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Compound Modification of Asphalt with SBS and Waste PET Functionalized Additives

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Abstract

The modification of asphalt binder using recycled plastics such as polyethylene terephthalate (PET) may improve its rheological characteristics while providing secondary environmental benefits. In this study, the chemical recycling of PET was conducted to synthesize additives and used in conjunction with styrene-butadiene-styrene (SBS) to modify asphalt binder. The properties of the modified asphalt binder (PS-MB) were characterized through both conventional binder tests, including penetration, softening point, viscosity, and storage stability tests, and Superpave binder tests, such as multiple stress creep recovery (MSCR), rutting factor (G*/Sinδ), fatigue factor (G*Sinδ), and low temperature creep stiffness tests. These properties were then compared with those of the unmodified asphalt binder and asphalt binder modified with SBS (S-MB). To study the effects of PET additives on the physical and chemical structures of S-MB, additional analyses were done using scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy. The outcomes of the laboratory investigation indicated that using waste PET derived additives as modifiers for SBS modified asphalt binder not only provides a functioning way to recycle waste PET, but also enhances the rheological properties of SBS modified asphalt binder as a paving material.

Keywords: SBS, value-added recycling, PET, modified asphalt

1. Introduction

With the rapid increase of axle load, traffic volume and severe climatic change, modification of asphalt often becomes necessary to enrich the functioning of asphalt pavement and prevent various pavement distresses, such as cracking, rutting and raveling. Polymer modification has shown to be one of the most efficient methods to advance pavement performance (Zhu et al.2014). Many research studies have implied that the engineering properties, both at high and low temperatures can be improved significantly by polymer modification (Padhan et al. 2019, Isacsson & Lu 1999). Two types of polymers have been used as a modifier for asphalt, namely thermoplastic elastomers, such as styrene-butadiene-styrene (SBS) and the other type called plastomers, such as ethylene vinyl acetate (EVA) and polyoctenamers (Ameri et al. 2012, Padhan et al. 2020, Isacsson & Lu 1999). Among the different types of polymers, SBS has been most frequently used, because of its excellent modification performance. However, previous research has indicated that SBS modified asphalt binder consistently displays thermodynamically unbalanced behaviour at high temperatures leading to premature phase separation and degradation of its long polymeric chain to smaller molecules (Pérez-Lepe et al. 2007; Soenen et al. 2008). Further, the superior manufacturing cost of SBS based modified asphalt also restricts its widespread use. To address these problems, studies have been performed to advance the compatibility, storage stability and rheological properties of SBS modified asphalt binder using new additives and other polymers in conjunction (Martín-Alfonso et al. 2008; Airey et al. 2003). From a commercial and environmental point of view, the reuse of waste materials such as waste plastic and waste tyres to partially substitute virgin polymeric materials would be obviously favored (Huang et al. 2007, Mohanta et al. 2019). An example of such as a polymer is polyethylene terephthalate (PET), which is a generic type of plastomer that is mainly used as a packaging material for containers and bottles. The widespread consumption of PET has created a major environmental hazard due to its poor biodegradable nature (El Mejjatti et al. 2014). PET recycling is hence widely encouraged and conducted using two modes of recycling: physical recycling and chemical recycling. Out of these, chemical recycling is more preferred as the recycled product does not need to be landfilled. Furthermore, the value-added products obtained after chemical recycling can increase the overall life cycle of PET (Silva et al. 2017). The use of PET based additives as a modifier for asphalt has been investigated by researchers and indicated mixed results. An advantage of using PET for such uses is that it does not need to be further purified or pretreated, such as removal of colors and other minor impurities to the same extent as other recycling applications might require. The prior studies which mainly involved the mixing of PET in asphalt mixtures used a dry method and reported an enhancement in rutting and fatigue related properties (Garcia-Morales et al. 2006; Ameri et al. 2016). Nevertheless, asphalt modified with PET has not generated much interest in the pavement community mainly as a result of its unstable nature, which may lead to phase separation issues at high temperatures due to deficient mixing (Zhu et al. 2014). A process involving homogenous mixing through a wet process is likely appropriate for real-world pavement applications (Gürü et al. 2014; Leng et al. 2018a). Such homogenous mixing of asphalt binder and PET can be achieved by the chemical pre-treatment of PET through reaction processes such as aminolysis and glycolysis. In particular, depolymerisation of PET using amine-based degradation i.e. aminolysis has been investigated in detail and shown to be an effective recycling method (Shukla and Harad, 2006; Padhan and Sreeram, 2019). In some previous studies, aminolysis methods have used for PET functionalization and used as a modifier for bitumen mixtures. It was reported that these additives can help in increasing the fatigue cracking resistance in mixtures with reclaimed asphalt pavement (RAP) while also improve antistripping characteristics (Leng et al. 2018a; Sreeram et al. 2018). Another form of these additives was also used to improve the phase integrity of crumb rubber and bitumen in crumb rubber modified asphalt (Leng et al. 2018b).

Nevertheless, no work has been conducted regarding the possibility of using of such additives in SBS modified asphalt binder. Accordingly, the primary objective of the present study is to assess the prospect of utilizing chemically synthesized additives from waste PET through an aminolysis process as a compound modifier for SBS modified asphalt binder to advance its properties as a paving material. Different types of asphalt binder samples were firstly prepared, including virgin asphalt binder without modification as a control binder, virgin binder modified with SBS, and virgin binder collectively modified with SBS and PET additives. Rheological property tests were then conducted on these binder samples for comparison purposes. Lastly, the probable modification mechanism of the additives in the binder were explored through scanning electron microscope (SEM) and Fourier transform infrared (FTIR) analyses.

2. Experimental Program

2.1 Materials

Asphalt binder with a penetration grade of 60/70 (Pen 60/70) was employed as the neat asphalt binder, referred to as virgin binder in this study to produce SBS modified binder (S-MB) and PET additives and SBS modified binder (PS-MB). A linear block co-polymer SBS was used and its application content was 4% by weight of virgin binder. The waste PET bottles were procured to produce PET derived additives, and two percentage contents of PET additives were considered, 3% and 5%, by weight of virgin binder. Industrial grade ethanolamine was purchased from a local company for the degradation of PET.

2.2 Chemical Recycling of PET

An aminolysis process was adopted for the chemical recycling of PET as per the process reported by other researchers (Leng et al. 2018a, Shukla et al. 2006). The ratio of ethanolamine to PET flakes was 2:1, and the reaction mixture was refluxed for around 4 hours. The degradation process was conducted till the mixture was homogeneous after which the product was filtered out. As the PET degradation was accomplished, it was noted that the mixture became homogeneous. The obtained white crystals after filtering was the final product, named bis (2-hydroxy ethylene) terephthalamide (referred to as PET additives in this study), and was used for subsequent binder modification. The schematic diagram to produce the PET additives is shown in Figure 1 and represented by the reaction scheme in Figure 2. The additives obtained as the end product of the PET degradation was studied using FTIR analysis. Two characteristic peaks were observed at 1503 cm^{-1}, 1540 cm^{-1} and 1630 cm^{-1} for the aromatic group and two amide groups respectively as shown in Figure 3, which indicates the successful amine substitution as reported in previous studies (Leng et al. 2018a, Leng et al. 2018b).

