

## Research Article

# High-Temperature Performance Enhancement of Bitumen by Waste PET-Derived Polyurethane

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Bitumen performance enhancement through modification by reactive polymers gained significant attention in the road construction industry. Polymeric bitumen additives, such as polyurethane, improve bitumen properties at low and high in-service temperatures. This research aimed to increase the polymer content (polyurethane) from 3% to 5%wt of bitumen by introducing cross-linking agent, sulfur. Synthesis of polyurethane was via in situ polymerization of bis (2-hydroxyethyl) terephthalamide (BHETA) in the presence of bitumen with sulfur as a cross-linking agent. BHETA was produced from polyethylene terephthalate (PET) by an aminolysis reaction. Penetration and softening point, frequency sweep test, performance grade (PG) and multiple stress creep recovery (MSCR) were evaluated to compare base and modified bitumen. Results show that the penetration and softening point of modified binders were reduced and increased, respectively, the frequency sweep test indicated improvement in viscoelastic properties of modified bitumen, PG of base bitumen was enhanced by two grades, i.e., from 58°C to 70°C, and the nonrecoverable creep compliance was increased by 81.82% at polymer content of 4% and sulfur content of 0.2%. The FTIR spectra of modified bitumen confirmed the formation of urethane linkages. Therefore, aminolysis of waste PET and in-situ polymerization to produce polyurethane can be applied to improve the performance of bitumen at high temperatures.

## 1. Introduction

Bitumen as a binder for pavement materials has a great impact on the performance of road pavements. The performance of asphaltic bitumen is highly dependent on the temperature of the area to be used; it is brittle and hard in cold conditions and soft in hot conditions [1]. These defective properties of bitumen can be overcome by different additives which endow bitumen with improved viscoelastic behavior [2–10]. Polymer modified bitumen (PMB) reduces the three causes of poor performance and loss of structural integrity of asphalt pavements: rutting; aggregate plastic deformation due to both high loads and high temperatures; fatigue cracking; caused by repetitive loading; thermal cracking; embrittlement caused by low temperature [11]. Therefore, bitumen additives could improve bitumen properties at low and high in-service temperatures [12].

Utilization of PMB has advantages of lower susceptibility to temperature fluctuation, high resistance to deformation at higher temperatures, better age resistance properties, better binding quality, and overall enhanced performance [8, 13–16].

One of the most widely utilized polymeric additives for modification of bitumen is styrene butadiene styrene (SBS) [2, 6, 10, 12, 17–22]. SBS copolymers acquire their strength and elasticity from physical and cross-linking of the molecules into a three-dimensional network. Styrene butadiene styrene can improve bitumen properties such as elastic responses, rutting resistance, low-temperature cracking resistance, and that is why SBS is accepted globally for modification of bitumen binder [23]. Nevertheless, it has been stated that SBS-modified bitumen often indicates thermodynamically unstable state when kept at high temperature which results in early phase separation [24].

Ethyl vinyl acetate (EVA)-based polymers are categorized as plastomer that modify bitumen by forming a tough, rigid, three-dimensional network to resist deformation [17]. Many pavement researchers have examined the properties of EVA-modified bitumen [8, 12, 25–27] and it is well understood that rheological characteristics such as permanent deformation and thermal cracking are improved when EVA copolymers are added to bitumen. Even though EVA polymers can improve bitumen properties, there are still some limitations which prevent widespread application such as phase separation, low elastic recovery, and less resistance to low-temperature cracking as compared to other elastomeric polymers.

The other polymer investigated for modification of bitumen is polyethylene terephthalate (PET), a thermoplastic polyester which covers 18% of the total polymer manufactured worldwide [28], that can be utilized in two ways. Physically, it can be used as aggregate directly in hot asphalt mixture to improve mechanical properties such as resilient modulus and rutting resistance [16, 29–32]. The other and the most important method of utilization of PET as road pavement is application through chemical conversion for chemical bonding with bitumen. Through this process, PET can be depolymerized using different solvents such as water, amines, alcohol, and acids to produce useful by-products which can be used as additive for bitumen modification [33]. Nowadays, pavement engineers are focusing on modification of bitumen through reactive agents, which can be chemically bonded with specific bituminous compounds [34]. They are aiming to impart inherent compatibility and long-term phase stability to the modified bitumen. New modifier such as reactive isocyanate [2, 34], polyurethane [35–37], and PET derived amides and polyurethane [16, 21, 38] are used in modification of bitumen and improve rheological properties, storage stability, and temperature susceptibilities of the binder.

For this study, waste PET is the raw material for preparing BHETA through aminolysis reaction [39–42], which further reacts with a diisocyanate to produce polyurethane in an in-situ polymerization reaction. This way of modification significantly improves the performance properties of the bituminous mixture due to the reaction of the isocyanate-based polymer with some bitumen compounds containing active groups (–OH, –SH, –NH, and –COOH). As a result, bitumen modified with isocyanate-based polymers is able to improve viscosity, storage stability, and rutting resistance [3, 43].

In addition to utilizing polymers as modifiers, cross-linking agents like sulfur can be used to further pavement property improvements. In particular, sulfur is used to enhance the properties of PMB by cross-linking molecules and chemically coupling polymer and bitumen through sulphide and/or polysulphide bonds [44], which reduces phase separation at high temperature storage of PMB. Many studies have been examined on sulfur modification with various kinds of bitumen and have been found to improve various performance properties such as elastic recovery, storage stability, and low temperature cracking [19, 20, 45]. Huang et al. [19] studied that addition of sulfur improves the

resistance to rutting in both cases of polyoctenamer and SBS-modified bitumen.

Although modification of bitumen by using PET-derived polyurethane was examined [21], the percentage replacement of bitumen by polymer was only about 3wt% of bitumen. In this work, the effects of further increasing polymer content to 5wt% by using sulfur as cross-linking agent was studied by an in-situ polymerization mechanism. The combined effects of PET-based polyurethane polymer and cross-linking agent on the performance of bitumen were studied. Among the performance characterization of bitumen, rutting resistance has been evaluated due to its aggravation by global warming and increasing heavy traffic loads. The rutting performance of the modified bitumen was examined by penetration and softening point determination, complex shear modulus and phase angle master curve analyses, and multiple stress creep recovery (MSCR) test.

## 2. Materials and Methods

**2.1. Materials.** The 60/70 penetration grade bitumen (supplied by Amhara enterprise group, Bahir Dar, Ethiopia) was used for this study and its physical properties are presented in Table 1.

Analytical grade ethanolamine (99.9%), sodium acetate (99.0%), sulfur (99.99%), and toluene diisocyanate (80:20, i.e., isomer of 2, 4-TDI to 2, 6-TDI) were used for this experimental work. Ethanolamine is used in the conversion of PET with sodium acetate as a catalyst. Toluene diisocyanate is used in the in-situ polymerization reaction, and sulfur is used as a cross-linking agent. The equipment/instruments used in this experimental work are presented in the Supplementary Materials.

### 2.2. Methods

**2.2.1. Synthesis of BHETA.** PET is first pretreated, and the method is presented in the Supplementary Information. The experimental procedure for waste PET aminolysis was designed according to the methods developed by Zhang et al. [39]. PET flakes and ethanolamine react in the ratio of 1:4 in a three-necked 500 ml round-bottomed flask. Sodium acetate (1.5% by weight of PET) was added as a catalyst. The aminolysis reaction was carried out at a temperature of 130–170°C and a mixing speed of 250 rpm. The mixture was refluxed, and at the end of the reaction, the unreacted PET pellets were quickly separated from the liquid phase before the product precipitated.

Distilled water was introduced in excess to the reaction mixture with vigorous agitation to crystallize the product, BHETA, which precipitates and was filtered. It was further refined by recrystallization in water and then dried out in an oven at 80°C. The product was characterized by FTIR and differential scanning calorimetry (DSC). The detailed experimental procedure for polyethylene terephthalate pretreatment (preparation of BHETA) is presented in the Supplementary Information (Figure S1).

TABLE 1: Physical properties of 60/70 bitumen.

Conventional tests	Test methods	Units	Specification	Values
Penetration @ 25°C	ASTM D5	mm/10	60–70	64.3
Ductility @ 25°C	ASTM D113	cm	100 min	100+
Softening point	ASTM D36	°C	46–56	48
Flash point	ASTM D92	°C	230 min	270

TABLE 2: Jnr based PG grading requirements [47].

Traffic levels	Description	Max. Jnr@ 3.2 kPa
Standard (S)	<10 million ESAL and >70 km/h traffic speed	4.0
Heavy (H)	10–30 million ESAL and 20–70 km/h traffic speed	2.0
Very heavy (V)	>30 million ESAL and 20 km/h traffic speed	1.0
Extreme (E)	For very heavy but around toll plazas and port facilities	0.5

**2.2.2. In-Situ Polymerization.** The in-situ polymerization of BHETA and toluene diisocyanate (TDI) was performed at various amounts of polymer (3, 4, and 5%) and sulfur (0.1, 0.2, and 0.3%) in the body of bitumen according to Rabintra and Gupta [21] in their respective weight ratios in an autoclave reactor with vigorous stirring at 600 rpm, a reaction time of 2 hours, and reaction temperature of 130°C. After 1 hour, the cross-linking agent, sulfur, was added to the reaction vessel. An in-situ polymerization reaction without sulfur was also performed to investigate the effect of cross-linking agent. The detailed process description of in-situ polymerization of BHETA and toluene diisocyanate is presented in the Supplementary Information (Figure S2).

