



Effect of polymer molecular weight on the rheology of SBS polymer-modified asphalt binder

Ikenna D. Uwanuakwa¹ · Musa Adamu^{2,3} · Shaban Ismael Albrka Ali¹ · Pinar Akpınar⁴ · Mohd Rosli Mohd Hasan⁵ · Khairul Anuar Shariff⁶ · Ibrahim Khalil Umar¹ · S. I. Haruna³

Received: 16 February 2022 / Accepted: 23 January 2023 / Published online: 5 February 2023
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Abstract

The properties of asphalt are known to change significantly when modified with polymer, and such shift is often attributed to polymer content, structure and density. On the other hand, there is a significant difference in polymers' properties with constant density and structure but varying molecular weight. In this research work, the effect of styrene butadiene styrene (SBS) polymer molecular weight on the hot storage stability, viscosity, rutting, and fatigue resistance of asphalt binder was investigated using the standard test methods on SBS-modified binders. Three SBS polymer with different molecular weight was used to modify 60/70 pen grade unmodified asphalt binder at 3%, 5%, and 7% by weight of the unmodified asphalt binder. It was found that increase in the polymer content and the molecular weight within the modified asphalt binder showed a significant improvement in the rutting resistance of the binder. The effect of the molecular weight on the rutting behaviour of the modified binder was more evident at 5% and 7% polymer content with up to 92% reduction from the unmodified non-recoverable creep compliance. The $IG^*l.\sin\delta$ parameter of the fatigue resistance analysis shows that the higher molecular weight of the polymer led to the improvement of the anti-fatigue performance parameter. The use of polymer with a high molecular weight value is not suitable for hot storage and reduces the viscosity of the binder.

Keywords Styrene butadiene styrene · Modified asphalt binder · Molecular weight

Introduction

Asphalt binder is a thermoplastic viscoelastic material used in the manufacturing of asphalt concrete for road paving. Natural asphalt and asphalt extracted from petroleum products are thermally sensitive and, therefore, susceptible to thermal-induced pavement distress [1–6]. One way to prolong the service life of the pavement is by modifying the asphalt with materials that have higher thermal change tolerance.

In the last four decades, a large interest has focused on improving asphalt binder's thermo-rheological properties. Materials such as polymer, clay, nanomaterials, recycled waste plastics, natural rubber, and other additives have been applied to polymer with each set of materials improving a given thermo-rheological parameter. Modified asphalt binder tends to behave differently unlike unmodified asphalt binder [7, 8]. For example, unmodified asphalt binder's viscosity measurement is independent of shear rate and directly proportional to temperature, whereas polymer-modified asphalt binder's viscosity measurement is

✉ Ikenna D. Uwanuakwa
Ikenna.uwanuakwa@neu.edu.tr

✉ Musa Adamu
madamu@psu.edu.sa

¹ Department of Civil Engineering, Near East University, Nicosia, Mersin-10, Turkey

² Engineering Management Department, College of Engineering, Prince Sultan University, Riyadh 11586, Saudi Arabia

³ Department of Civil Engineering, Bayero University Kano, Kano, Nigeria

⁴ Department of Civil Engineering, Bahçeşehir Cyprus University, Nicosia, Mersin-10, Turkey

⁵ School of Civil Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

⁶ School of Material and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

dependent on both shear rate and temperature. As a result of these differences in behaviour, the SHRP-A-369 report stated that the linear viscoelastic model of asphalt could be applied to “unmodified” and modified asphalt, but “the model should be applied with caution to modified asphalt cement” [9]. Furthermore, specification standards developed for unmodified asphalt binder material design have been reported to have a lower correlation for designs with modified asphalt binder [10].

One approach to understanding the complexity of asphalt behaviour is the use of the colloidal theory of asphalt. Asphalt is made up of asphaltene and maltene. The maltene component can be further disassociated into saturates, aromatics, and resins. Each component possesses a distinctive property that controls the behaviour of the asphalt binder. The molecular weight (M_w) of these asphalt components is one of the dominant properties. On the other hand, asphaltene, which represents between 5 and 20 wt.% of paving grade asphalt, has the highest Mn up to 3500 g/mol [7]. Asphaltene exists in asphalt as a dispersed solid particle (micelles) in the maltene and dominates the stiffness properties of the paving grade asphalt [7]. Also, the asphaltene requires the peptization of resins to remain stable in the maltene matrix [11].

Research carried out over the years has shown that asphaltene controls the stiffness behaviour of asphalt [12]. However, polymers and other materials used in asphalt modification have a large molecular weight of 500,000 g/mol.

Available literature has not investigated the effect of the molecular weight of polymer on the behaviour of asphalt binder while maintaining a constant density. In this research, the change in molecular of SBS polymers with the same density was investigated on the hot storage stability, viscosity, rutting, and fatigue performance criteria of asphalt binder.

Materials and methods

Materials

This study utilised a 60/70 Pen grade asphalt for the unmodified binder and in the production of the modified binders. The SBS polymers used were Kraton® D1152 ESM and D1101 ASM polymers designated as PMB-I and PMB-II, respectively. The properties of the asphalt and the polymers are summarised in Table 1 and composition of the polymer modified bitumen (PMB) is presented in Fig. 1.

Characterisation of SBS polymers

The characterisation of the polymer molecular weight was carried out using the gel permeation chromatography (GPC) technique. The samples were prepared by dissolving 0.1% wt. of tetrahydrofuran (THF) solution in a 1.5- μ m vial and taken through a 0.2- μ m filter to remove the undissolved polymer [13]. The characterisation was carried out with Agilent 1260 Infinity Quaternary LC gel permeation chromatography as shown in Fig. 2.

Sample preparation

The addition of SBS polymer was made by the weight of the asphalt. For each SBS polymer, 3%, 5%, and 7% wt. were used to modify the 60/70 Pen grade asphalt with a lower shear mixer (2000 revolutions per minute -RPM) at a temperature of 175 °C. The polymer content was selected based on the results from previous literature that specified 5 to 6% as the optimal SBS content [14, 15]. The SBS polymer used was milled powder which was added at a temperature lower than the disassociation temperature of SBS to achieve phase inversion.