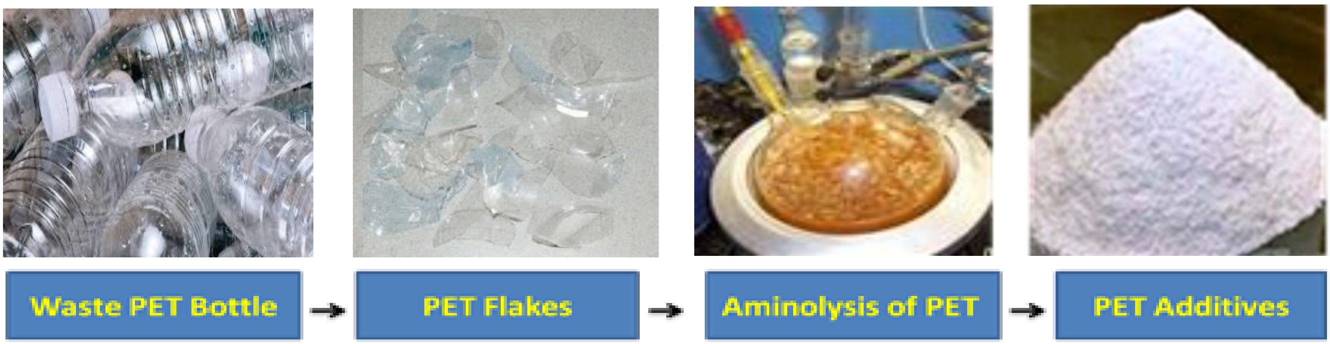

Figure 1. Schematic diagram for the production of PET additives (Sreeram et al. 2018)

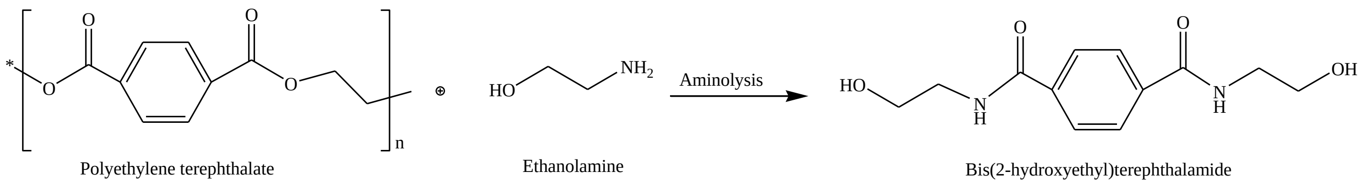

Figure 2. Aminolysis reaction of PET

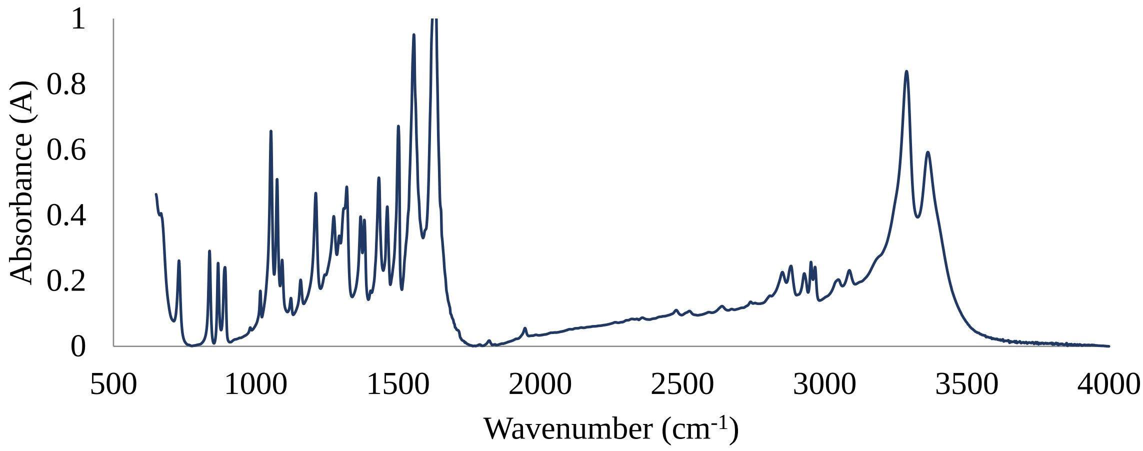

Figure 3. FTIR spectra of synthesized additive (400–4000 cm^{-1})

2.3 Asphalt Binder Modification

High shear mixing was employed to prepare the binders. The mixing speed used was around 5000 rpm for a duration of 2 hours at a temperature between 170 ^oC and 180 ^oC. The control S-MB was prepared with an SBS content of 4% and labeled as S-MB4. Two PS-MB binders with 3% and 5% of PET additives, and 4% of SBS, were prepared, and labelled as PS-MB3 and PS-MB5, respectively.

2.4 Experimental Procedure

Both rheological and microscopic characterization were conducted on the virgin binder, S-MB4, PS-MS3, and PS-MB5. To study the rheological behaviour of the prepared binders, conventional binder tests such as penetration, softening point, viscosity, storage stability tests and Superpave binder tests, including multiple stress creep recovery (MSCR), rutting factor (G*/Sinδ) and fatigue factor (G*Sinδ) tests using a dynamic shear rheometer (DSR) and low temperature tests using a bending beam rheometer (BBR), were conducted. The probable modification mechanism of the additives in the binders were analyzed through SEM and FTIR analyses. The experimental program of the study is detailed in Figure 4.