**2.2.3. Characterization of Base and Modified Bitumen.** The conventional test such as penetration and softening point of base and modified binders were performed by ASTM methods as described in Table 1. Frequency sweep tests were conducted to examine the rheological properties of base and modified binders at intermediate and high temperatures. A performance-grade test was carried out to determine bitumen's high-temperature susceptibility and to grade its performance. Multiple stress creep recovery analysis was performed to determine the rutting performance of bitumen at high temperature. MSCR-based grading of bitumen which simulates traffic level, weight of vehicle, and speed is stated in Table 2. FTIR analysis was performed to confirm the urethane linkages created by the in-situ reaction. AASHTO standards of bitumen characterization [46, 47] were considered to perform these fundamental tests. The detailed process descriptions of frequency sweep test, performance grade, multiple stress creep recovery, and master curves of complex modulus and phase angle are presented in the Supplementary Information.

### 3. Results and Discussion

#### 3.1. Characterization of BHETA

**3.1.1. FTIR Analysis of BHETA.** From Figure 1, the functional groups of the product were identified by the FTIR spectra with sharp peaks. In the FTIR spectra, the peaks at

3364  $\text{cm}^{-1}$  correspond to  $-\text{NH}$  in hydrogen bonding, and peaks at 1547.2  $\text{cm}^{-1}$  indicate secondary amide stretching [48]. The FTIR spectrograph of the monomer at peaks 1049.7 and 3288  $\text{cm}^{-1}$  denotes the presence of primary alcohol. The disappearance of the ester group at 1735  $\text{cm}^{-1}$  (encircled region) [49] and the formation of amide peaks at 1547.2 and 3364  $\text{cm}^{-1}$  denote the conversion of PET to BHETA. This analysis agrees with pure BHETA spectra as compiled by NIST Webbook [50].

**3.1.2. Thermal Properties of BHETA.** The DSC analysis of the BHETA white powder was performed from 40 to 400°C at a heating rate of 10°C/min, and two significant endothermic peaks were obtained (Figure 2). The thermogram from 40 to 190°C indicates that the molecular arrangement of the product is highly ordered (crystalline). The peak formed at a temperature of 202.76°C shows the melting point, whereas 236.5°C represents the destruction of interchain hydrogen bonding. The sharp peak at the melting temperature manifests monomer formation [51]. The patterns of peak formation in melting and interchain hydrogen bonding destruction temperatures of DSC analysis of this study agree with previous research works [51, 52]. The highly ordered crystal formation was revealed in this study by the slightly higher melting temperature, which will be suitable for application in road pavement at higher temperatures.

#### 3.2. Performance Evaluation of Base and Modified Bitumen

**3.2.1. Conventional Test Results.** The penetration value of base and modified bitumen plotted in Figure 3, shows all the modified binders have a reduction in penetration. The penetration values of sulfur-controlled binders were higher than others; this indicates that sulfur addition has a noticeable effect in high temperature performance of bitumen. In sulfur-controlled binders, increasing polymer content, cause a decrease in penetration; however, this trend could not be seen in sulfur containing sample because of the interaction effects of polymer and sulfur. The minimum value of penetration was obtained at 0.2%S and 4%P, which is due to appropriate proportion of modifiers. For sulfur content of 0.1 and 0.2%S, increasing polymer content from 3 to 4%

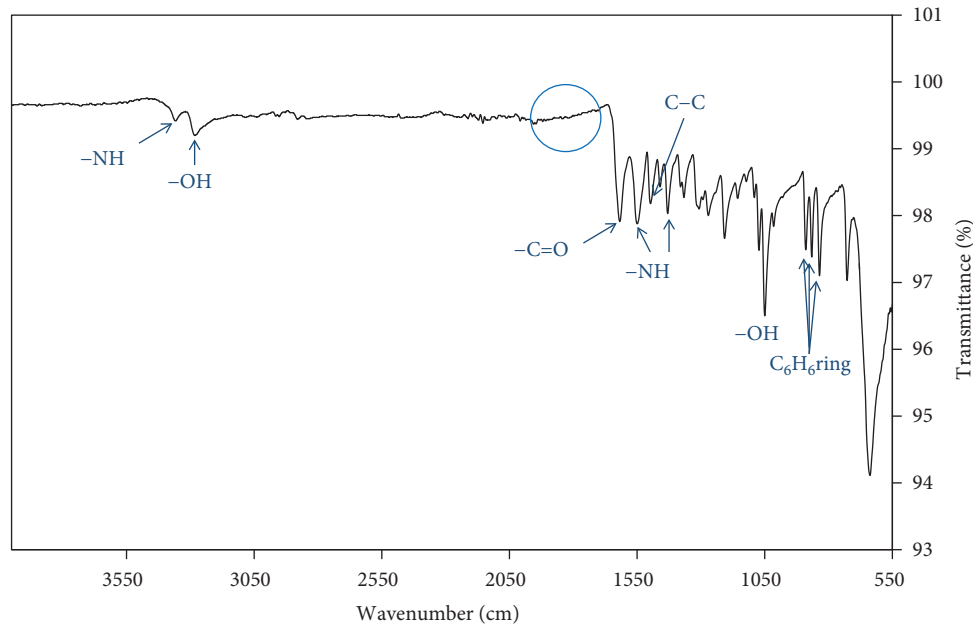


FIGURE 1: FTIR spectra analysis of BHETA.

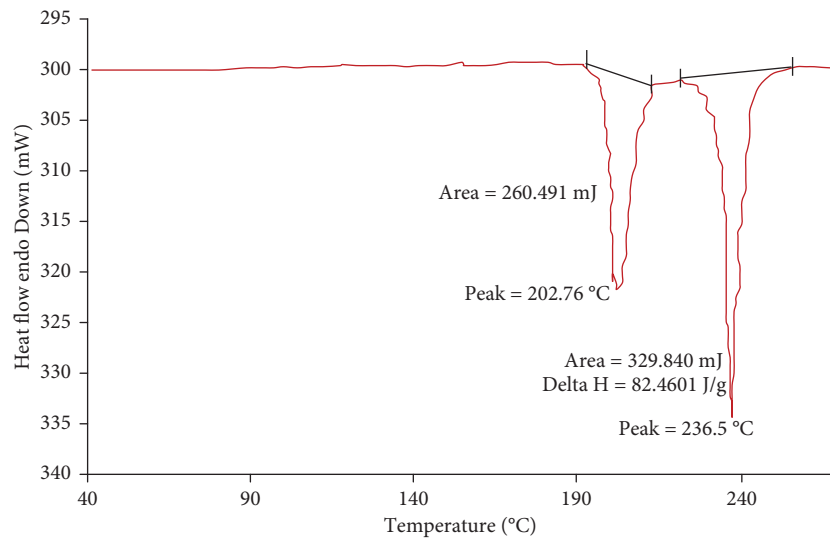


FIGURE 2: DSC analysis of BHETA.

causes a reduction in penetration, but further addition in polymer has no improvement.

The effects of polymer and sulfur contents on softening point are illustrated in Figure 4. The softening point values of modified bitumen indicates an increment relative to the control. For constant polymer content increasing sulfur content from 0 to 0.2%, the softening point increases from 48 to 73°C. Therefore, this physical test indicates that modification of bitumen by polymers with cross-linking agent reduces high temperature susceptibility.

**3.2.2. Rheological Properties.** From the rheological parameters of dynamic shear tests, complex modulus ( $G^*$ ) and phase angle ( $\delta$ ) are more important to simulate the stiffness

and elasticity of binders, respectively. The frequency sweep tests were performed to see the effect of frequency on binders' rheological properties since traffic loading is a dynamic loading with a varying frequency and temperature environments [53]. The rheological properties of unmodified and modified bitumen at intermediate and high temperature were determined using master curves of  $G^*$  and  $\delta$  as shown in Figure 5. The time-temperature superposition principle was applied for temperatures of 21.1, 37.8, and 54.4°C with frequency from 0.1 to 25 Hz. The master curves of  $G^*$  and  $\delta$  were developed at a reference temperature of 21.1°C, a temperature which is near to ambient conditions, and the shifting factors were  $G^*$  master curves.

As shown in Figure 5, for both base and modified binders, as frequency increases (decrease in temperature),

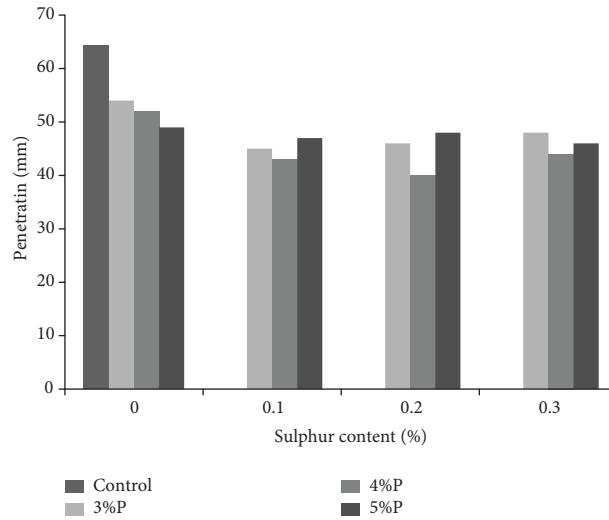


FIGURE 3: Penetration of base and modified bitumen.