Table 1 Physical and chemical properties of asphalt and polymers

Parameters	Asphalt	D1152 ESM PMB-I	D1101 ASM PMB-II	D1184 ASM PMB-III
Penetration @25 °C (dmm)	63	–	–	–
Softening point (°C)	–	–	–	–
Viscosity @135 (Pa s)	–	–	–	–
Solution viscosity @25% (Pa s)	–	1.0	1.24	4.2
Structure	–	Linear	Linear	Branch
Styrene–butadiene ratio	–	29.5/70.5	31/69	30/70
Melt flow rate 200 °C/5000 g (g/10 min)	–	7.2	–	–
Particle size < 200 μ m% wt	–	4.8	10	7
Molecular weight, M_w (g/mol)	–	158, 270	357, 600	506, 920

Fig. 1 Composition of a prepared polymer-modified binder (PMB)

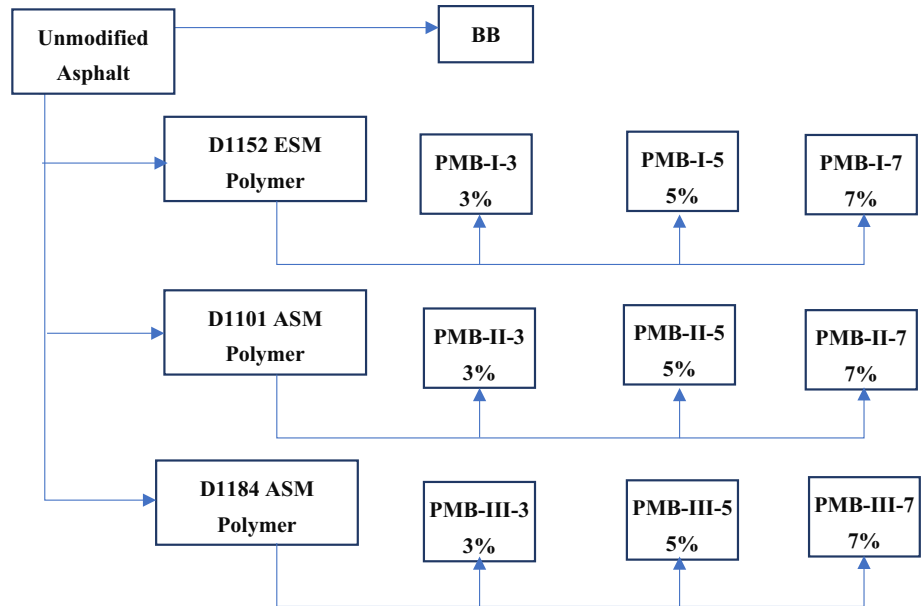


Fig. 2 GPC experimental setup Agilent 1260 Infinity Quaternary LC equipment

Storage stability

The hot storage stability of SBS and asphalt was evaluated by comparing the top polymer-rich-phase (PRP) and the bottom asphalt-rich-phase (ARP) samples taken from oven-conditioned samples. The blended samples were placed in an aluminium tube of 36 mm in diameter and 150 mm in height. The preparation of the samples for the hot storage stability of the polymer-modified binder was in accordance with BS EN 13,399:2010. The aluminium tube was filled between 100 and 120 mm in height and allowed to cool to room temperature and thereafter stored vertically in the oven for 48 and 72 h at

163 °C and 180 °C, respectively. The hot stored samples were removed from the oven and cooled to room temperature and thereafter stored for 4 h at – 5 °C. After the removal of the aluminium foil, the samples were divided into three equal portions and the softening point test was performed on the top and bottom parts in accordance with ASTM D36-11.

Rheological measurements

Mechanical Dynamic Analysis consists of the viscosity and viscoelastic rheological test.

Using a Brookfield rotational viscometer (RV), the viscosity test was performed on samples with 5% polymer content at 135 °C, 155 °C, and 175 °C between 3.3 and 16.9 1/s shear rate. 5% polymer content was chosen based on reports from the literature that indicated optimum SBS content [14, 15]. The test was conducted according to procedures outlined in the ASTM D4402-11 [16]. The Brookfield rotational viscometer only measures the torque in revolution per minute (rpm). Equation 1 was used to calculate the shear rate. The viscosity measurements were obtained in centipoises with spindle No. 27 rotating in the thermo-cell containing the asphalt and 5% SBS-modified asphalt binder.

The shear rate was calculated using the Newton law for viscosity;

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{1}$$

Where shear stress $\tau = \frac{T}{2\pi R_s^2 L}$, (2)

$$\text{and shear strain } \gamma = \frac{2\omega R_c^2 R_s^2}{x^2 (R_c^2 - R_s^2)} \quad (3)$$

ω is the rotational speed in radians/second, R_s is the spindle radius, R_c is the radius of the mould and x radial location where the shear rate is measured.

The viscoelastic rheological analysis was measured using a HAAKE Rheostress 6000 dynamic shear rheometer (DSR). The test was conducted according to the ASTM D7175-11 specification guideline [17].

The viscoelastic rheological test was carried out on un-aged, short-term, and longer-term aged binders. A frequency sweep test was performed on each sample for un-aged, short-term, and longer-term aged conditions. The frequency sweep for the un-aged and short-term aged samples was performed with a 25 mm parallel plate and 1 mm gap, whereas an 8-mm parallel plate with a 2-mm gap was used on long-term aged samples.

Assessment of $G^*/\sin\delta$ parameter: The variation of the parameter was investigated on an un-aged binder at temperatures between 46 and 76 °C at 6 °C increments. The test was carried out according to the procedures specified in SHRP-410 [18] and evaluated at a frequency of 10 rad/s.

The Multiple Stress Creep Recovery Test (MSCRT): The MSCRT was investigated at a temperature of 64 °C. The test was carried out in accordance with the specification of the AASHTO MP19 on samples conditioned with a rolling thin film oven (RTFO) [19].

Fatigue property test: The long-term aged samples conditioned with a pressure-ageing vessel (PAV) test was used on an 8-mm parallel plate with a 2-mm gap to measure the parameters for fatigue property evaluation. The test was carried out in accordance with the ASTM D7175-11 standard specification between 16 and 31 °C at 3 °C increments [17, 18].

Results and discussion

Effect of SBS molecular weight on the storage stability of PMB

In this research, a hot storage test was used to determine the degree of phase separation between the asphalt and polymer-rich phases. The test was conducted at temperatures 163 and 180 °C for 48 and 72 h to evaluate short and medium storage. The temperatures and storage duration were selected and captured based on the conditions specified in ASTM D36-11 and BS EN13399:2010 [20, 21]. The results were evaluated based on the softening point difference between ARA and PRP on the modified binder samples.