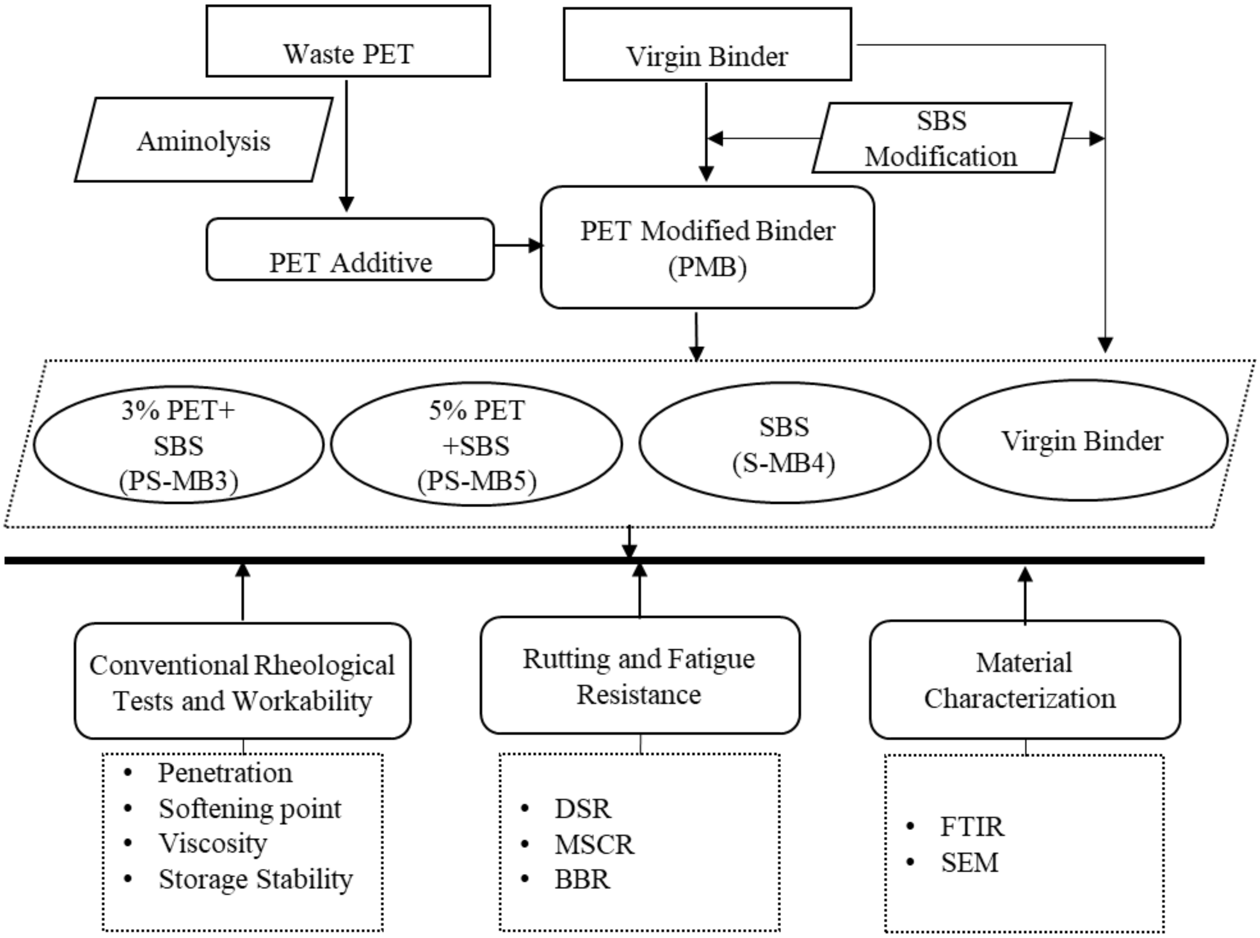

Figure 4. Experimental program flow chart

3. Results and Discussion

3.1 Conventional Rheological Tests

3.1.1 Penetration, Softening Point and Viscosity

The results of the penetration, softening point and viscosity tests are presented in Figure 5 and Figure 6, respectively. The penetration values of the S-MB4, PS-MB3 and PS-MB5 binders were decreased and their corresponding softening point were increased as compared to the virgin binder. The viscosities of the S-MB were also enhanced at the testing temperatures with the increase in the concentration of PET additives. Thus, it is expected that such PS-MB binders would offer improved performance in warmer environments as a result of the increased stiffness and higher viscosity.