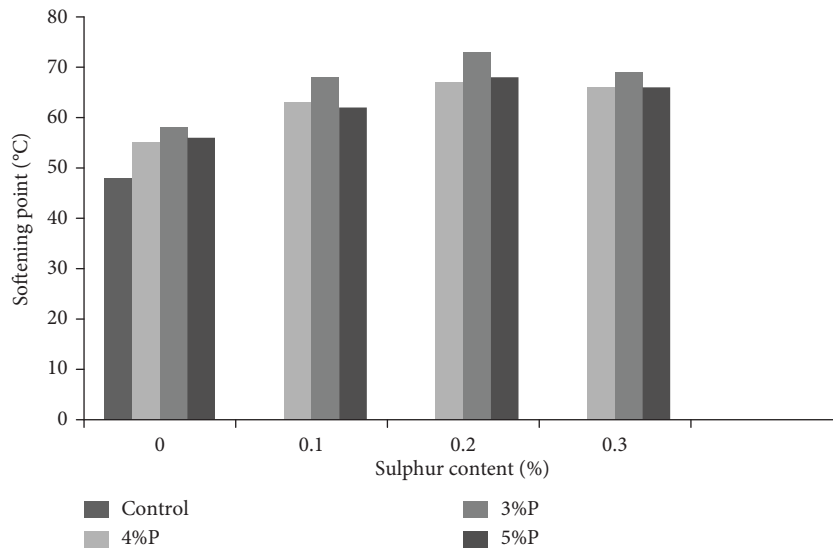


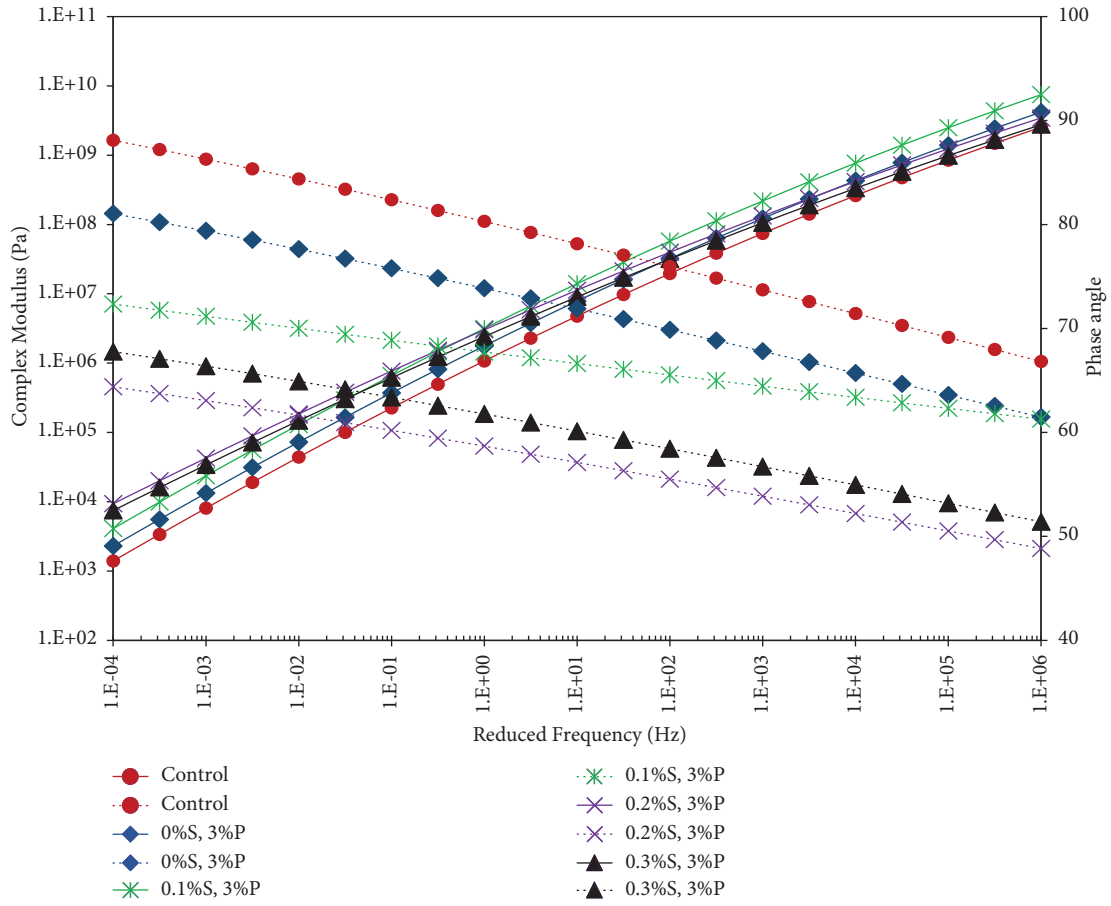
FIGURE 4: Softening point of base and modified bitumen.

the  $G^*$  increases irrespective of sulfur and polymer contents. Thus, higher temperature condition corresponds to longer loading time which is prone to rutting and lower temperature conditions correspond to shorter loading time which is susceptible to fatigue cracking. As depicted in Figure 5(a), the modulus of unmodified bitumen was significantly improved specially for low frequency levels and higher temperature zones. The maximum  $G^*$  was obtained at 0.2%S and 3%P for low frequency levels, and sulfur-controlled binder (0%S and 3%P) was the second least stiff next to neat bitumen. Thus, the cross-linking agent has shown its meaningful impact on the stiffness of binders.

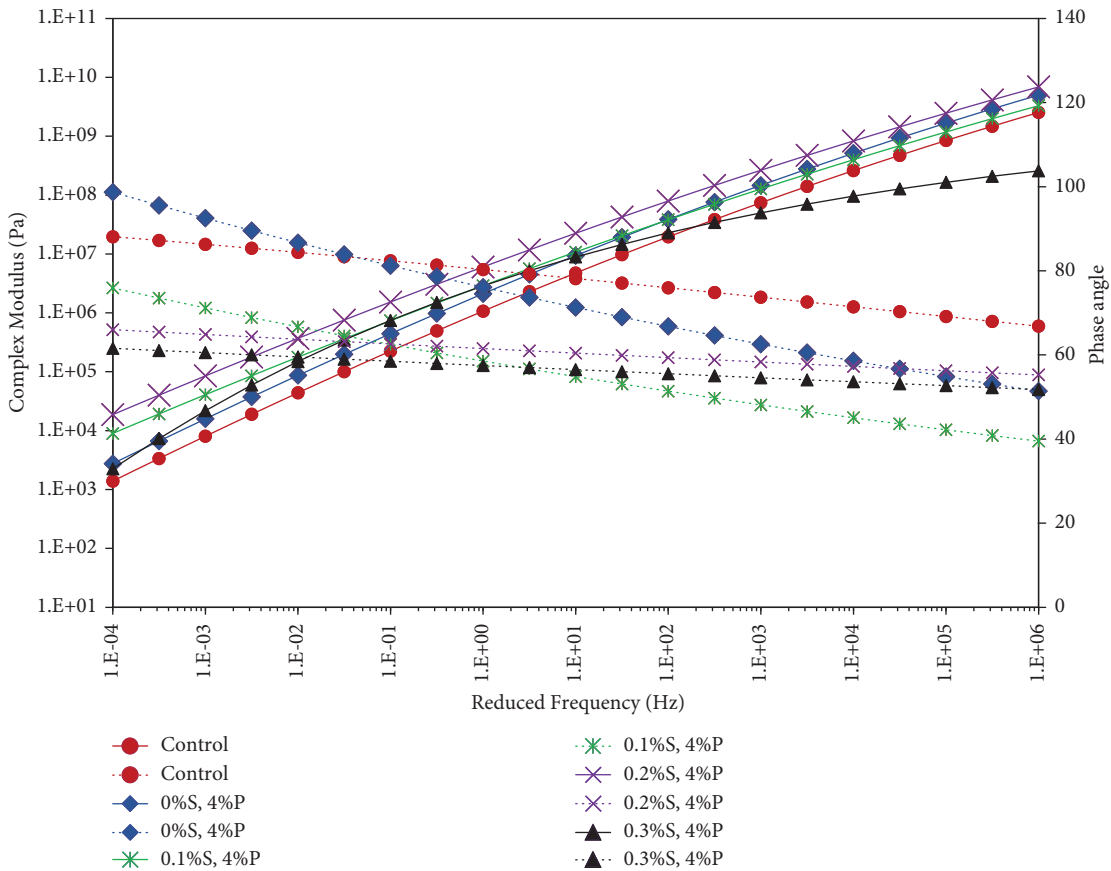
Figures 5(b) and 5(c) have also similar profiles of  $G^*$  master curves with Figure 5(a). The largest  $G^*$  throughout the frequency ranges was obtained at polymer content of 4% and 0.2% sulfur content (Figure 5(b)). The degree of modification here was prominent relative to the control, and

the effect of sulfur content was also influential; whereas in Figure 5(c), the unmodified bitumen was better in stiffness than sulfur controlled and 0.3%S modified binder in frequencies less than 10 Hz (rutting susceptible region).

The master curve for phase angle ( $\delta$ ) of base and modified binders are also plotted on Figure 5 together with master curve of  $G^*$ . The phase angle decreases as the frequency increases; for all binders, the differences of  $\delta$  values between them are also notable. The level of decrement in  $\delta$  was significant for modified bitumen relative to the base bitumen. The lower the  $\delta$ , the higher the elastic component of the binder and is desirable property for resisting permanent deformation. As the polymer content increases from 3 to 4%, the phase angle decreases and further increasing to 5% does not show significant differences (Figures 5(a)–5(c)). For constant polymer contents, the effect of sulfur content was remarkable; thus, the cross-linking agent has substantial



(a)



(b)

FIGURE 5: Continued.