Figures 3 and 4 illustrate the behaviour of the samples. The effect of polymer density was kept constant throughout the experiment by selecting polymers with the same density and allowing for effective measurement of the molecular weight effect on storage stability. Figure 3 shows the softening point difference of the top and bottom sections after 48 h of hot storage at 163 °C and 180 °C. At 163 °C storage temperature, all the samples except PMB-I-3 were unstable for hot storage. Similarly, only PMB-I-3 at 163 °C was stable after 72 h of storage. It can be observed that the softening point difference of the top and bottom sections increased with the increase in SBS M_w . According to evidence in published literature [22, 23], resins and maltenes fraction of asphalt are responsible for peptising and stabilising asphaltene in asphalt colloidal systems and polymer in polymer-modified asphalt. Therefore, more maltenes will be required to maintain the thermodynamic stability of a blend when the molecular weight of the polymer is increased in the blend. Furthermore, the increase in storage temperature and duration did not have a significant effect on the phase separation compared to the M_w of the SBS polymer. Since the mixing temperature did not exceed the disassociation temperature of

Fig. 3 Storage stability of samples stored for 48 h

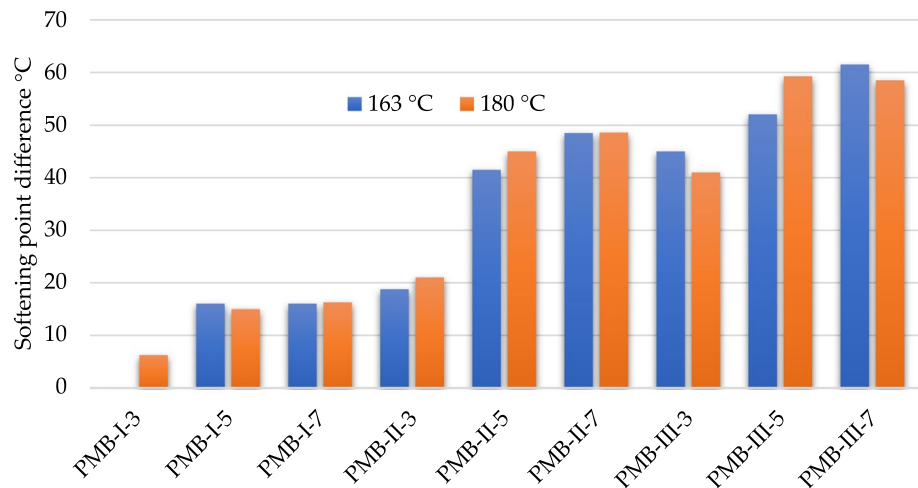
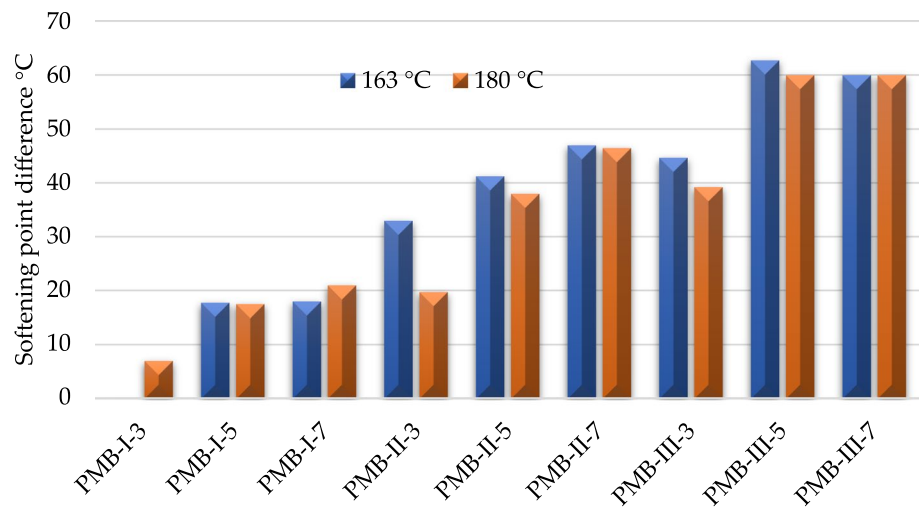


Fig. 4 Storage stability of samples stored for 72 h



the polymer, the SBS polymer existed as micelles. In addition to the asphaltene present in the asphalt, it increased the M_w of micelles within the PMB. At higher storage temperatures, un-peptised micelles due to excessive molecular weight disassociate from the matrix and float under gravity as a result of weaker London-van der Waals force which held the colloidal dispersion phase resulting in phase separation. For example, PMB-I-3, PMB-II-3 and PMB-III-3 contain 3 wt.% of SBS polymer. However, only PMB-I-3 achieved a stable storage at 163 °C hot storage temperature.

Effect of molecular weight on the viscosity PMB

The quiviscous temperature for asphalt concrete construction was developed by the Asphalt Institute in 1962 which recommended the mixing and compaction temperatures for a binder with a viscosity of 0.17 ± 0.02 and 0.28 ± 0.03 Pa s, respectively. These values are applied to both the Marshal mix and SuperPave mix designs [10]. However, the SuperPave manual noted that these viscosity value ranges are not valid to be used for modified binder mixing and compaction temperatures. The manual recommended the manufacturers' specifications for modified binders [10].

The effect of the molecular weight on the binder viscosity was investigated at 135 °C using a Brookfield viscometer between 3.38 and 16.91 1/s shear rate.

The results in Fig. 5 show the behaviour of the samples. It also confirms the Newtonian behaviour of unmodified asphalt. Furthermore, in samples with low M_w , the results show a slight deviation in the values of the viscosity from the Newtonian region towards the non-Newtonian region which is governed by the shear rate. The dependency on the shear rate increased with molecular weight. The same effect was also observed in the unmodified binder.

Furthermore, the results showed the relationship between the M_w and shear rate. The modification of the asphalt

altered the molecular structure of the asphalt from Newtonian to a non-Newtonian fluid. The behaviour of non-Newtonian fluid is a complex one, and the stress tensor, as well as its derivatives, is a function of the velocity gradient [24].

The increase in the shear rate was observed to decrease the dependency of the viscosity on the M_w . At a high shear rate, the intermolecular forces are destroyed, and this results in a decrease in the viscosity at a particular temperature.

In the case of unmodified asphalt which has a weak bond between the asphalt molecules [25], the bonds were broken at much lower shear rates and temperatures when compared with PMB held together by networks of polymer entanglement.

Furthermore, the polymer structure also influences the viscosity. PMB-III modified with branched polymer has a lower viscosity at a high temperature despite its high molecular weight. The behaviour can be attributed to the lower melting point associated with branched polymer chains [14, 15].

Rutting parameter characterisation of SBS-modified asphalt binder

The $G^*/\text{Sin}\delta$ of an asphalt binder extracted from the DSR test is recognised by SuperPave specification for the evaluation of the rutting performance of a binder. The specification requires a minimum value of 1.0 and 2.2 kPa for the un-aged and RTFOT binder, respectively, at a reference pavement temperature (AASHTO M 320, 2010) to meet the rutting resistance performance of asphalt pavement [18]. The results obtained for varying SBS polymer molecular weight are presented in Fig. 6 for the RTFOT samples.