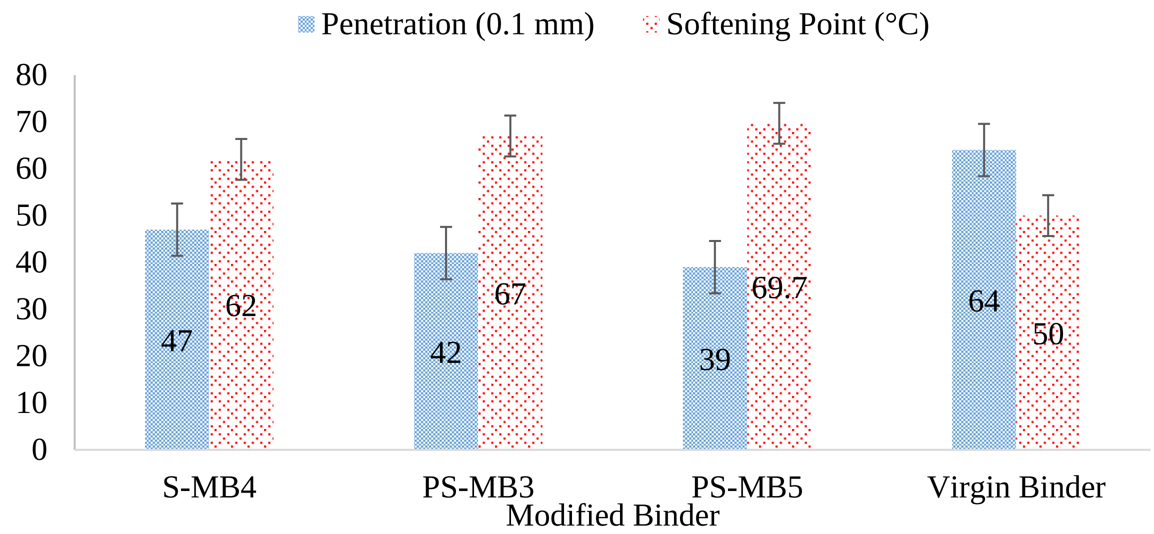

Figure 5. Penetration and Softening point test results

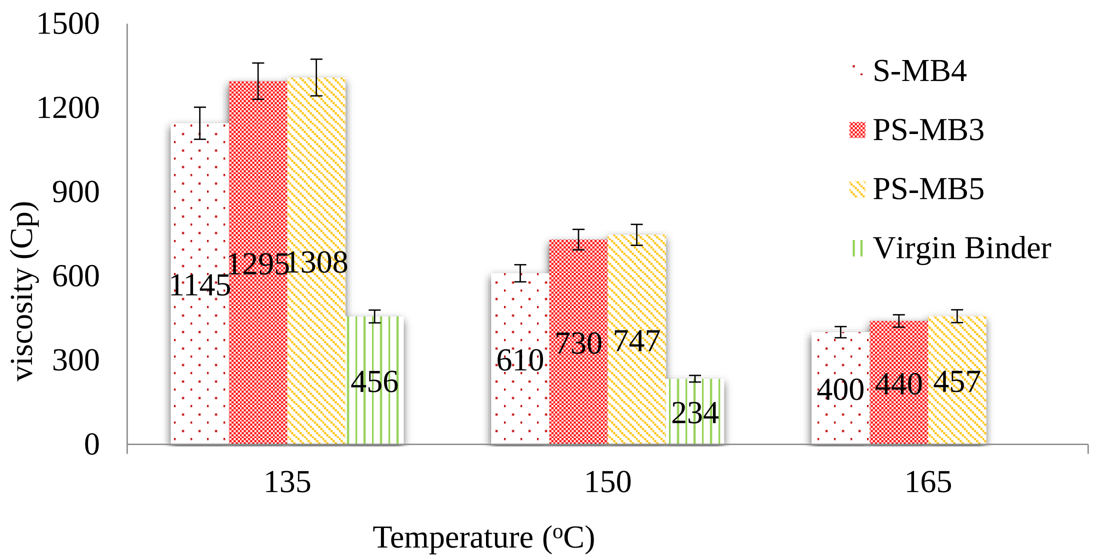

Figure 6. Viscosity test results

3.1.2 Storage Stability

The high temperature stability of SBS-PET modified binders was measured using traditional storage stability tests. To evaluate the storage stability, the PS-MB and S-MB binders was first dispensed into a cylindrical aluminum tooth paste tube with dimensions of 160 mm in height and 30 mm in diameter. Subsequently, the tube was kept perpendicularly in an oven at 163 °C for 48 hours, cooled and then cut into three equivalent segments (ASTM D5892). The lower and upper fractions were used to estimate the extent of phase separation of SBS-PET modified binders by measuring their softening points. The storage stability of binders is deemed good when the difference in softening point is low which designates that the polymer is dispersed equally (Polacco et al. 2015). As indicated in Figure 7, the supplementation of the PET additives efficiently reduced the difference between the softening point in the modified binders. It is likely that certain components in the PET additive can interacts chemically with styrene parts of SBS to form a more stable microstructure, which would help in the enhancement of storage stability of the tested binders. This is further discussed in the microscopic characterization section.

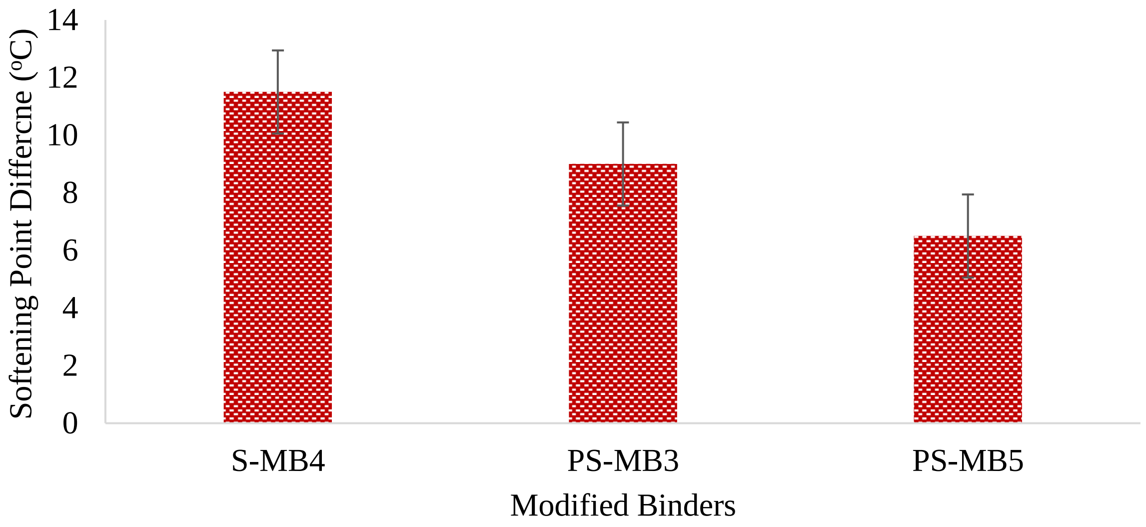

Figure 7. Storage stability results

3.2 Superpave Binder Characterization

3.2.1 DSR Test Results

Rheological measurements were conducted using the DSR for the original (unaged), RTFO-aged, and RTFO+PAV-aged binders to evaluate the parameters of rutting factor, G*/Sinδ, and fatigue factor, G*. Sinδ for each type of binder. Superpave specifications mandate that the lowest value for G*/Sinδ must be above 2.20 kPa and 1.00 kPa for RTFO-aged and unaged asphalt binders respectively. As per the test results shown in Figure 8 and Figure 9, S-MB4, PS-MB3, PS-MB5 were able to fulfil these requirements at 70 ^{o}C, 76 ^{o}C and 82 ^{o}C, respectively, designating that the two PS-MB binders have higher service temperatures than the S-MB binder and virgin binder. The parameter for evaluating the fatigue resistance is G*.Sinδ which is specified to have a value no greater than 5000 kPa for PAV aged binders. As shown in Figure 10, S-MB4, PS-MB3, and PS-MB5 met this fatigue criterion up to 16 ^{o}C, respectively. It was observed that 3% PET additives offered better resistance to fatigue damage by decreasing G*.Sinδ of the SBS modified binders at all test temperatures. At 13 ^{o}C, SBS modified binders were unable to fulfill the specification limit with a G*.Sinδ value of 5,860 kPa, but 3% PET additives brought it inside the restriction by reducing G*.Sinδ to 4760 kPa. With 5% of PET additives, its fatigue resistance is similar to that of S-MB, but worse than that of the PS-MB with 3% PET derived additives. Hence, the integration of the PET additives can potentially further improve the fatigue resistance of S-MB.