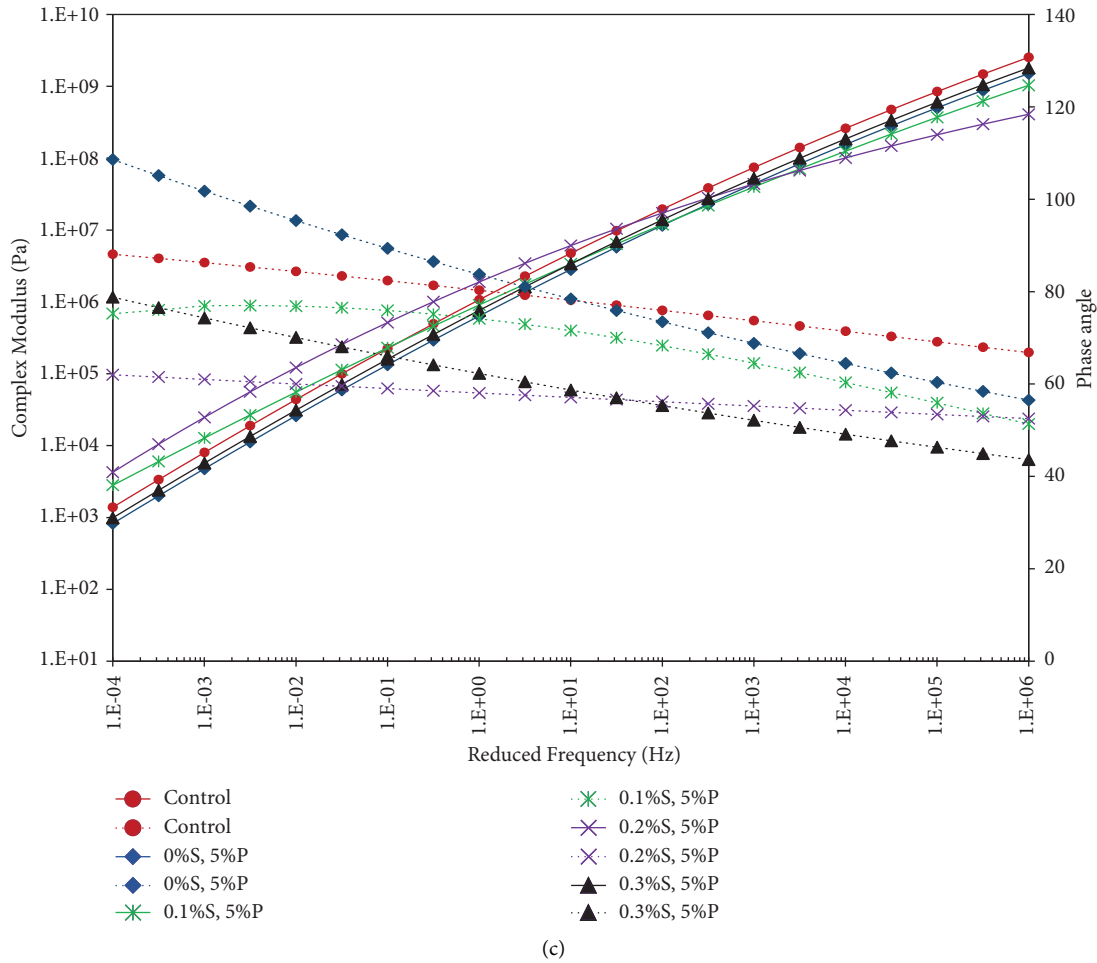


FIGURE 5: Complex modulus and phase angle master curves drawn on logarithmic scale at different sulfur content for polymer content of 3% P (a), 4%P (b), and 5%P (c) at reference temperature = 21.1°C.

contribution to increase the storage modulus of bitumen and the sulfur-controlled sample shows large phase angle which is closely similar to the base bitumen.

As observed in conventional (penetration and softening point) tests, when the sulfur content increases from 0 to 0.3% S, values of results were higher at sulfur content of 0.2% regardless of polymer contents. Similarly, from master curves of modified bitumen (Figures 5(a)–5(c)), the stiffer binder was obtained at 0.2% sulfur content, at lower frequency (less than 10 Hz) and higher temperature which is highly rutting susceptible region. However, at relatively higher polymer content (Figure 5(c)), the modulus of binders with 0% and 0.3% sulfur content were lower than the base bitumen at frequencies less than 10 Hz. In general, the correlation between conventional and fundamental (master curve) test results has a good agreement except at 0%S and 0.3%S samples. This slight difference in the test results is tolerable in bitumen characterization and happened due to the difference in testing conditions; fundamental tests are performed at various temperature, frequency, and loading conditions.

**3.2.3. Performance Grade.** The PG of bitumen was examined by the superpave rutting parameter. The PG is designated by the rutting factor criterion when it can withstand the testing temperature of bitumen. For example, the value of  $G^*/\sin\delta$  at a testing temperature of 64°C is 3.1 kPa (greater than 2.2 kPa for aged bitumen), and the performance grade can be represented as PG64-yy. Since the result of this method of analysis is described in the range, the performance grade of the bitumen could be described in terms of pass-fail temperature at which the rutting factor ( $G^*/\sin\delta$ ) is 2.2 kPa [46]. Throughout this discussion, the pass-fail temperature was taken as the response variable of the PG.

**(1) Effect of Sulfur and Polymer Contents.** As depicted in Figure 6, the pass-fail temperature increased as the polymer content increased from 3 to 4% and the pass-fail temperature decreased as the polymer content increased from 4 to 5%. It indicates that 4% of polymer content was sufficient to modify bitumen properties. At this polymer content, bitumen is a continuous phase while polymer is dispersed in the bitumen matrix. At high service temperatures, the property

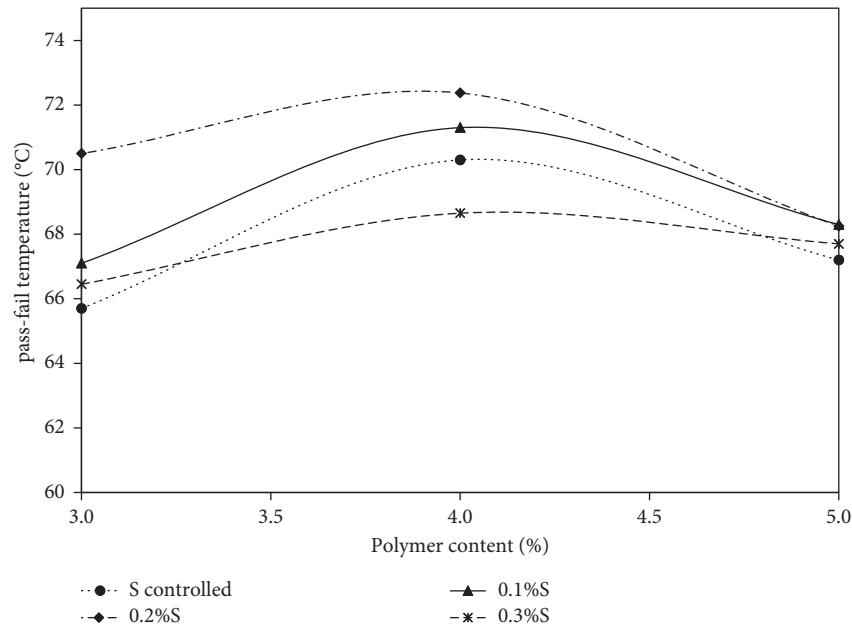


FIGURE 6: Pass-fail temperature of modified bitumen.

TABLE 3: High temperature performance grades of base and modified bitumen.

Sulfur contents (%)	Polymer contents (%)	Pass-fail T (°C)	PG	Remarks
0	0	63.75	PG 58-yy	Control
0	3	65.7	PG 64-yy	Modified
0	4	70.3	PG 70-yy	Modified
0	5	67.2	PG 64-yy	Modified
0.1	3	67.1	PG 64-yy	Modified
0.2	3	71.3	PG 70-yy	Modified
0.3	3	68.3	PG 64-yy	Modified
0.1	4	70.5	PG 70-yy	Modified
0.2	4	72.37	PG 70-yy	Modified
0.3	4	68.25	PG 64-yy	Modified
0.1	5	66.45	PG 64-yy	Modified
0.2	5	68.65	PG 64-yy	Modified
0.3	5	67.7	PG 64-yy	Modified

of bitumen was improved as the stiffness of the polymer phase is higher than that of the matrix, which enhanced the temperature susceptibility of modified bitumen [54]; whereas in polymer contents around 5%, both polymer and bitumen are continuous phases and interlocked which is difficult to control and pose stability problems.