The results show that increase in the testing temperature led to a decrease in the $G^*/\text{Sin}\delta$ value, while increase in the molecular weight of the polymer increased the $G^*/\text{Sin}\delta$ value. Beyond 64 °C, the unmodified binder did not meet the

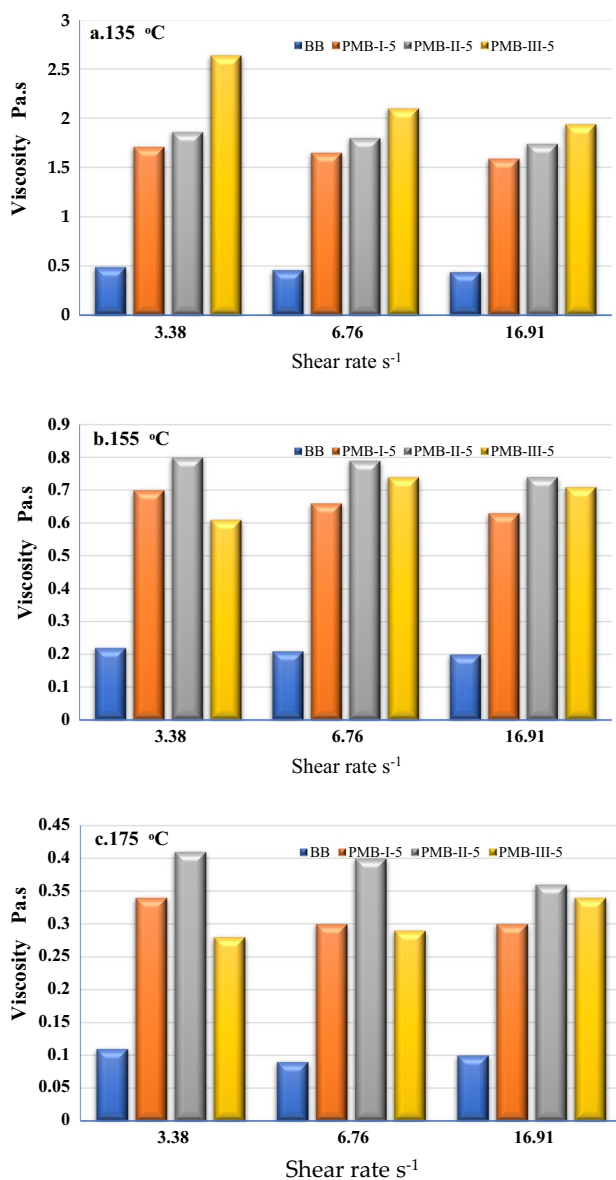


Fig. 5 Effect of shear rate on the viscosity of the samples at a 135, b 155, and c 175 °C

minimum requirement of 2.2 kPa specified for RTFOT-aged samples. The PMB-II and III met the requirement of up to 76 °C temperatures indicating a good resistance to rutting in the pavement.

The higher value of the $G^*/\text{Sin}\delta$ parameter associated with PMB-III with a higher M_w indicates the dependency of binder stiffness on the M_w for a given PMB at constant density.

Further analysis shows that the glass transition temperature of the SBS monomers influences the rutting parameter. The PMB-II with 31% polystyrene content of SBS polymer has higher rutting resistance. This could be attributed to the behaviour of the polystyrene monomer in SBS. It is

important to note that SBS exhibits two glass transition temperatures: $-100\text{ }^\circ\text{C}$ and $70\text{ }^\circ\text{C}$ for polybutadiene and polystyrene phases, respectively, and is expected to shift the glass transition temperature of asphalt [26]. This phenomenon was observed between 46 and 70 °C at 5% polymer content. PMB-II recorded the height $G^*/\text{Sin}\delta$ value.

Multiple Stress Creep Recovery (MSCR) characterisation of SBS-modified asphalt binder

The Multiple Stress Creep Recovery Test is generally used in the evaluation of the rutting performance of an asphalt binder [27–30]. In this research, the commonly used standard stress levels of 0.1 and 3.2 kPa were applied at 64 °C, and the corresponding induced strains were measured accordingly.

The importance of the MSCR test is to investigate the stress sensitivity of an asphalt binder for a given traffic load condition using the non-recoverable creep compliance (J_{nr}) parameter. The parameter (J_{nr}) can be calculated using Eq. (4) for both 0.1 and 3.2 kPa stress levels;

$$J_{nr} (\text{kPa}^{-1}) = \frac{1}{10} \left\{ \sum_{i=1}^{10} \left(\frac{e_{10}}{\tau} \right)_i \right\} \tag{4}$$

where e_{10} = adjusted strain after recovery for each cycle and τ is the applied stress level.

A detailed approach for the estimation of the J_{nr} is given in [31].

The non-recoverable creep compliance (J_{nr}) parameter measures the ratio of the strain that is not recovered at the end of the recovery section of the applied strain. The results of the J_{nr} at 1.0 and 3.2 kPa stress levels which corresponds to what is recommended by AASHTO MP19 [19] for the evaluation of binders for different traffic conditions are presented in Fig. 7. It is observed that increase in the molecular weight of the SBS resulted in a decrease in J_{nr} values. There was a significant reduction in the value of the unmodified J_{nr} and the modified binders.

Figure 7 further shows that at 5% SBS content, there was a 71%, 90%, and 92% reduction from the unmodified binder J_{nr} at 1.0 kPa for PMB-I-5, PMB-II-5, and PMB-III-5, respectively. Further, at 3.2 kPa stress level, the J_{nr} reduction from the unmodified binder for PMB-I-5, PMB-II-5, and PMB-III-5 were 84%, 88%, and 90%, respectively. With respect to the adjusted strain recovery (e_{10}) at the end of 0.1 kPa and 3.2 kPa applied stress, the unmodified binder's adjusted strain recovered was 0.216 and 9.059, respectively. However, with the addition of 5% SBS polymer, there was an 85%, 92%, and 93% reduction in the adjusted strain recovered at 0.1 kPa for PMB-I-5, PMB-II-5, and PMB-III-5, respectively. With an increase in the stress to 3.2 kPa, the adjusted strain recovered at the end was 83%, 88%, and

89% for PMB-I-5, PMB-II-5, and PMB-III-5, respectively. This indicates that the increase in the SBS molecular weight decreases the J_{nr} parameter of the binder and improves its susceptibility to permanent deformation. Furthermore, Kumar et al. [32] reported higher elastic recovery with binder modified with branch polymer when compared with those modified with linear polymer.