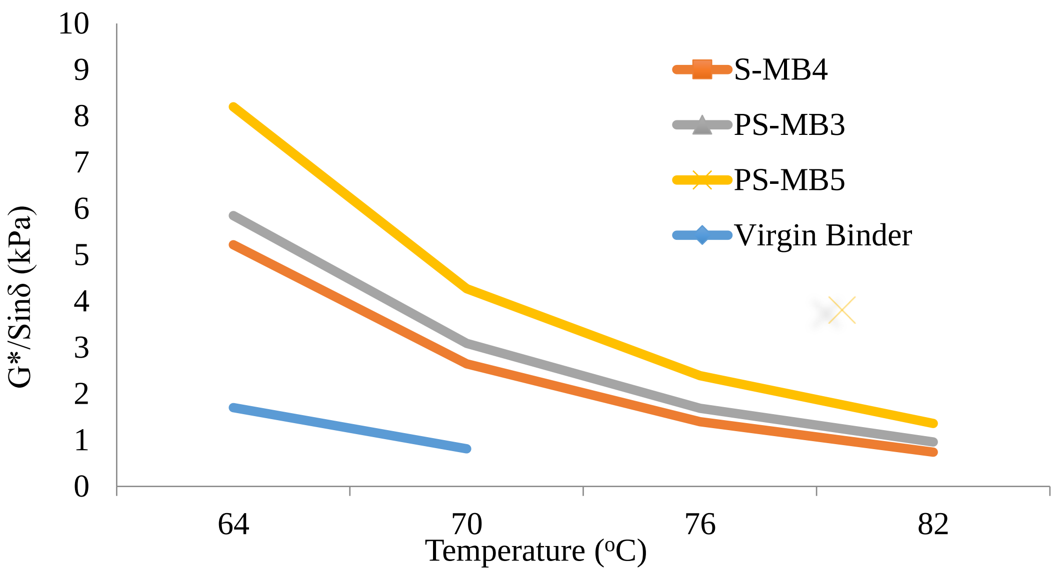

Figure 8. G*/Sin(δ) (kPa) vs Temperature of unaged binder

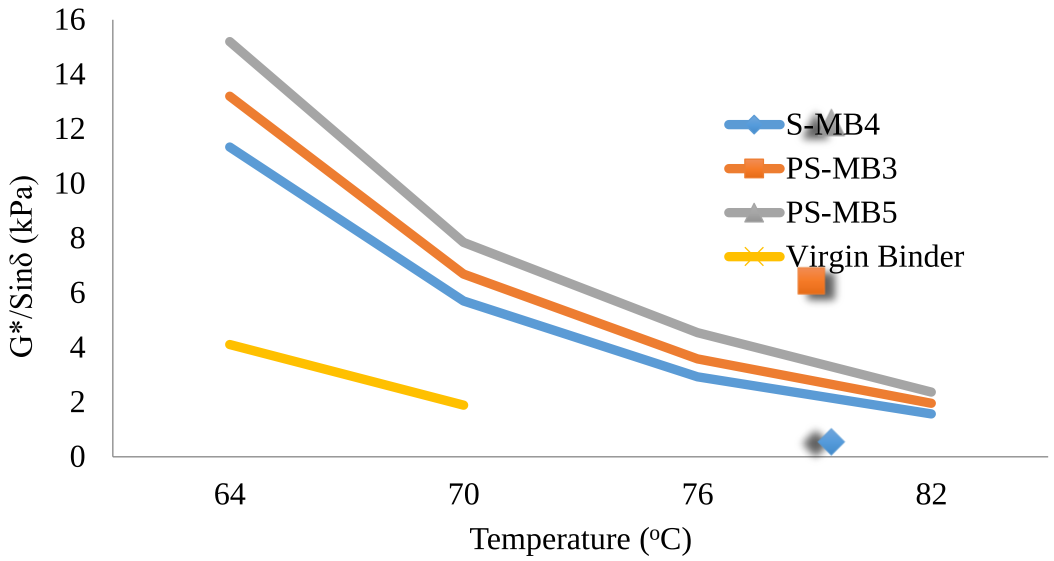

Figure 9. G*/Sin(δ) (kPa) vs Temperature of RTFO-aged binder

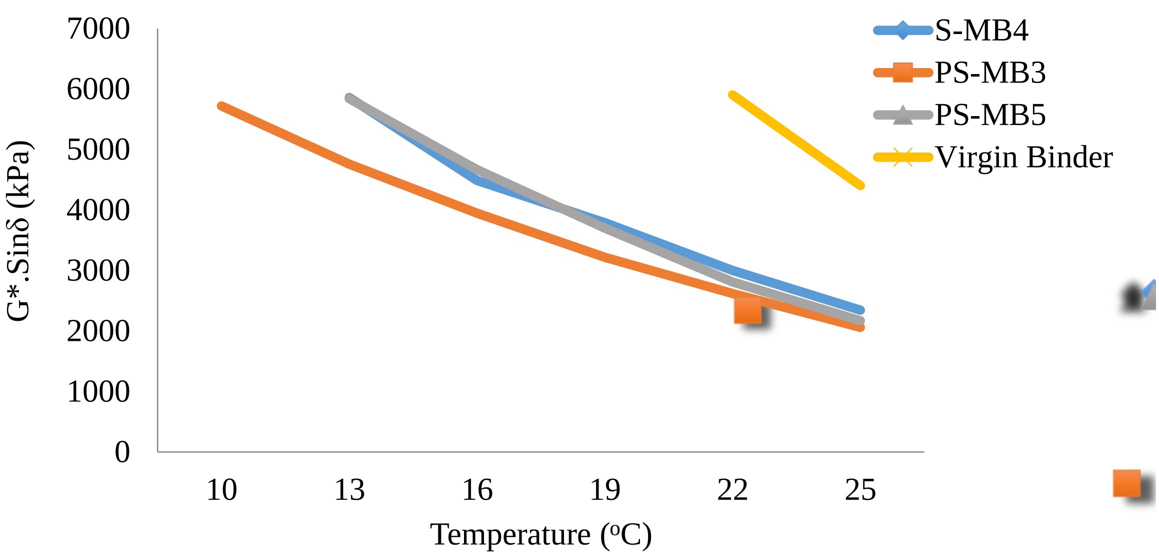

Figure 10. *G**.Sin(*δ*) (kPa) vs temperature of PAV-aged binder

3.2.2 MSCR Test Results

The elastic response of the tested binders at the shear stress levels of 0.1 and 3.2 kPa was characterised using the MSCR tests. Figure 11 and Figure 12 present the results in relation to the % recovery and non-recoverable compliance (J_{nr}) at 70 °C for distinctive stress levels. From Figure 11, it can be recognized that the increase of PET additive contents has insignificant benefit to the percentage recovery results of SBS modified binder. As detected from Figure 12, the values of J_{nr} increased when the level of stress was also amplified. At 0.1 kPa, the modified binders S-MB4, PS-MB3 & PS-MB5 have J_{nr} values of 0.957, 0.861 and 0.723 kPa^{-1}, respectively, while at 3.2 kPa, these values were significantly increased to 1.419, 1.214 and 1.092 kPa^{-1}, respectively. In addition, it can be noted that the J_{nr} values of PS-MB3 and PS-MB5 are lower than those of S-MB4 at both stress levels. Furthermore, when the PET additive percentage increased from 3% to 5%, the J_{nr} values of PS-MB decreased. Overall, the test results indicated that incorporating PET additives to S-MB4 will largely improve its rutting resistance. These results were coherent with the G*/sin(δ) values attained from the PG grading tests.