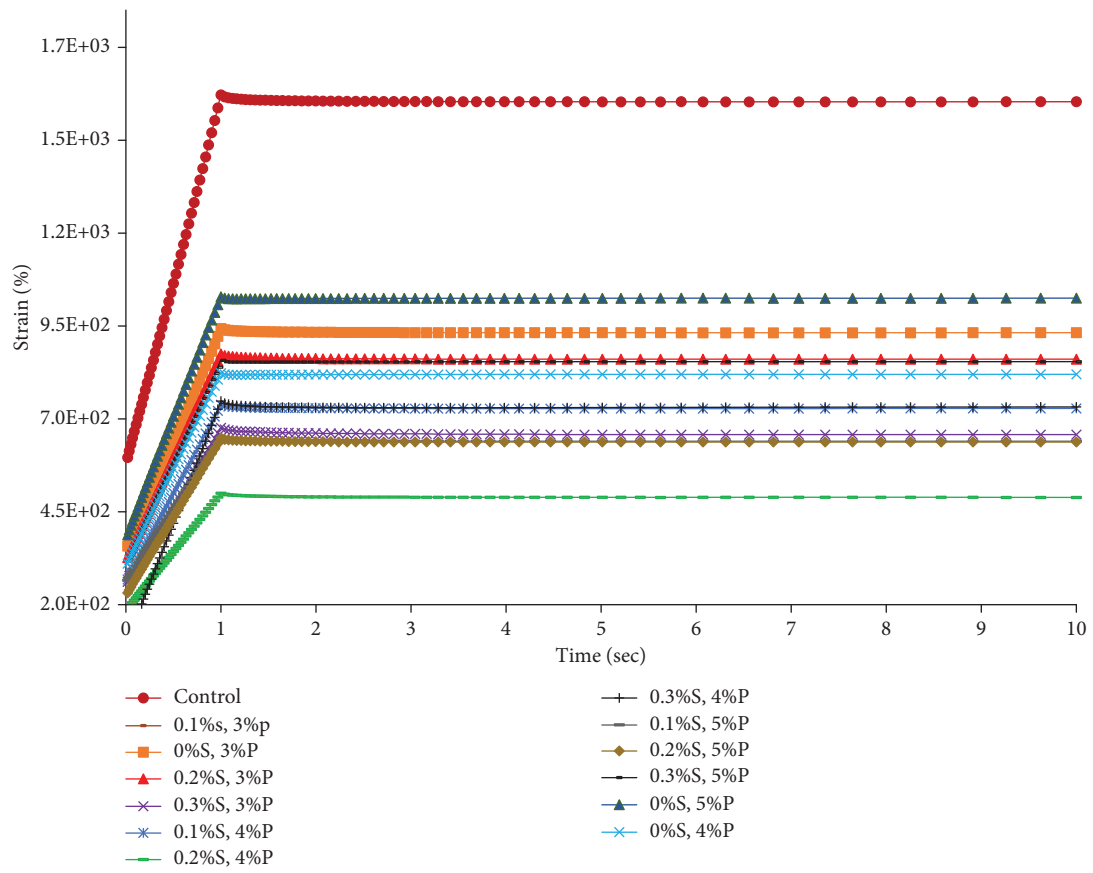
When sulfur content increased for specific polymer content, the performance was improved significantly at 0.2% of sulfur content. The low sulfur content of 0.1% was insufficient to create cross-linking between bitumen and polymer chains, and as studied by the patent US 2003/0171460 A1 [55], at higher sulfur content, the polymer undergoes over cross-linking and produces gels with undesired consequences. The control samples (0% sulfur) were evaluated for higher temperature performance, and their values were lower than the corresponding sulfur-containing samples at 0.1 and 0.2%S. However, it was better when compared with the sample prepared at 0.3% sulfur content and 4% polymer content. At the highest polymer content

(5%), the effect of the cross-linking agent was reduced; it was not important to use sulfur of more than 0.1% (Figure 6). In general, the performance grades of most of the modified bitumen were improved in one grade (58 to 64°C) and some of them in two grades (58 to 70°C) as shown in Table 3.

**3.2.4. Multiple Stress Creep Recovery Analysis.** This test was performed to determine the actual performance of the bitumen against rutting using constant loading stress levels and temperature as input parameters. The MSCR results were analyzed by the accumulated strain and nonrecoverable creep compliance. Multiple stress creep recovery was conducted at three levels of testing temperatures for a single sample to obtain its performance within the specified temperature range.

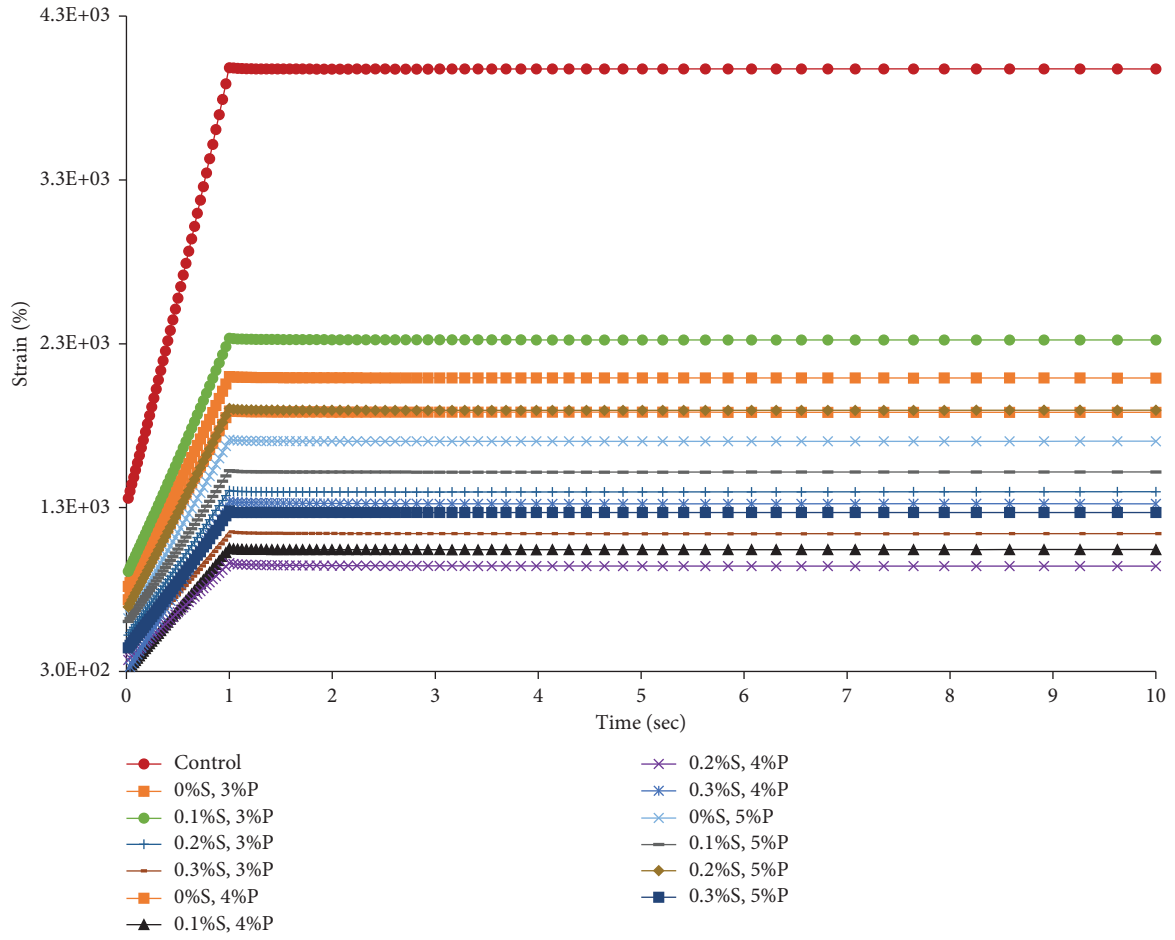
(1) *Accumulated Strain.* Accumulated strain indicates the performance of bitumen against deformation with





(a)

FIGURE 7: Continued.



(b)  
FIGURE 7: Continued.

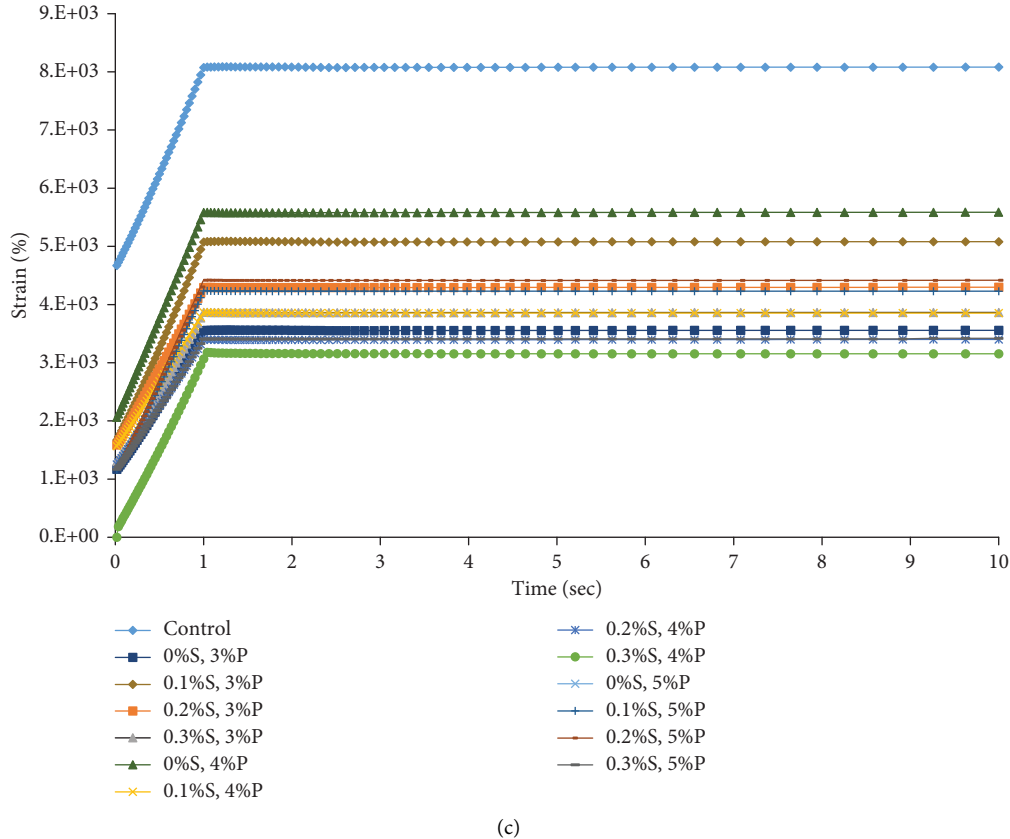


FIGURE 7: Single-cycle strain of base and modified binders for different contents of sulfur and polymer tested at a stress level of 3.2 kPa for testing temperatures of (a) 58°C, (b) 64°C, and (c) 70°C.

continuous loading and recovery operation. It was analyzed by calculating the cumulative strain from generated strain at the conditioning (0.1 kPa and 3.2 kPa) stages of loading. As shown in Figure 7, deformation is plotted for the first single cycle at testing temperatures of 58, 64, and 70°C.