The results of the statistical analysis of two-factor ANOVA on the variation test samples with Jnr100 and Jnr3200 are presented in Table 2. The higher variation between F -value and F -critical, and the reduced P value (0.02) lower than the alpha value resulted in the rejection of the proposed null hypothesis that the mean of observation is the same, in favour of the alternative that there is a variation

Fig. 6 Variation $G^*/\text{Sin}\delta$ with temperature for RTFOT samples

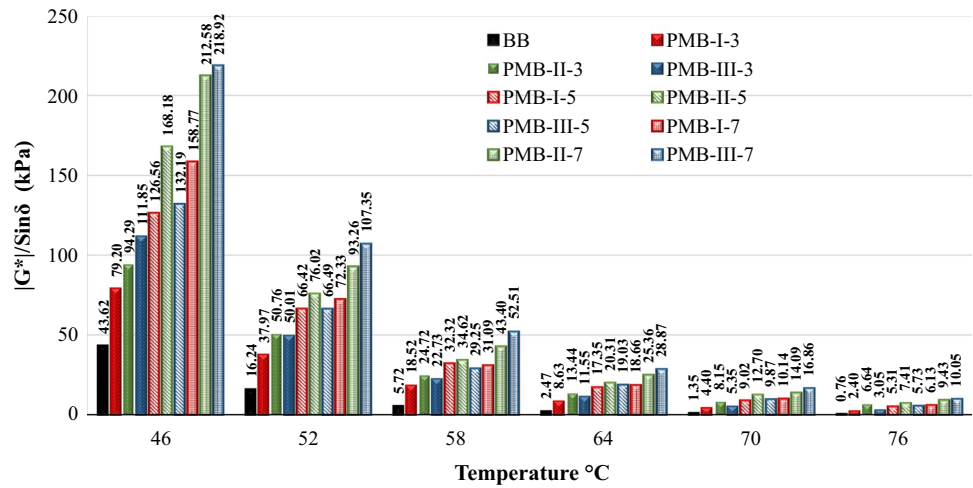


Fig. 7 J_{nr} Values for study samples

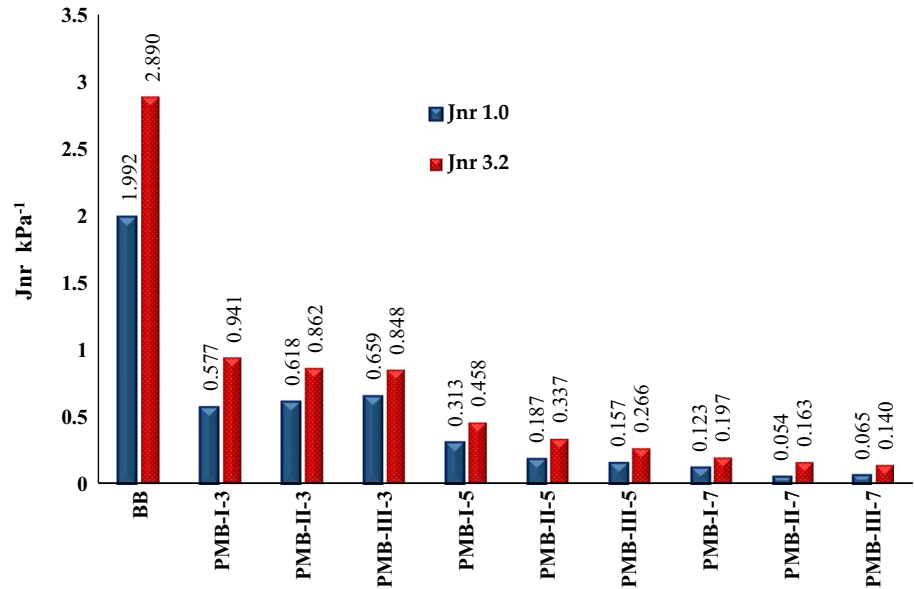


Table 2 Two-factor ANOVA on the samples Jnr100 and Jnr320

Source of variation	SS	df	MS	F	P-F crit value
Rows	8.900934	9	0.988993	31.94582	8.97E-06
Columns	0.277348	1	0.277348	8.958731	0.015124
Error	0.278626	9	0.030958		
Total	9.456908	19			

in the mean. This suggests that the increase in M_w has a significant effect on the variation of J_{nr} of the asphalt binder.

Fatigue parameter characterisation of SBS-modified asphalt binder

Figure 8 shows the variation of $|G^*| \cdot \sin \delta$ parameter with the temperature for all studied samples. The $|G^*| \cdot \sin \delta$ parameter of an asphalt binder is used in the evaluation of the fatigue property of the binder as detailed in the AASHTO M 320 specification [18]. The standard specified a maximum $|G^*| \cdot \sin \delta$ value of 5000 kPa for a given asphalt binder to meet the anti-fatigue performance criteria. All the study samples were not suitable for resisting fatigue at 16 °C. In general, with the increase in temperature, the study shows that an increase in the polymer content which increases the stiffness of the binder reduces its potential for resisting fatigue in pavement. Furthermore, it can be observed that PMB-III-3 performed better in fatigue resistance. Also, PMB-III modified with branched polymer chain from the 5000 kPa limiting line in Fig. 8, and within each SBS content, PMB-III with a higher M_w was observed to have a reduced $|G^*| \cdot \sin \delta$ parameter when compared with the corresponding PMB-I and PMB-II. This tends to indicate resistance to binder ageing.

The fatigue failure for PMB-I and PMB-III at 5% SBS polymer content is expected to occur at a temperature below 25 °C. Both modifiers have a similar polystyrene-polybutadiene ratio of approximately 30/70. However, the PMB-II fatigue failure at 5% polymer content is expected to occur at a temperature below 28 °C.

Cost-benefit analysis

In this section, the principles of cost-benefit analysis are outlined. The cost-benefit analysis (CBA) of the modification of asphalt with polymers of varying molecular weight was analysed and the results are discussed with respect to the rutting properties of asphalt binder.

The philosophy of cost-benefit analysis is to provide an economic outlook on an alternative system based on the evaluation of the cost, benefit, and effectiveness of the system. The cost-benefit analysis in this research was estimated to ascertain the economic suitability of modifying 60/70 penetration grade asphalt with SBS polymer of different molecular weights. The analysis considered only the rutting properties.

The polymer material cost was obtained from Kraton polymer and the asphalt cost was obtained from Alibaba.com. The price of asphalt obtained from Alibaba.com did vary with location and suppliers. Although there are limited 60/70 pen grade suppliers on Alibab.com online market, the price range difference in each location is within 15 €/Mt. The average price obtained from suppliers in Turkey is 224.49 €/Mt [33].

Other costs that were associated with polymer modification include heating and mixing of the polymer and asphalt. The estimation was carried out based on technical data of IKA PMB Plant DR 2000/10 PB, electricity tariff, and labour in Turkey. According to Enerjisa 2019 Annual Report, Turkey’s average electricity tariff was 0.063 €/kWh and the IKA PMB electricity input and production output are 25 kW and 2500 L/h [34].