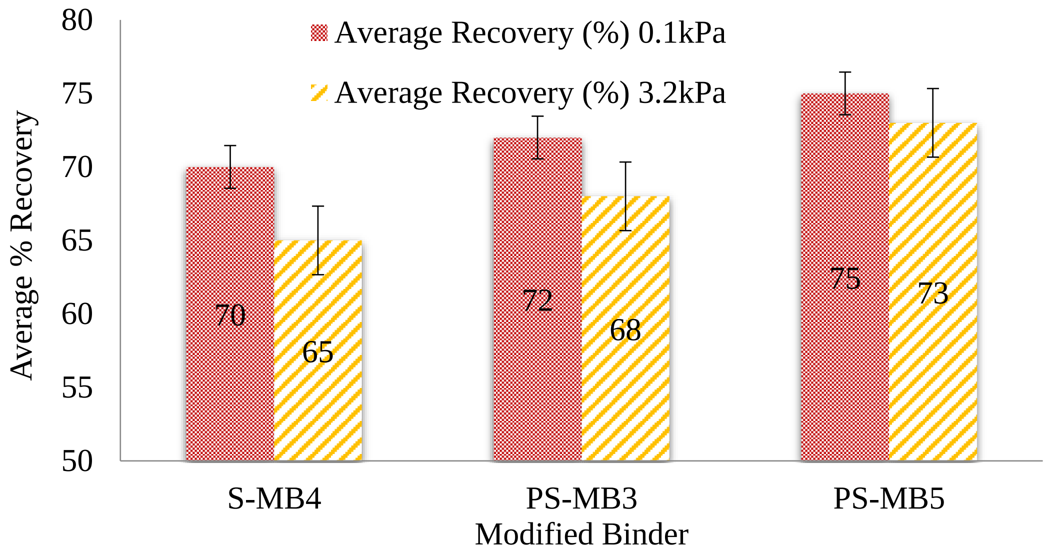

Figure 11. Average % recovery at 70 °C

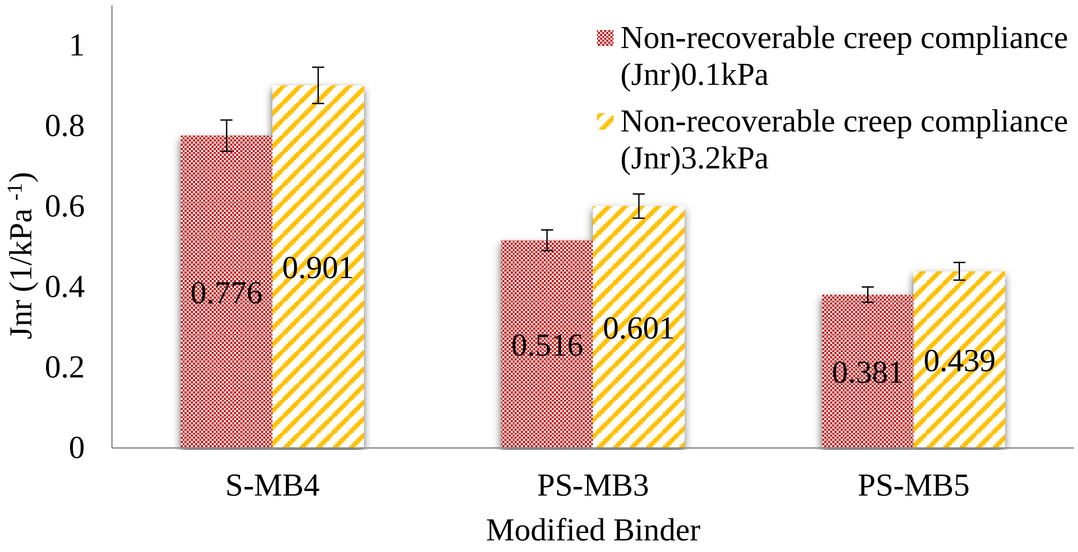

Figure 12. J_{nr} values at 70 °C

3.2.3 Frequency Sweep Test

A frequency range between 0.01 to 600 rads/sec was utilised to conduct the frequency sweep tests. The tests were implemented using the DSR at 60°C using a 25mm diameter plate and 1 mm gap. The addition of PET additives led to modified binders that have higher G* values and showed superior performance at higher temperatures and low frequencies as compared to the virgin binder and SBS modified binders (Figure 13). Also, a noteworthy difference between phase angles ((δ (°)) of the virgin binder and S-MB4 (Figure 14) was also observed. PET modified asphalt binders on the other hand show similar values of δ (°) as S-MB4 which indicates comparable elastic response behaviour.