The first one second is the duration of the loading and the remaining nine seconds for recovery. For all testing temperatures, the strain of the base binder was reduced in a large extent with clear difference among binders, especially at testing temperatures of 58 and 64°C (Figures 7(a)–7(b)). As the testing temperature increases, it is obvious that the deformation of binders increases, which means in application it will deform due to dominance of viscous phase. For testing temperatures of 58 and 64°C, the lowest accumulated strain of modified bitumen was obtained at a polymer content of 4% and sulfur content of 0.2%; whereas for testing temperature of 70°C, larger amount of sulfur (0.3%S) for all polymer contents demonstrated relatively lower deformation. Thus, the higher sulfur content made the modified binder more resistant to deformation by its intrinsic thermal properties.

From Figure 8, it is depicted that the base bitumen resulted in the highest deformation, more than six times of highly modified bitumen at last cycles of loading. By analysis of the accumulated strain, there is no sharp rule in which the performance of bitumen is limited by the strain level.

However, it indicates the relative performance of bitumen against deformation tested at the same condition.

(2) *Nonrecoverable Creep Compliance.* Nonrecoverable creep compliance ( $J_{nr}$ ), which is the ratio of unrecovered strain to the applied stress, can directly be correlated to the rutting potential of bitumen as follows [56].

$$J_{nr_{0.1}} = \frac{\sum_{N=1}^{10} [J_{nr}(0.1, N)]}{10} \left( \frac{1}{\text{kPa}} \right), \quad (1)$$

$$J_{nr_{3.2}} = \frac{\sum_{N=1}^{10} [J_{nr}(3.2, N)]}{10} \left( \frac{1}{\text{kPa}} \right), \quad (2)$$

where  $J_{nr}(0.1, N)$  and  $J_{nr}(3.2, N)$  are the nonrecoverable creep compliances at 0.1 kPa and 3.2 kPa at cycle number  $N$ , respectively, and  $N$  is the cycle number at each stress level.

The average  $J_{nr}$  values were calculated using equations 1 and 2 for stress levels of 0.1 kPa and 3.2 kPa, respectively. The values were used to identify the bitumen grade. Lower  $J_{nr}$  values indicate better resistance to rutting of the modified bitumen at that level of the applied load. The value of  $J_{nr}$  for each specimen is indicated in Figure 9, which demonstrates the effect of sulfur content and polymer content on non-recoverable creep compliance at the stress level of 3.2 kPa and testing temperature of 64°C. This test method is

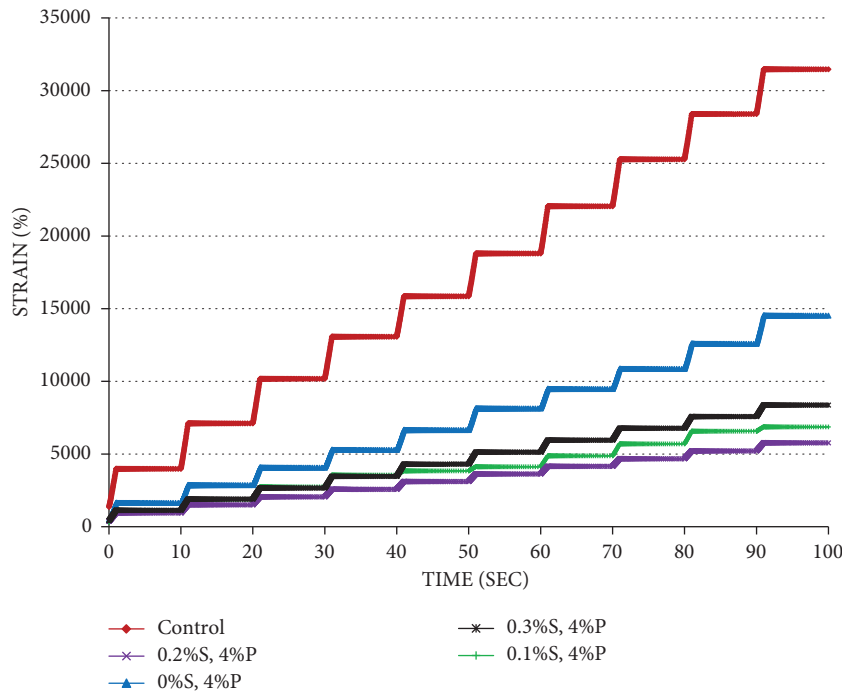


FIGURE 8: Accumulated stains of modified bitumen for different sulfur contents and 4% polymer content tested at 64°C.

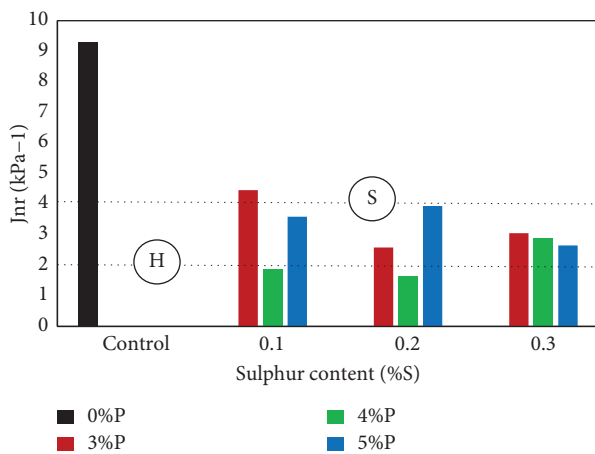


FIGURE 9: Nonrecoverable creep compliance ( $J_{nr}$ ) values of base and modified bitumen at different sulfur and polymer contents tested at 64°C.

AASTHO specification to grade the performance of bitumen based on rutting resistance potential.

The  $J_{nr}$  value of base bitumen was almost more than five times of modified bitumen with 4% polymer content. This was due to microstructural modification of bitumen with reactive isocyanate (-NCO) ends of polyurethane reacting with some active components of bitumen [3]. Thus, the incorporation of polymer with the formation of chemical bonds in the bitumen matrix can increase the viscosity of the modified bitumen at high service temperature and magnify its role in increasing the elastic nature of the polymer-bitumen system [57, 58]. Furthermore, cross-linking agent

(sulfur) could make the system to be highly integrated through coupling polymer molecules and bitumen by sulphide bonds [26]. Therefore, it can be noted that the base bitumen was modified by 81.82% in its  $J_{nr}$  values at 0.2% sulfur content and 4% polymer content.

As shown in Figure 9, six specimens met the standard traffic level, which was suitable for vehicle speeds greater than 70 km/hr and less than 10 million ESAL (Table 2), and the remaining two specimens could satisfy heavy traffic levels (traffic speed of 20–70 km/h and 10–30 million ESAL) at 64°C. The lowest value of  $J_{nr}$  was at 0.2% of sulfur with 4% of polymer. Thus, this polymer modification condition was the superlative of this experimental investigation which can withstand heavier loads. Since the goal of this study was to increase the polymer content from 3% to 5% by introducing cross-linking agent, at 5% of polymer content, 0.3% of sulfur addition was able to decrease the  $J_{nr}$  value from 4.34  $\text{KPa}^{-1}$  to 2.65  $\text{KPa}^{-1}$  [59]. Therefore, using sulfur as a cross-linking agent in polyurethane polymer enhancement of bitumen brings significant modification of bitumen properties.

**3.3. FTIR Analysis of Base and Modified Bitumen.** FTIR spectra analysis of base and modified bitumen were conducted to confirm the formation of urethane linkage. Wave numbers from  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  were used at a resolution of  $4\text{ cm}^{-1}$ . Figure 10 shows FTIR spectra of base and modified bitumen at 4% and 0.2% polymer and sulfur contents, respectively.