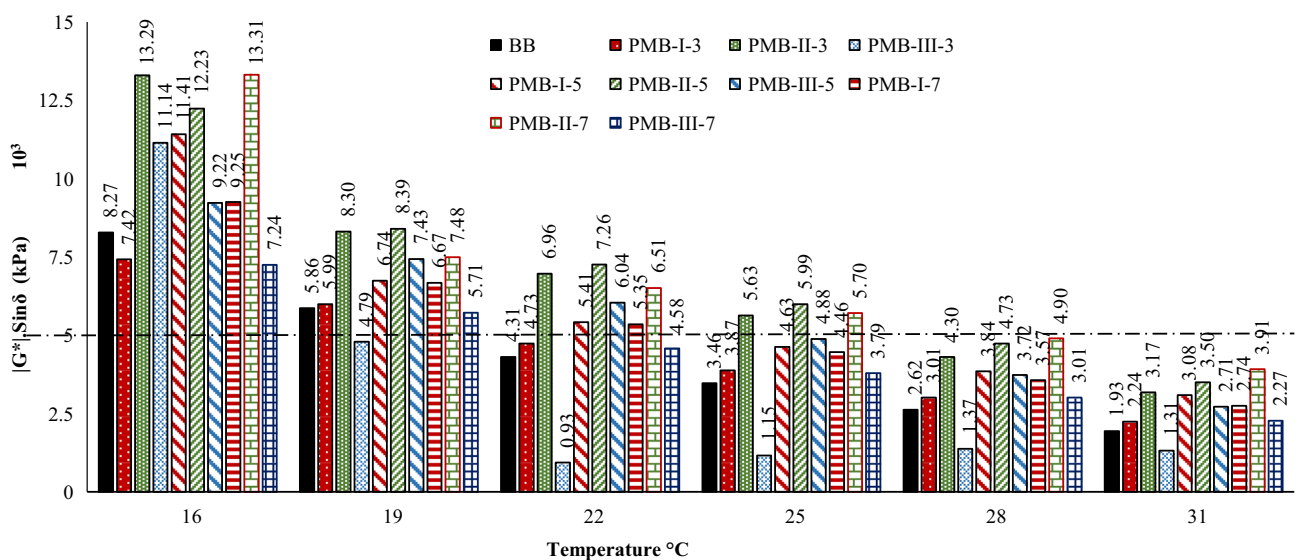


Fig. 8 Variation $|G^*| \cdot \sin \delta$ with temperature

Estimation cost of electricity per hour = 25 * 0.063 = 1.575€/ Totaloutput per hour = 2500L

The volumes were converted to mass by multiplying them by the density. The density of the two mixtures is estimated as follows:

$$\frac{1}{\rho} = \frac{\text{mass fraction of polymer}}{\text{density of polymer}} + \frac{\text{mass fraction of asphalt}}{\text{density of asphalt}} \tag{5}$$

Determination of mass fraction at varying polymer content:

$$= \% \text{ conc} * 1000\text{cm}^3 * \text{density} \tag{6}$$

Assume 5 € for labour per hour to produce PMB. Therefore, the cost of producing PMB with different polymer content is 302 €/mt for PMB-I and PMB-II, and 312 €/mt for PMB-III for all polymer content. The machine's hourly rate was 5 € per hour.

The cost-effectiveness analysis was carried out by comparing the cost incurred to obtain the benefit and cost of the existing system. In this study, a simplified approach was adopted to calculate the cost-effectiveness;

$$\text{cost-effectiveness} = \frac{\text{expected performance}}{\text{unit cost}} \tag{7}$$

The cost-benefit was determined by taking the ratio of the cost-effectiveness of the unmodified binder to that of the modified binder. The ratio was estimated between 46 and 64 °C for rutting resistance and the J_{nr} parameter.

The results of the cost-effectiveness of modifying asphalt with SBS polymer with varying molecular weights with respect to rutting resistance are presented in Fig. 9.

In the figure, it can be observed that at 46 °C pavement temperature, the benefits of modifying 60/70 pen grade asphalt with Kraton D1152 polymer at 3, 5, and 7% polymer content were 1.53, 2.23, and 2.5, respectively. Further, for binder PMB incorporated with Kraton D1184, which has a high molecular weight, the gained benefits at 46 °C were 2.12, 2.26, and 3.30 for 3, 5, and 7% polymer content, respectively. This is an indication that increased polymer content has a significant increase in economic benefit. Also, the increase in the molecular weight of the polymer was observed to yield a significant benefit across the test temperatures.

At high temperatures, the cost-benefit was observed to increase significantly with an increased molecular weight of the polymer. For example, the cost-effectiveness ratio of PMB-III-7 increases at an average of 1.46 from 46 to 64 °C temperatures. The PMB-II-7 and PMB-I-7 increased at an average of 1.24 and 0.89 respectively from 46 to 64 °C temperatures. Similarly, the trend was also observed with 3 and 5% polymer content. The results of the cost-effectiveness ratio are in agreement with data presented in [35, 36] which reported a 2.6 cost-effectiveness ratio for polymer-modified asphalt concrete.

The gained benefits calculated using the J_{nr} parameter are presented in Fig. 10. The cost-effectiveness values obtained for 3% polymer content show 4.09, 3.82, and 3.66 gain for using PMB-I, PMB-II, and PMB-III respectively. However, at 5% and 7% polymer content, PMB-III shows 17.05 and 63.20 respectively for 1.0 kPa stress level, and at 3.2 kPa, 14.60 and 31.37. The benefit decreased as the SBS molecular weight decreased. It is worth noting that using SBS with high molecular weight would increase the cost-benefit of pavement surfacing.

