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Influence of bitumen type and polymer dosage on the relaxation spectrum of styrene-butadiene-styrene (SBS)/styrene-butadiene (SB) modified bitumen

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Abstract

Modification using elastomeric thermoplastic polymers is commonly adopted to improve the high-temperature performance of paving bitumen. The performance of modified bitumen classified under the same grade is highly variable depending on the type of base bitumen, the polymer architecture, and its dosage. The current specification parameters are insensitive to such variability. Identification of a suitable set of parameters that can quantify the changes in rheological properties due to various interaction mechanisms of bitumen with modifier thus becomes necessary. In this study, the base bitumen obtained using two different processes, namely air rectification and component blending, are considered. Though the same grade of bitumen produced using both processes is considered, the material compositions are different, and this necessitated the use of different polymer architectures (diblock and triblock SBS) for the two binders. Three different dosages are used for each modifier. A stress relaxation experiment is conducted, and the peak modulus and stress relaxation time are determined. In addition, the continuous relaxation spectrum and the associated parameters are computed. The base bitumen and the polymer architecture of the corresponding polymer influenced the stress relaxation response substantially. These factors also influenced the response of the material captured using the relaxation spectrum and exhibited interesting insights regarding the influence of temperature.

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1 Introduction

The increasing traffic volume and axle loads in recent days have necessitated the use of polymer-modified binders for the construction of bituminous pavements. There are a variety of modifiers available for this purpose, and amongst those, the use of elastomers, plastomers, and crumb rubber are common (Bahia et al. 2001; Airey 2004; Zhu et al. 2014). The choice of the type of modifier, however, depends on the environmental and traffic conditions of the locality and the pavement composition, the combined influence of which determines the likely mode of distress. For locations where rutting in bituminous layers is the predominant mode of failure, bitumen modification with elastomeric polymers is suggested (Chen et al. 2002; Tayfur et al. 2007). This class of modifiers is said to improve the high temperature ‘stiffness’ properties of the binder in addition to the enhancement of its elastic recovery properties (Lu and Isacsson 1997; Zhu et al. 2014).

Styrene and butadiene-based triblock and diblock copolymers are commonly used elastomeric modifiers for bitumen modification (Lu and Isacsson 1997). The triblock copolymer based on styrene and butadiene (SBS) consists of polystyrene block followed by polybutadiene block followed by polystyrene block. The polystyrene block is hard and rigid, while the polybutadiene block is in the form of a rubbery matrix. At room temperature, the polystyrene end blocks join together to form hard, rigid domains allowing the formation of a physically entangled three-dimensional network. Here, the polystyrene end imparts strength to the material, while the polybutadiene rubbery matrix imparts elasticity to the material. The cross-linked network is prevalent up to the glass transition temperature of polystyrene, which is about 100 °C beyond which the polystyrene end domains begin to dissociate (Kumar et al. 2020). However, as the temperature reduces, the end domains are re-formed, and SBS regains its three-dimensional network (Gahvari 1997; Airey 2004). The diblock copolymer based on styrene and butadiene (SB) consists of a polystyrene block followed by a polybutadiene block. The three-dimensional network is missing here owing to the absence of the second polystyrene end block. The diblock SB copolymers form radial or star-shaped clusters rather than a three-dimensional network (McKay et al. 1995).

When added to bitumen, SBS undergoes a physical interaction wherein the elastomeric phase of the copolymer absorbs the lighter fractions present in bitumen and swells to approximately five to nine times its initial volume (Masson et al. 2003; Sengoz et al. 2009). This nature of interaction influences the morphology of SBS modified bitumen (Brule 1996; Becker et al. 2001). At low concentrations ($\lesssim 4\%$), the polymer is dispersed in the bituminous matrix; at intermediate dosages ($\sim 5\%$), an unstable co-continuous matrix is observed, and at higher dosages ($\gtrsim 7\%$), the polymer volume increases substantially such that bitumen is dispersed in the polymer matrix (Brule 1996). The morphology wherein bitumen is dispersed in the polymer matrix is said to provide the maximum beneficial effects for the polymer-modified system. However, Kluttz et al. (2012) have observed a phase inversion when the dosage of SBS was increased to about 7 to 8%. This modified bitumen was observed to result in an increased fatigue life based on the 3-D model simulations and field data (Kluttz et al. 2012). For the polymer-modified systems to be stable, the maltene content of the base bitumen is considered to be important (Airey 2004). The molecular weight of the SBS/SB block copolymers is generally considered to be identical to that of asphaltenes, and hence, for a stable modified binder system, sufficient maltenes must be available for the interactions to develop. However, higher aromatic content is considered detrimental as its higher solvency power could dissolve the polystyrene blocks (Airey 2004).

The factors that influence the interaction of bitumen with a modifier can be classified as the properties of the modifier, such as type and dosage of the modifier, architecture of the modifier, and the properties of base bitumen such as the crude source, processing methodologies, and its grade (Airey and Brown 1998; Lu et al. 1999; Polacco et al. 2006; Xu et al. 2016; Kumar et al. 2020). The blending variables, including temperature, shear rate, and duration of blending, also play a crucial role (Keyf et al. 2007; Navarro et al. 2007, 2009). In addition to the factors mentioned above, the rheological response of the material depends on the testing conditions such as the test temperature, the magnitude of the load, and the rate of loading (Airey 2004; Lu and Isacsson 1998; Nivitha et al. 2018; Kumar et al. 2020).