From this analysis, it can be observed that the absence of the band in the  $2260\text{ to }2310\text{ cm}^{-1}$  range confirms the nonexistence of the free NCO group in the polymer

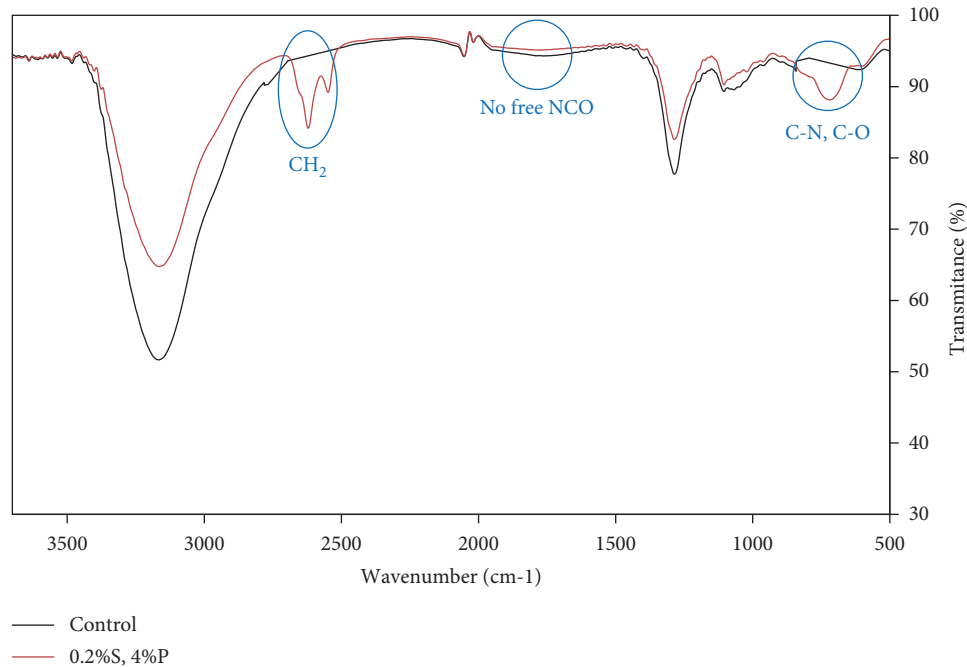


FIGURE 10: FTIR spectra of base and modified bitumen.

structure, which indicates the complete urethane reaction [60]. The most important characteristic features of the polyurethane were the presence of bands at  $1090\text{ cm}^{-1}$  (C–N stretching vibrations),  $1123\text{ cm}^{-1}$  (C–O stretching vibrations),  $2855\text{--}2927\text{ cm}^{-1}$  ( $\text{CH}_2$  symmetric and asymmetric), and  $3446\text{ cm}^{-1}$  (free O–H and N–H stretching from urethane group stretching vibrations) [61]. These vibrational bands show the formation of urethane linkage, NH–COO, in the in situ polymerization.

#### 4. Conclusion

Chemical modification of bitumen through the in-situ polymerization reaction of PET-derived polyurethane with the cross-linking agent in the body of bitumen was carried out at various combinations of polymer and sulfur contents. The parameter effects were examined through performance analysis of modified and base bitumen by penetration, softening point, complex modulus and phase angle master curves, performance grade, and multiple stress creep recovery tests.

Conventional tests (penetration and softening point) show improvement in performance of modified bitumen. The viscoelastic properties of the modified binder in terms of complex modulus and phase angle were also enhanced. From performance grade analyses, a two-grade improvement (PG58-yy to PG70-yy) with the highest pass-fail temperature was realized at a polymer content of 4% and sulfur content of 0.2%. The accumulated strain of bitumen modified at the optimum condition (4% polymer and 0.2% sulfur) was reduced by five times compared to the base bitumen. The grading based on multiple stress creep recovery was performed through the nonrecoverable compliance tests, and most of the analysis results fall under the

standard traffic level, and the best grade for this modification was heavy traffic level at 4% polymer and 0.2% sulfur contents for the testing temperature of  $64^\circ\text{C}$ . In summary, the present work primarily focuses on the performance-based analysis of modified bitumen, and the results demonstrate that the product can be used in standard traffic levels.

#### Data Availability

All data generated or analyzed during this study are included in this published article (and its supplementary information file).

#### Conflicts of Interest

All authors declare that there are no conflicts of interest.

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#### Supplementary Materials

It describes the details of the equipment list, the methods (polyethylene terephthalate pretreatment (Figure S1), experimental set up for the in situ polymerization (Figure S2), frequency sweep test (FST), master curves of complex modulus and phase angle, performance grade, multiple

stress creep recovery, and master curves of complex modulus and phase angle). (*Supplementary Materials*)

## References

- [1] M. Naskar, T. K. Chaki, and K. S. Reddy, "Effect of waste plastic as modifier on thermal stability and degradation kinetics of bitumen/waste plastics blend," *Thermochimica Acta*, vol. 509, no. 1–2, pp. 128–134, 2010.
- [2] F. J. Navarro, P. Partal, M. García-Morales, F. J. Martínez-Boza, and C. Gallegos, "Bitumen modification with a low-molecular-weight reactive isocyanate-terminated polymer," *Fuel*, vol. 86, no. 15, pp. 2291–2299, 2007.
- [3] J. Zhu, B. Birgisson, N. Kringos, and B. Kringos, "Polymer modification of bitumen: advances and challenges," *European Polymer Journal*, vol. 54, pp. 18–38, 2014.
- [4] A. F. Kemalov, R. A. Kemalov, I. M. Abdrafikova, P. S. Fakhretdinov, and D. Z. Valiev, "Polyfunctional modifiers for bitumen and bituminous materials with high performance," *Advances in Materials Science and Engineering*, vol. 2018, Article ID 7913527, 15 pages, 2018.
- [5] R. S. Souza, L. L. Y. Visconte, A. L. N. da Silva, and V. G. Costa, "Thermal and rheological formulation and evaluation of synthetic bitumen from reprocessed polypropylene and oil," *International Journal of Polymer Science*, vol. 2018, Article ID 7940857, 6 pages, 2018.
- [6] M. Cappello, S. Filippi, Y. Hung, M. Losa, and G. Polacco, "Apparent molecular weight distributions for investigating aging in polymer-modified bitumen," *Advances in Polymer Technology*, vol. 2021, Article ID 3660646, 14 pages, 2021.
- [7] L. Zhang, X. Gao, W. Wang, H. Wang, and K. Zheng, "Laboratory evaluation of rheological properties of asphalt binder modified by nano-TiO<sub>2</sub>/CaCO<sub>3</sub>," *Advances in Materials Science and Engineering*, vol. 2021, Article ID 5522025, 13 pages, 2021.
- [8] M. H. Dehnad, B. Damyar, and H. Z. Farahani, "Rheological evaluation of modified bitumen by EVA and crumb rubber using RSM optimization," *Advances in Materials Science and Engineering*, vol. 2021, Article ID 9825541, 8 pages, 2021.
- [9] K. A. Masri, N. S. Shamimi Mohd Zali, R. P. Jaya, M. A. Seman, and M. R. Mohd Hasan, "The influence of nano titanium as bitumen modifier in stone mastic asphalt," *Advances in Materials Science and Engineering*, vol. 2022, Article ID 4021618, 19 pages, 2022.
- [10] C. Chu, J. Zhu, and Z. a. Wang, "Investigation of the road performance of AH-30 bitumen and its mixture: comparison with AH-70 and SBS-modified bitumen," *Advances in Materials Science and Engineering*, Article ID 3124047, 11 pages, 2021.
- [11] F. H. A. National Highway Institute, "Superpave Fundamentals," *Reference Manual*, vol. 131053, 2008.
- [12] L. Zanzotto, J. Stastna, and O. Vacin, "Thermomechanical properties of several polymer modified asphalts," *Applied Rheology*, vol. 10, no. 4, pp. 185–191, 2000.
- [13] H. Fazaeli, H. Behbahani, A. A. Amini, J. Rahmani, and G. Yadollahi, "High and low temperature properties of FT-paraffin-modified bitumen," *Advances in Materials Science and Engineering*, vol. 2012, Article ID 406791, 7 pages, 2012.
- [14] A. H. Ali, N. S. Mashaan, and M. R. Karim, "Investigations of physical and rheological properties of aged rubberised bitumen," *Advances in Materials Science and Engineering*, vol. 2013, Article ID 239036, 7 pages, 2013.
- [15] S. D. Srivastava, S. A. Ahmad, N. P. Rao, and S. A. Husain, "Comparative analysis of modification of bitumen by use of poly vinyl chloride and ethyl vinyl acetate," *International Journal of Renewable Energy Technology*, vol. 04, no. 08, pp. 389–391, 2015.
- [16] D. R. Merkel, W. Kuang, D. Malhotra et al., "Waste PET chemical processing to terephthalic amides and their effect on asphalt performance," *ACS Sustainable Chemistry & Engineering*, vol. 8, no. 14, pp. 5615–5625, 2020.
- [17] B. Sengoz and G. Isikyakar, "Evaluation of the properties and microstructure of SBS and EVA polymer modified bitumen," *Construction and Building Materials*, vol. 22, no. 9, pp. 1897–1905, 2008.
- [18] G. Wen, Y. Zhang, Y. Zhang, K. Sun, and Y. Fan, "Improved properties of SBS-modified asphalt with dynamic vulcanization," *Polymer Engineering & Science*, vol. 42, no. 5, pp. 1070–1081, 2002.
- [19] W. Huang and N. Tang, "Characterizing SBS modified asphalt with sulfur using multiple stress creep recovery test," *Construction and Building Materials*, vol. 93, pp. 514–521, 2015.
- [20] W. Zhang, L. Ding, and Z. Jia, "Design of SBS-Modified bitumen stabilizer powder based on the vulcanization mechanism," *Applied Sciences*, vol. 8, no. 3, p. 457, 2018.
- [21] R. K. Padhan and A. A. Gupta, "Preparation and evaluation of waste PET derived polyurethane polymer modified bitumen through in situ polymerization reaction," *Construction and Building Materials*, vol. 158, pp. 337–345, 2018.
- [22] Y. Yildirim, "Polymer modified asphalt binders," *Construction and Building Materials*, vol. 21, no. 1, pp. 66–72, 2007.
- [23] M. Chen, J. Geng, C. Xia, L. He, and Z. Liu, "A review of phase structure of SBS modified asphalt: affecting factors, analytical methods, phase models and improvements," *Construction and Building Materials*, vol. 294, Article ID 123610, 2021.
- [24] H. Soenen, X. Lu, and P. Redelius, "The morphology of bitumen-SBS blends by UV microscopy an evaluation of preparation methods," *Road Materials and Pavement Design*, vol. 9, no. 1, pp. 97–110, 2008.
- [25] C. Brovelli, L. Hilliou, Y. Hemar, J. Pais, P. Pereira, and M. Crispino, "Rheological characteristics of EVA modified bitumen and their correlations with bitumen concrete properties," *Construction and Building Materials*, vol. 48, pp. 1202–1208, 2013.
- [26] R. K. Padhan, A. A. Gupta, and A. Sreeram, "Effect of cross-linking agent on ethylene vinyl acetate/polyoctenamer modified bitumen," *Road Materials and Pavement Design*, vol. 20, no. 7, pp. 1615–1623, 2019.
- [27] G. D. Airey, "Rheological evaluation of ethylene vinyl acetate polymer modified bitumens," *Construction and Building Materials*, vol. 16, no. 8, pp. 473–487, 2002.
- [28] L. N. Ji, "Study on preparation process and properties of polyethylene terephthalate (PET)," *Applied Mechanics and Materials*, vol. 312, pp. 406–410, 2013.
- [29] M. E. Abdullah, S. Aminah, A. Kader, and R. P. Jaya, "Effect of Waste Plastic as Bitumen Modified in Asphalt Mixture," *Transportation Infrastructures and Highway Engineering*, vol. 103, 09018.
- [30] A. Hassani, H. Ganjidoust, and A. A. Maghanaki, "Use of plastic waste (poly-ethylene terephthalate) in asphalt concrete mixture as aggregate replacement," *Waste Management & Research: The Journal for a Sustainable Circular Economy*, vol. 23, no. 4, pp. 322–327, 2005.
- [31] E. Ahmadinia, M. Zargar, M. R. Karim, M. Abdelaziz, and E. Ahmadinia, "Performance evaluation of utilization of waste Polyethylene Terephthalate (PET) in stone mastic asphalt," *Construction and Building Materials*, vol. 36, pp. 984–989, 2012.