Fig. 9 Cost-effectiveness ratio for rutting parameter

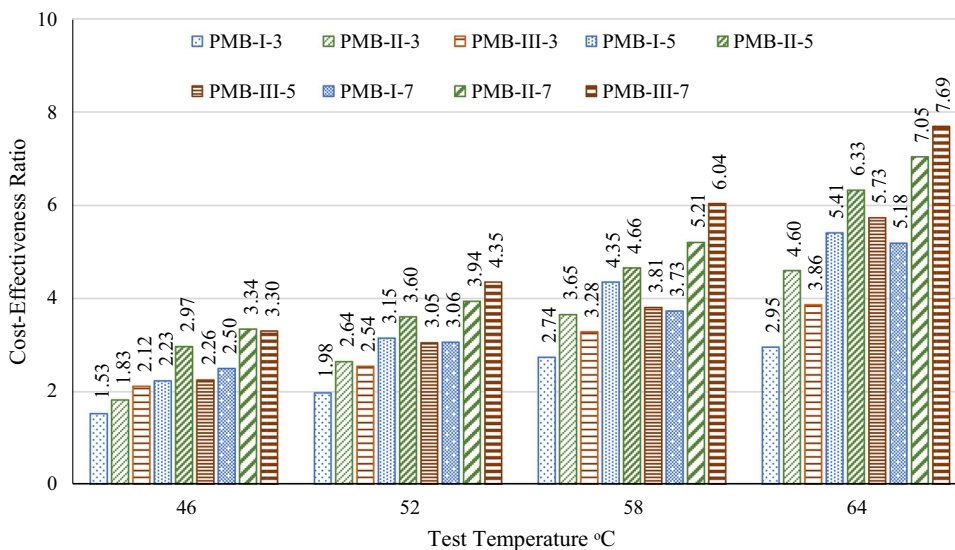
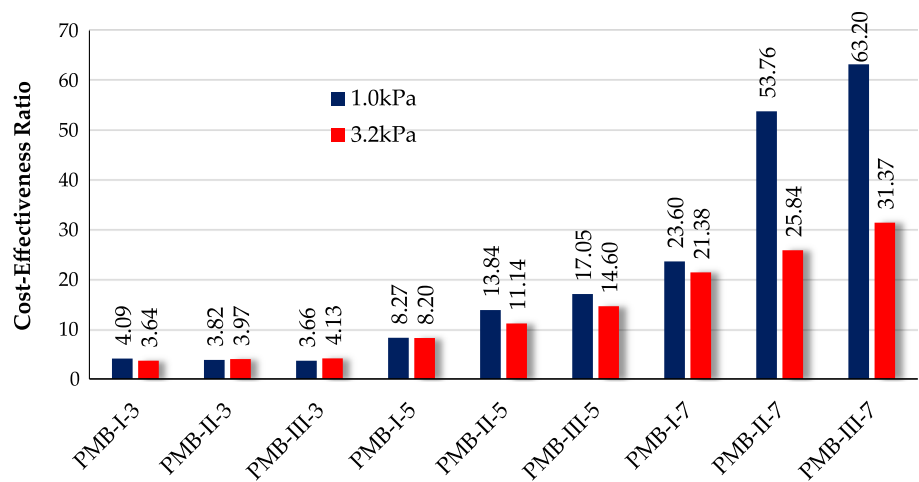


Fig. 10 Cost-effectiveness ratio for J_{nr} parameter



Conclusions

The study investigated the effect of polymer molecular weight on the thermal-rheology behaviour of SBS polymer-modified asphalt binder. Nine SBS polymer-modified asphalt binder samples were prepared by modifying the unmodified binder with three different SBS polymers at 3, 5, and 7 wt.%. The influence of the SBS polymer molecular weight was investigated on the hot storage stability, viscosity, rutting, and fatigue performance of the modified binder.

- The hot storage stability results show that the SBS polymer molecular weight has a significant influence on the degree of modified binder stability stored at elevated temperatures. The results supported the colloidal theory of asphalt which requires the resins to peptise the high molecular weight micelles in order to stabilise the sample.
- The viscosity evaluation of the modified binder indicated the dependency of the value on the SBS polymer molecular weight and shear rate at 135 and 155 °C. However, at 175 °C, a test temperature close to the disassociation temperature of SBS, the viscosity value is controlled by the butadiene/styrene content.
- The result of the rutting performance of the SBS-modified binder shows that at lower polymer content of 3%, there is no appreciable influence of M_w on the $G^*/\sin\delta$ and recovery strain for both 0.1 and 3.2 kPa stress. However, with the increasing polymer content, a significant difference was observed in the M_w influence on the rutting performance parameters.
- Furthermore, the non-recoverable creep compliance (J_{nr}) parameter analysis shows that there was a significant reduction in the value of the unmodified J_{nr} , which is proportional to polymer content and molecular weight. Also, the ANOVA analysis indicated that increase in M_w assists in improving the J_{nr} of the binder.
- The increase in the M_w was observed to induce lower $G^*/\sin\delta$ parameter at intermediate temperature.
- The analysis of the cost-benefit of using SBS polymer with high molecular weight indicated that there is a significant benefit to using high molecular weight SBS polymer. For the $G^*/\sin\delta$ parameter, the cost-effectiveness ratio of PMB-III-7 increases at an average of 1.46 from 46 to 64 °C temperatures. The PMB-II-7 and PMB-I-7 increased at an average of 1.24 and 0.89, respectively, from 46 to 64 °C temperatures. For the J_{nr} parameter, for PMB-III with an average molecular weight of 500 kDa at 5% and 7% for 1.0 kPa stress level was 17.05 and 63.20, respectively. At a higher stress level of 3.2 kPa, the benefit increased to 14.60 and 31.37, respectively. The PMB-II and PMB-I cost-effectiveness value was lower than that of PMB-III indicating the economic potential of using SBS with high molecular weight.

Acknowledgements The authors thank Kraton Polymers Nederland BV for supplying the SBS used in this research. Furthermore, we acknowledge the Highway laboratory of the School of Civil Engineering and Materials laboratory of School of Material and Mineral Resources Engineering, Universiti Sains Malaysia, for the equipment. Additionally, the authors wish to acknowledge the Structures and Materials (S&M) Laboratory, Prince Sultan University, Riyadh, Saudi Arabia, for their viable support.

Declarations

Conflict of interest The authors declare no conflict of interest.

References

- Atul Narayan SP, Murali Krishnan J, Little DN, Rajagopal KR (2017) Mechanical behaviour of asphalt binders at high temperatures and specification for rutting. *Int J Pavement Eng* 18:916–927. <https://doi.org/10.1080/10298436.2015.1126272>

