphalt (PMA) binder with 5% TPU and SIS at 25 °C.

The statistical significance of the $G^\ast \sin \delta$ value according to the addition of TPU and SIS content was investigated. The results are shown in Table 7. The results showed that the SIS content had a significant effect on the binder’s $G^\ast \sin \delta$ value. Moreover, the incorporation of TPU with SIS PMA binder was found to have a statistically significant difference in the $G^\ast \sin \delta$ value at the 5% confidence level. There was no statistically significant difference between SIS5% and TPU5% and SIS10% and SIS5%+TPU5%, showing that the addition of TPU has a similar level of crack improvement effect as the addition of SIS.

Table 7. Statistical analysis results of the $G^\ast \sin \delta$ value as a function of the addition of TPU and SIS content ($\alpha = 0.05$).

| SIS content | Control | TPU5% |
|-------------|---------|-------|
| $G^\ast \sin \delta$ at 25 °C (RTFO+PAV) | SIS Content | 0% 5% 10% 15% 0% 5% 10% 15% |
| Control | 0% | - S S S S S S |
| | 5% | - S S N S S S |
| | 10% | - S S N S S S |
| | 15% | - S S S S N |
| TPU5% | 0% | - S S S |
| | 5% | - S S S |
| | 10% | - S S S |
| | 15% | - |

N: non-significant; S: significant.
3.5. Thermal Cracking Property

Superpave asphalt binder specifications include a maximum 300 MPa or less for creep stiffness. The decrease in stiffness reduces the tensile stress in the asphalt binder to prevent thermal cracking. A BBR test was conducted at \(-18 \, ^\circ C\) to investigate the effects of SIS content and the addition of TPU on low-temperature cracking performance. The stiffness and \(m\)-values of the PMA binders with SIS added with or without TPU were measured. Both results, stiffness and \(m\)-value, are shown in Figures 8 and 9, respectively. In general, similar trends were found, such as in the fatigue cracking results. When SIS was added to the base binder and 5% TPU-modified binder, the stiffness values of the binders were reduced. In addition, all the SIS-modified binders containing 5% TPU showed lower stiffness values compared to the general SIS-modified binders. It is worth noting that in the binder with 10% SIS, after the addition of 5% TPU, the stiffness value decreased by approximately 37%. In addition, unlike the fatigue strength results in which the effect of TPU was not evident in the SIS15% binder, the thermal cracking characteristics result showed a stiffness value that was about 28% lower in the binder with TPU compared to the same SIS15% binder. The SIS15% (with and without 5% TPU) modified binder and TPU5%+SIS10% binder satisfy the maximum rigidity of 300 MPa at \(-18 \, ^\circ C\). However, the binders that met the minimum \(m\)-value of 0.3 were binders modified with SIS 15%.

![Stiffness of the PMA binders with 5% TPU and SIS at \(-18 \, ^\circ C\).](image1)

![\(m\)-values of the PMA binders with 5% TPU and SIS at \(-18 \, ^\circ C\).](image2)
Table 8 represents the statistical analysis results of stiffness with varying TPU and SIS content. The results illustrate that there is a statistically significant difference in SIS content with respect to stiffness. This indicates that an increase in the SIS content results in a considerable change in the stiffness value. Statistical results of $m$-values are presented in Table 9. The data showed a significant difference in the $m$-value by the addition of the SIS content. Still, there was no significant difference, as some of the data in the general SIS-modified binders showed similar values with those of the SIS-modified binders including 5% TPU.

Table 8. Statistical analysis results of the stiffness as a function of the addition of TPU and SIS content ($\alpha = 0.05$).

| Stiffness | Control | TPU5% |
|-----------|---------|-------|
|           | SIS Content |       |
| 0%        | - | S | S | S | S | S | S |
| 5%        | - | N | S | N | N | N | S |
| 10%       | - | S | N | N | S | S |
| 15%       | - | S | S | S | N |
| TPU5%     |           |       |
| 0%        | - | N | S | S |
| 5%        | - | S | S |
| 10%       | - | S |
| 15%       | - | - |

N: non-significant; S: significant.

Table 9. Statistical analysis results of the $m$-value as a function of the addition of TPU and SIS content ($\alpha = 0.05$).

| $m$-value | Control | TPU5% |
|-----------|---------|-------|
|           | SIS Content |       |
| 0%        | - | N | S | S | N | S | S |
| 5%        | - | S | S | N | N | S | S |
| 10%       | - | S | S | N | N | S |
| 15%       | - | S | S | S |
| TPU5%     |           |       |
| 0%        | - | N | S | S |
| 5%        | - | S |
| 10%       | - | S |
| 15%       | - | - |

N: non-significant, S: significant.

4. Summary and Conclusions

The performance characteristics of polymer-modified asphalt binders, improved by the addition of TPU and SIS, were evaluated. The study was conducted with a 5% TPU content set, and three different percentages of SIS contents were applied. All binders were prepared by a wet process and aged using RTFO and PAV. A series of Superpave asphalt binder tests were performed using a rotational viscometer, DSR, and BBR in order to evaluate the physical and rheological properties of the binders. In addition, the plastic deformation characteristics were assessed through an MSCR test. From the results, the following conclusions were drawn:
1. The SIS modifier significantly increased the binder viscosity, but the addition of TPU had an insignificant effect on viscosity. This means that unlike conventional polymeric materials, TPU makes it possible to produce improved mixtures without increasing the binder viscosity.

2. The results of $G^*/\sin \delta$ values showed that the addition of TPU and SIS significantly improved the rutting resistance of the PMA binders.

3. In the MSCR test results, as the SIS content increased, the $J_{nr}$ value significantly decreased. Furthermore, it was observed that TPU had little influence on improving binder elasticity.