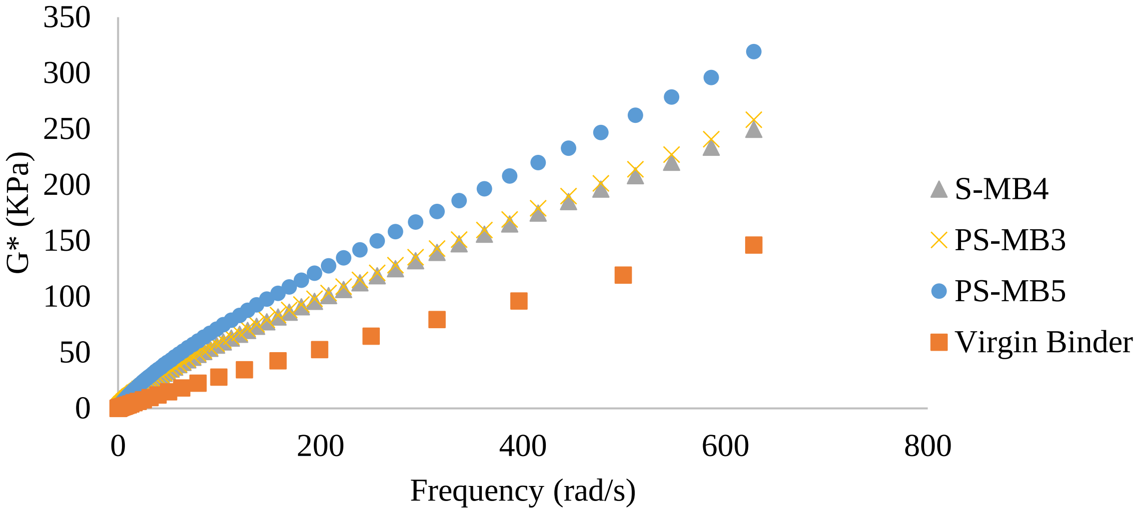

Figure 13. G* vs Frequency at 60 °C

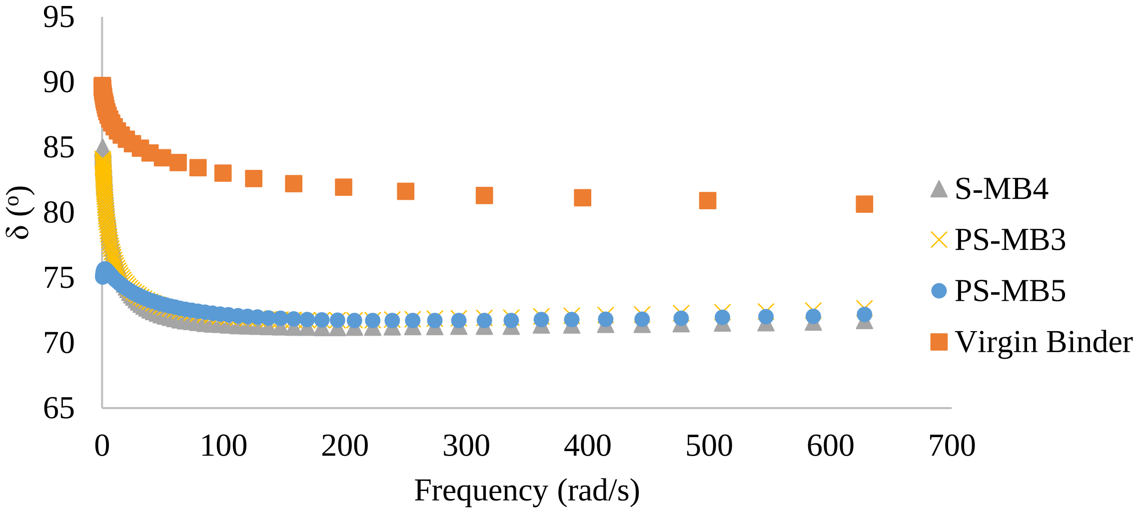

Figure 14. Phase angle (δ) vs Frequency at 60 ºC

3.2.4 BBR Test

The BBR test was utilised to identify the low temperature performances of S-MB4, PS-MB3 and PS-MB5. The test temperatures ranged from -6 ºC to -18 ºC; and the concerned parameters of creep stiffness (S-value) and creep rate (m-value) of the various binders were evaluated. As indicated in Figure 15, when the content of PET additive was increased, the S-value of S-MB4 increased gradually. Among the functionalized binders, PS-MB3 exhibited the greatest capability to counter low temperature cracking, satisfying the specification standard of 300 MPa up to -12^{o}C. For m-value, a number larger than 0.3 is commonly desired which all the test specimens met up to -12^{o}C as shown in Figure 16. It should be stated that the modified binders did not outperform the virgin binder and was seen to be in same performance grade. Overall, the results demonstrated that binders containing PET additives can provide marginally better properties as compared to conventional SBS modified binders when it comes to low temperature cracking.

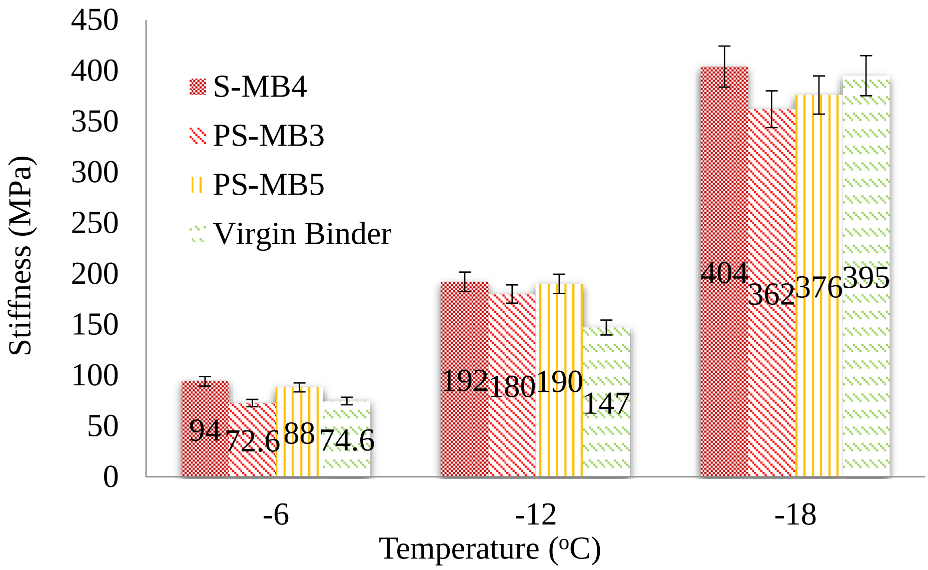

Figure 15. Stiffness vs Temperature

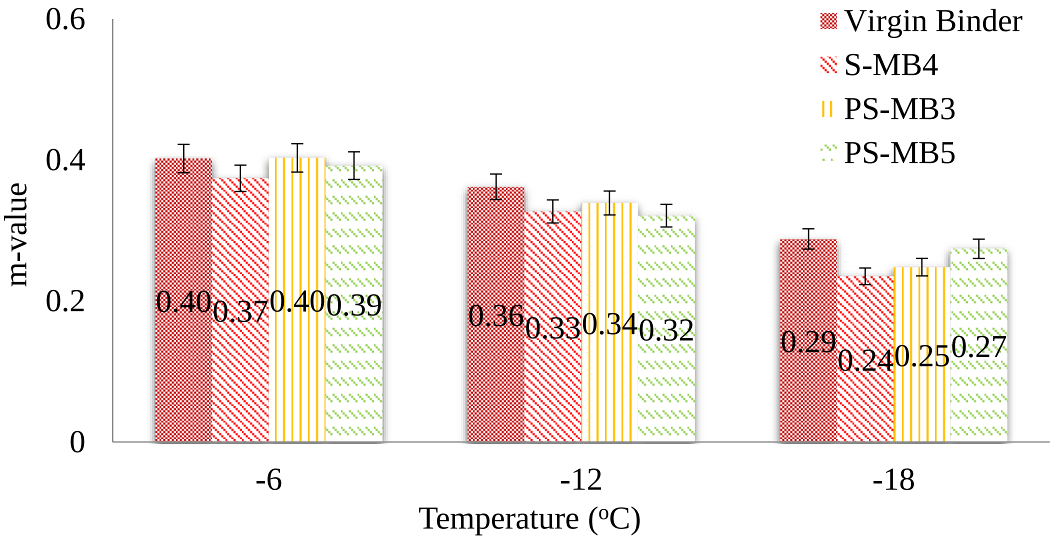

Figure 16. m-value vs Temperature

3.4 Microscopic Characterization

3.4.1 FTIR Test Results

The FTIR spectra of the different binder samples are shown in Figure 17. The peaks observed at around 1030 cm^{-1} for the virgin binder, S-MB binder and PS-MB binder are attributed to the sulfoxide bonds (S=O) due to the oxidation effects of short-term aging. Additionally, the absorbance peaks of butadiene and styrene were characterised around 966 cm^{-1} and 700 cm^{-1}, respectively. SBS co-polymer is constituted of styrene and butadiene, such functional groups are not present in the virgin binder. Consequently, the absorbance peaks around 966 cm^{-1} and 700 cm^{-1} can be utilized to pinpoint SBS modified binders. Furthermore, the FTIR spectra of PS-MB show the presence of new absorbance bands at around 930 cm^{-1}, which do not occur in either the PET additives or S-MB. Hence, it can be postulated that there is not only physical interaction taking place, but also the probability of some chemical interaction between SBS and PET additives (Wu et al. 2009, Masson et al. 2001). Nevertheless, more rigorous chemical tests are required to confirm this and is outside the scope of this work.