- [32] D. Movilla-Quesada, A. C. Raposeiras, and J. Olavarría, "Effects of recycled polyethylene terephthalate (PET) on stiffness of hot asphalt mixtures," *Advances in Civil Engineering*, vol. 2019, Article ID 6969826, 6 pages, 2019.
- [33] P. Rabindra Kumar and A. Sreeram, "Chemical Depolymerization of PET Bottles via Combined Chemolysis Methods," pp. 135–147, 2019.
- [34] M. A. Izquierdo, F. J. Navarro, F. J. Martínez-Boza, and C. Gallegos, "Novel stable MDI isocyanate-based bituminous foams," *Fuel*, vol. 90, no. 2, pp. 681–688, 2011.
- [35] M. Motamedi, G. Shafabakhsh, and M. Azadi, "Evaluation of fatigue and rutting properties of asphalt binder and mastic modified by synthesized polyurethane," *Journal of Traffic and Transportation Engineering*, vol. 8, no. 6, pp. 1036–1048, 2021.
- [36] T. Yao, S. Han, C. Men, J. Zhang, J. Luo, and Y. Li, "Performance evaluation of asphalt pavement groove-filled with polyurethane-rubber particle elastomer," *Construction and Building Materials*, vol. 292, Article ID 123434, 2021.
- [37] P. Partal and F. J. Martínez-Boza, "Modification of Bitumen Using Polyurethanes," *Polymer Modified Bitumen*, pp. 43–71, 2011.
- [38] A. K. Bhatnagar, R. K. Padhan, and A. A. Gupta, *Preparation of Polymer Modified Bitumen (Pmb) from Polyethylene Terephthalate (Pet) Derived Polyamido Amine*, European Patent Application, Munich, Germany, 2015.
- [39] L. N. Zhang, L. Z. Liu, Q. F. Yue, and C. C. Zhu, "From aminolysis product of PET waste to value-added products of polymer and assistants," *Polymers and Polymer Composites*, vol. 22, no. 1, pp. 13–16, 2014.
- [40] P. Gupta and S. Bhandari, "Chemical Depolymerization of PET Bottles via Ammonolysis and Aminolysis," *Recycling Of Polyethylene Terephthalate Bottles*, pp. 109–134, Elsevier, 2019.
- [41] R. Shamsi, M. Abdouss, G. M. M. Sadeghi, and F. A. Taromi, "Synthesis and characterization of novel polyurethanes based on aminolysis of poly(ethylene terephthalate) wastes, and evaluation of their thermal and mechanical properties," *Polymer International*, vol. 58, no. 1, pp. 22–30, June 2008.
- [42] Y. S. Parab, N. D. Pingale, and S. R. Shukla, "Aminolytic depolymerization of poly (ethylene terephthalate) bottle waste by conventional and microwave irradiation heating," *Journal of Applied Polymer Science*, vol. 125, no. 2, pp. 1103–1107, 2011.
- [43] R. K. Padhan, A. A. Gupta, R. P. Badoni, and A. K. Bhatnagar, "Improved performance of a reactive polymer-based bituminous mixes – effect of cross-linking agent," *Road Materials and Pavement Design*, vol. 16, pp. 37–41, 2015.
- [44] G. Wen, Y. Zhang, Y. Zhang, K. Sun, and Y. Fan, "Rheological characterization of storage-stable SBS-modified asphalts," *Polymer Testing*, vol. 21, no. 3, pp. 295–302, 2002.
- [45] J. Zhu, B. Birgisson, and N. P. Kringos, "Postprint polymer modification of bitumen: advances and challenges," *Digitale Vetenskapliga Arkivet*, vol. 54, pp. 18–38, 2014.
- [46] A. Designation, "AASHTO designation," *Standard Specification for Performance Graded Asphalt Binder*, Astm Standard, PA, USA, 2007.
- [47] A. S. Mp19, *Standard Specification for Performance Graded Asphalt Binder Using Multiple Stress Creep Recovery (MSCR) Test*, AASHTO, Washington, D.C, 2014.
- [48] S. R. Shukla and A. M. Harad, "Aminolysis of polyethylene terephthalate waste," *Polymer Degradation and Stability*, vol. 91, no. 8, pp. 1850–1854, 2006.
- [49] P. Mhaske, "Synthesis of Tetra(2,2-Hydroxyethylene) Terephthalamide from PET Waste and its Application in Synthesis of Polyesteramide Coating," *Pigment and Resin Technology*, vol. 46, 2017.
- [50] Coblantz Society Inc, "Terephthalamide, n,n'-bis(2-hydroxyethyl)- - the NIST WebBook," 2018, <https://webbook.nist.gov/cgi/inchi?ID=C18928626&Mask=80>.
- [51] S. B. E. M. E. Tawfik and N. M. Ahmed, "Aminolysis of poly(ethylene terephthalate) wastes based on sunlight and utilization of the end product [Bis(2-hydroxyethylene) terephthalamide] as an ingredient in the anticorrosive paints for the protection of steel structures magda," *Journal of Applied Polymer Science*, vol. 116, no. 5, pp. 2658–2667, 2010.
- [52] A. P. More, R. A. Kute, and S. T. Mhaske, "Chemical conversion of PET waste using ethanolamine to bis(2-hydroxyethyl) terephthalamide (BHETA) through aminolysis and a novel plasticizer for PVC," *Iranian Polymer Journal (English Edition)*, vol. 23, no. 1, pp. 59–67, 2014.
- [53] S. Wu, J. Zhu, J. Zhong, and D. Wang, "Experimental investigation on related properties of asphalt mastic containing recycled red brick powder," *Construction and Building Materials*, vol. 25, no. 6, pp. 2883–2887, 2011.
- [54] B. Brûlé, "Polymer-modified asphalt cements used in the road construction industry: basic principles," *Transportation Research Record*, vol. 1535, no. 1, pp. 48–53, 1996.
- [55] G. Moises Cisneros Rached and E. Mazzone, "Cabvaliere, "method for crosslinking asphalt compositions and the product resulting therefrom," *United States Patent, Appl. Publ.*, vol. 1, p. 19, 2003.
- [56] X. Yang and Z. You, "High temperature performance evaluation of bio-oil modified asphalt binders using the DSR and MSCR tests," *Construction and Building Materials*, vol. 76, pp. 380–387, 2015.
- [57] F. J. N. Simona Senise, A. A. Cuadri, and P. Pedro, "Hybrid rubberised bitumen from reactive and non-reactive ethylene copolymers," *Polymers*, vol. 9, 2019.
- [58] L. M. B. Costa, H. M. R. D. Silva, J. Peralta, and J. R. M. Oliveira, "Using waste polymers as a reliable alternative for asphalt binder modification – performance and morphological assessment," *Construction and Building Materials*, vol. 198, pp. 237–244, 2019.
- [59] T. Mandal, R. Sylla, and H. U. Bahia, "Road Materials and Pavement Design Effect of cross-linking agents on the rheological properties of polymer- modified bitumen," *Road Materials and Pavement Design*, vol. 16, pp. 37–41, 2015.
- [60] S. Thakur and N. Karak, "Castor oil-based hyperbranched polyurethanes as advanced surface coating materials," *Progress in Organic Coatings*, vol. 76, no. 1, pp. 157–164, 2013.
- [61] S. Ibrahim, A. Ahmad, and N. S. Mohamed, "Characterization of novel Castor oil-based polyurethane polymer electrolytes," *Polymers*, vol. 7, no. 4, pp. 747–759, 2015.