2. Jamal Hafeez I, Yaseen G, Aziz A (2018) Influence of cereclor on the performance of aged asphalt binder. *Int J Pavement Eng*. <https://doi.org/10.1080/10298436.2018.1542694>
3. Dalhat MA, Al-Abdul Wahhab HI (2017) Performance of recycled plastic waste modified asphalt binder in Saudi Arabia. *Int J Pavement Eng* 18:349–357. <https://doi.org/10.1080/10298436.2015.1088150>
4. Ziari H, Babagoli R (2015) Evaluation of fatigue and rutting behavior of asphalt binder containing warm additive. *Pet Sci Technol* 33:1627–1632. <https://doi.org/10.1080/10916466.2015.1084320>
5. Shafabakhsh G, Motamedi M, Firouznia M, Isazadeh M (2019) Experimental investigation of the effect of asphalt binder modified with nanosilica on the rutting, fatigue and performance grade. *Pet Sci Technol* 37:1495–1500. <https://doi.org/10.1080/10916466.2018.1476534>
6. Mirzababaei P, Nejad FM, Vanaei V (2017) Investigation of rutting performance of asphalt binders containing warm additive. *Pet Sci Technol* 35:79–85. <https://doi.org/10.1080/10916466.2016.1247173>
7. Lesueur D (2009) The colloidal structure of bitumen: consequences on the rheology and on the mechanisms of bitumen modification. *Adv Colloid Interface Sci* 145:42–82. <https://doi.org/10.1016/J.CIS.2008.08.011>
8. Polacco G, Filippi S, Merusi F, Stastna G (2015) A Review of the fundamentals of polymer-modified asphalts: asphalt/polymer interactions and principles of compatibility. *Adv Colloid Interface Sci* 224:72–112. <https://doi.org/10.1016/J.CIS.2015.07.010>
9. Anderson DA, Christensen DW, Bahia HU, Dongre R, Sharma MG, Antle CE (1994) Binder characterization and evaluation volume 3: physical characterization
10. Yildirim Y, Ideker J, Hazlett D (2006) Evaluation of viscosity values for mixing and compaction temperatures. *J Mater Civ Eng* 18:545–553. [https://doi.org/10.1061/\(ASCE\)0899-1561\(2006\)18:4\(545\)](https://doi.org/10.1061/(ASCE)0899-1561(2006)18:4(545))
11. Lian H, Lin JR, Yen TF (1994) Peptization studies of asphaltene and solubility parameter spectra. *Fuel* 73:423–428. [https://doi.org/10.1016/0016-2361\(94\)90097-3](https://doi.org/10.1016/0016-2361(94)90097-3)
12. Eberhardsteiner L, Füssl J, Hofko B, Handle F, Hospodka M, Blab R, Grothe H (2015) Influence of asphaltene content on mechanical bitumen behavior: experimental investigation and micromechanical modeling. *Mater Struct Constr* 48:3099–3112. <https://doi.org/10.1617/S11527-014-0383-7/FIGURES/15>
13. Ding Y, Deng M, Cao X, Yu M, Tang B (2019) Investigation of mixing effect and molecular aggregation between virgin and aged asphalt. *Constr Build Mater* 221:301–307. <https://doi.org/10.1016/j.conbuildmat.2019.06.093>
14. Chen JS, Liao MC, Tsai HH (2002) Evaluation and optimization of the engineering properties of polymer-modified asphalt. *Pract Fail Anal* 2:75–83. <https://doi.org/10.1007/BF02719194>
15. Sun DQ, Zhang LW (2013) A quantitative determination of polymer content in SBS modified asphalt. Part I: state of the art. *Pet Sci Technol* 31:2636–2642. <https://doi.org/10.1080/10916466.2011.580302>
16. ASTM D4402 (2011) Standard test method for viscosity determination of asphalt at elevated temperatures using a rotational viscometer. West Conshohocken
17. ASTM D7175 (2011) Standard test method for determining the rheological properties of asphalt binder using a dynamic shear rheometer. West Conshohocken
18. AASHTO M (2010) 320 standard specification for performance-graded asphalt binder. American Association of State Highway and Transportation Officials, Washington, pp 1–8
19. AASHTO (2010) Specification for performance-graded asphalt binder using multiple stress creep recovery (Mscr) test MP19. Mp19
20. BSI (2010) Bitumen and bituminous binders. Determination of storage stability of modified bitumen, p 13399
21. ASTM (2011) Standard test method for softening point of bitumen (Ring-and-ball apparatus). West Conshohocken
22. Pauli AT (1999) Asphalt compatibility testing using the automated Heithaus titration test. *Am Chem Soc Div Fuel Chem*. <https://doi.org/10.2172/778911>
23. Fu X, Finley A, Carpenter S (2018) Formation damage problems associated with CO2 flooding. In: Yuan B, Wood D (eds) Formation damage during improved oil recovery: fundamentals and applications. Elsevier, Amsterdam, pp 305–359
24. Binesh AR, Mousavi SM, Kamali R (2015) Effect of temperature-dependency of Newtonian and Non-Newtonian fluid properties on the dynamics of droplet impinging on hot surfaces. *Int J Mod Phys C*. <https://doi.org/10.1142/S0129183115501065>
25. Jones DR, Kennedy TW (1991) The asphalt model: results of the SHRP asphalt research program. In: Proceedings of the strategic highway research program and traffic safety on two continents, part four. Transportation Research Board, Gothenburg
26. Nivitha MR, Murali Krishnan J (2016) What is transition temperature for bitumen and how to measure it? *Transp Dev Econ* 2:1–8. <https://doi.org/10.1007/s40890-015-0009-y>
27. García-Travé G, Tauste R, Moreno-Navarro F, Sol-Sánchez M, Rubio-Gámez MC (2016) Use of reclaimed geomembranes for modification of mechanical performance of bituminous binders. *J Mater Civ Eng*. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0001507](https://doi.org/10.1061/(ASCE)MT.1943-5533.0001507)
28. Jafari M, Akbari Nasrekani A, Nakhaei M, Babazadeh A (2017) Evaluation of rutting resistance of asphalt binders and asphalt mixtures modified with polyphosphoric acid. *Pet Sci Technol*. <https://doi.org/10.1080/10916466.2016.1248776>
29. Shafabakhsh GH, Ani OJ, Talebsafa M (2015) Artificial Neural network modeling (ANN) for predicting rutting performance of nano-modified hot-mix asphalt mixtures containing steel slag aggregates. *Constr Build Mater* 85:136–143. <https://doi.org/10.1016/j.conbuildmat.2015.03.060>
30. Ashish PK, Singh D (2018) High- and intermediate-temperature performance of asphalt binder containing carbon nanotube using different rheological approaches. *J Mater Civ Eng* 30:04017254. [https://doi.org/10.1061/\(asce\)mt.1943-5533.0002106](https://doi.org/10.1061/(asce)mt.1943-5533.0002106)
31. Soenen H, Blomberg T, Pellinen T, Laukkanen OV (2013) The multiple stress creep-recovery test: a detailed analysis of repeatability and reproducibility. *Road Mater Pavement Des* 14:2–11. <https://doi.org/10.1080/14680629.2013.774742>
32. Kumar Y, Singh SK, Oberoi D, Kumar P, Mohanty P, Ravindranath SS (2020) Effect of molecular structure and concentration of styrene-butadiene polymer on upper service temperature rheological properties of modified binders. *Constr Build Mater*. <https://doi.org/10.1016/j.conbuildmat.2020.118790>
33. Bitumen Turkey Trade, Buy Turkey Direct From Bitumen Factories at Alibaba.com. <https://www.alibaba.com/countrysearch/TR/bitumen.html>. Accessed 23 Nov 2022
34. Enerjisa (2019) Enerjisa annual report 2019
35. Souliman MI, Mamlouk M, Eifert A (2017) Mechanistic analysis and cost-effectiveness of rubber and polymer modified asphalt mixtures. *Adv Civ Eng Mater* 6:20160069. <https://doi.org/10.1520/ACEM20160069>
36. Souliman MI, Mamlouk M, Eifert A (2016) Cost-effectiveness of rubber and polymer modified asphalt mixtures as related to sustainable fatigue performance. *Procedia Eng*. 145:404–411

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