4. The fatigue cracking results showed that both polymer materials of TPU and SIS are effective in improving crack resistance at intermediate temperature.

5. According to the results of the BBR test measured at $-18$ °C, the stiffness value was found to decrease with 5% TPU and the higher percentage of SIS. It indicated that both additives have a positive effect on low temperature cracking property.

6. Through the overall results, both additives were found to upgrade the performance of the base binder. It is considered that the blending of the two polymer modifiers increased the elongation and tensile strength of the binder.

7. TPU is a polyester-based material with excellent wear resistance, low-temperature properties, and high hardness as an elastomer with perfect thermoplastic properties; on the other hand, SIS (styrene-b-isoprene-b-styrene) has isoprene as a rubbery midblock. The SIS molecule chain is composed of isoprene. It increases the complex modulus at high temperatures, and due to its branch methyl in the isoprene group, it has better tenacity and compatibility with other materials. Due to that, it can be observed that the addition of 5% TPU improved the rutting and cracking properties when added with SIS, without increasing the viscosity. The use of polymer modifiers results in the increase in binder and mixture viscosity properties, which leads to a decrease in workability during production and paving operations. TPU can be a good material to overcome this challenge.

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References

1. Cao, M.; Li, Y.; Fang, M. To discuss the asphalt pavement’s early damages. In Proceedings of the International Conference on Civil Engineering and Urban Planning, Yantai, China, 18–20 August 2012; pp. 795–798.

2. Chen, D.H.; Bilyeu, J.; Scullion, T.; Nazarian, S.; Chiu, C.T. Failure investigation of a foamed-asphalt highway project. J. Infrastruct. Syst. 2006, 12, 33–40. [CrossRef]

3. Bazmara, B.; Tahersima, M.; Behravan, A. Influence of thermoplastic polyurethane and synthesized polyurethane additive in performance of asphalt pavements. Constr. Build. Mater. 2018, 166, 1–11. [CrossRef]

4. Fuensanta, M.; Jofre-Reche, J.A.; Rodriguez-Llansola, F.; Costa, V.; Martín-Martinez, J.M. Structure and adhesion properties before and after hydrolytic ageing of polyurethane urea adhesives made with mixtures of waterborne polyurethane dispersions. Int. J. Adhes. Adhes. 2018, 85, 165–176. [CrossRef]

5. Tantisattayakul, T.; Kanchanapiya, P.; Methacanon, P. Comparative waste management options for rigid polyurethane foam waste in Thailand. J. Clean. Prod. 2018, 196, 1576–1586. [CrossRef]
6. Gonzalez, M.N.G.; Levi, M.; Turri, S. Development of polyester binders for the production of sustainable polyurethane coatings: Technological characterization and life cycle assessment. *J. Clean. Prod.* 2017, 164, 171–178. [CrossRef]

7. Dobslaw, D.; Woiski, C.; Winkler, F.; Engesser, K.H.; Dobslaw, C. Prevention of clogging in a polyurethane foam packed biotrickling filter treating emissions of 2-butoxyethanol. *J. Clean. Prod.* 2018, 200, 609–621. [CrossRef]

8. Xia, L.; Cao, D.W.; Zhang, H.Y.; Guo, Y.S. Study on the classical and rheological properties of castor oil-polyurethane prepolymer (C-PU) modified asphalt. *Constr. Build. Mater.* 2016, 112, 949–955. [CrossRef]

9. Xu, C.; Zhang, Z.; Zhao, F.; Liu, F.; Wang, J. Improving the performance of RET modified asphalt with the addition of polyurethane prepolymer (PUP). *Constr. Build. Mater.* 2019, 206, 560–575. [CrossRef]

10. Polacco, G.; Stastna, J.; Biondi, D.; Antonelli, F.; Vlachovicova, Z.; Zanzotto, L. Rheology of asphalts modified with glycidyl methacrylate functionalized polymers. *J. Colloid Interface Sci.* 2004, 280, 366–373. [CrossRef]

11. Navarro, F.J.; Partal, P.; García-Morales, M.; Martinez-Boza, F.J.; Gallegos, C. Bitumen modification with a low-molecular-weight reactive isocyanate-terminated polymer. *Fuel* 2007, 86, 2291–2299. [CrossRef]

12. Becker, M.Y.; Muller, A.J.; Rodriguez, Y. Use of rheological compatibility criteria to study SBS modified asphalts. *J. Appl. Polym. Sci.* 2003, 90, 1772–1782.

13. Zhu, J.; Birgitsson, B.; Krings, N. Polymer modification of bitumen: Advances and challenges. *Eur. Polym. J.* 2014, 54, 18–38. [CrossRef]

14. Kim, H.H.; Mazumder, M.; Lee, M.S.; Lee, S.J. Evaluation of high-performance asphalt binders modified with SBS, SIS, and GTR. *Adv. Civ. Eng.* 2019, 2019, 1–11. [CrossRef]

15. Zhang, F.; Hu, C.; Zhang, Y. The research for SIS compound modified asphalt. *Mater. Chem. Phys.* 2018, 205, 44–54. [CrossRef]

16. Mazumder, M. *Characterization of Crack Sealant Materials and Implementation Techniques*; ProQuest: Ann Arbor, MI, USA, 2019.

17. Bahia, H.U. Critical evaluation of crack modification using strategic highway research program concepts. *Transp. Res. Rec.* 1995, 1488, 82–88.

18. AASHTO T 313. *Standard Method of Test for Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer (BBR)*; ASTM International: West Conshohocken, PA, USA, 2016. Available online: https://www.fhwa.dot.gov/pavement/materials/hmec/pubs/module_f/lab_manual_asphalt.pdf (accessed on 30 November 2020).

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