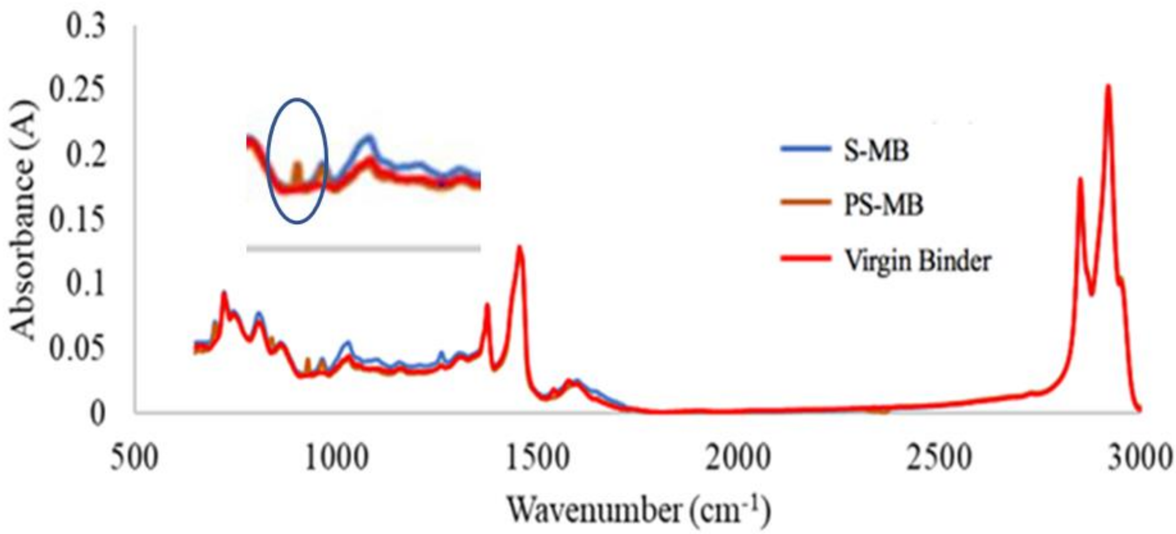

Figure 17. FTIR spectrum of binder samples

3.4.2 SEM Image Analysis

The morphological characteristics of the binders were evaluated by the means of a Tescan VEGA3 scanning electron microscope, operating at 20 kV with a magnification of 100,000X at ambient temperature. The samples were coated with gold plating using a SCD 005 sputter coater before testing. Figure 18 shows the SEM images of the PET additives, S-MB, and PS-MB samples. It was noted from the SEM image of PS-MB that PET additives were seen to be in a state of good dispersion in the asphalt binder matrix. After mixing the PET additives with S-MB, possible new structures were detected in the modified binder. The PET additives (white particles in asphalt matrix) were seen to be glued uniformly with the S-MB binder.

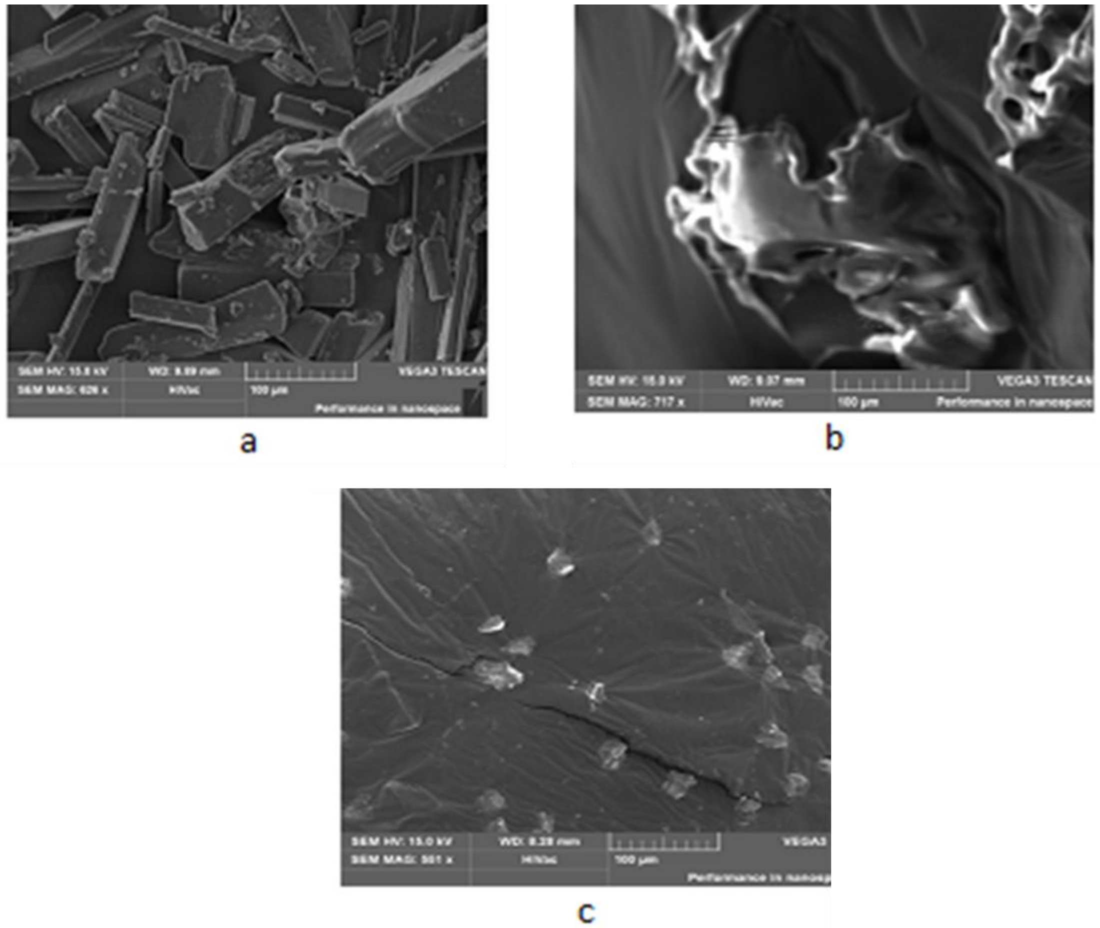

Figure 18. SEM image of: a) PET derived additives; b) S-MB; c) PS-MB

4. Conclusions

In this work, PET based additives were chemically synthesized from waste PET bottles and utilized as a performance enhancing modifier for SBS modified asphalt binder. The results of PET derived additives on the SBS modified binder were examined through both rheological property tests and material characterization. The key findings of this work are summarized below:

- PET derived additives were seen to increase the viscosity and softening point, and lower the penetration of S-MB4.
- Modified binders were seen to have better storage stability after the addition of the PET additives.
- PET additives enhanced the rutting performance of SBS modified binders. The rutting resistance properties of the PS-MB binders rises with the increase in the % of PET additive dosage.
- PS-MB3 provided better fatigue cracking resistance compared with S-MB. Thus, PET additives can also improve the fatigue resistance of SBS modified binder depending on the amount of additive used.
- The MSCR test results of PS-MB binders designated that the J_{nr} values of the PS-MB binders are larger than the S-MB binder. With the increase of PET additive percentage, the J_{nr} values of the PS-MB binders increase.
- FTIR and SEM analysis indicated that there could be some chemical interaction between the SBS polymer and PET additives, which in turn may validate the rheological results observed.

Overall, from the result of the experiments in this study it can be ascertained that the integration of PET additives has substantial positive consequences on the rheological properties of SBS modified binder at different temperature ranges. Future studies will be fixated on performing mixture tests to determine the feasibility for field applications.

5. Acknowledgement

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