Among these factors, the type of base bitumen is critical as it could also dictate the choice of polymer and the associated factors such as its type and dosage (Xu et al. 2016). In India, the vacuum residue obtained from the vacuum distillation tower is post-processed by the refineries to meet the specification requirements using either of the two processes, namely, air rectification or component blending (Rajan et al. 2008; Nivitha et al. 2019). The bitumen obtained from the two processes is different in terms of their chemical composition and hence the rheological response. In the air rectification (also termed as air blowing) process, the vacuum residue is subjected to continuous hot air blowing, which induces oxidation in the material. The resulting bitumen has a higher viscosity compared to the vacuum residue. In the component blending process, the vacuum residue is mixed with propane in the deasphalting unit to separate deasphalted oil from the Propane Deasphalted (PDA) pitch. This pitch is then blended with heavy oil to reduce its viscosity to meet the specification requirements (Rakow 2003; Chakkoth et al. 2020). The thermal history associated with both these bitumen production processes is different. In the case of air rectification, the low viscous material at elevated temperatures is converted into a high viscous one, while in the case of component blending, the high viscous PDA pitch is blended with lighter extracts to achieve the required viscosity.

The difference in the processing methodologies has been observed to influence the rheological properties of bitumen and its subsequent aging characteristics (Rajan et al. 2008; Nivitha et al. 2019). In this regard, when bitumen from two different processes is used to prepare polymer-modified bitumen, it is expected to have a significant impact on the interaction mechanisms. Scarcely any study has attempted to ascertain the influence of the type of base bitumen on the interaction mechanisms and the rheological properties of polymer-modified bitumen. While one can hypothesize about the interaction of polymers with bitumen and, verify it with morphological measurements, the sensitivity of currently available rheological measurements is questionable. Most of these measurements are specification-driven and do not capture the influence of the various interactions between the two constituents (base binder and the modifier) on the rheological characteristics. This necessitates the use of tests that are sensitive to the influence of base bitumen, different types of polymers, and bitumen-polymer interactions.

While many studies have focussed on different parameters to quantify the changes in rheological response arising from the interaction of bitumen and polymer, only limited studies are available that focus on the stress relaxation response. How the stresses relax has been reported to be quite sensitive to the network structure observed for many polymer systems (Doi and Edwards 1986). It will be worthwhile to investigate the applicability of such a response to capturing the effect of bitumen-polymer interaction and its dosage sensitivity. One could identify a few standard parameters that could be calculated from the stress relaxation data. Relaxation modulus calculated in the linear regime from the stress relaxation experiment is considered as one of the basic parameters to characterize viscoelastic materials.

Researchers have attempted the use of relaxation modulus for the constitutive modeling of bituminous binders and mixtures (Elseifi et al. 2002; Liu et al. 2018; Nivitha et al. 2018). The other fundamental parameter representing the viscoelastic characteristics of different materials is the relaxation spectrum generally calculated from the relaxation modulus data (Tschoegl 1989; Winter 2000). One can hypothesize that a relaxation spectrum will be able to capture the response of the modified binder due to different types of interactions in terms of relaxation modes, which are generally not captured by other experiments.

Studies have evaluated the relaxation spectrum using the dynamic modulus data owing to the ease with which such tests can be performed for bitumen (Baumgartel and Winter 1989; Huang and Baird 2002; Bhattacharjee et al. 2011; Liu et al. 2018). It should be noted here that evaluating the relaxation spectrum from dynamic modulus data is considered to be a non-trivial inverse problem (Takeh and Shanbhag 2013). Here, the dynamic modulus is collected only at discrete frequencies, limited to a certain frequency range by experimental requirements and masked by noise in some cases. In such cases, the determination of a unique relaxation spectrum is considered to be a complicated task (Takeh and Shanbhag 2013). Further, for tests conducted in the frequency domain, various approximations regarding the determination of dynamic modulus in the linear regime, preparing a master curve, and regularization for collecting the spectral data are involved. Most of these issues could be avoided by using the stress relaxation data to obtain the relaxation spectrum. However, conducting a stress relaxation experiment is challenging as relaxation response may not be quantifiable at different temperatures and shear rates. Limited studies are available that have used stress relaxation tests to compute the relaxation time for bitumen (Xu et al. 2016).

In this study, an attempt is made to assess the influence of polymer dosage and temperature on the relaxation behavior of SB/SBS polymer-modified bitumen prepared from base binders manufactured by two different processes, namely air blowing and component blending. Three dosages of polymers, namely 1, 3, and 5%, were used for each case. A stress relaxation study was conducted at three different temperatures and three different strain levels. The relaxation modulus and the continuous relaxation spectrum were used to assess the influence of base binder, polymer dosage, strain level, and temperature.

2 Experimental investigation

2.1 Materials

Two different binders conforming to Viscosity Grade 30 (VG30) as per IS 73:2018 (2018) were used as base binders in this study. As per the IS 73:2018 specifications, VG30 indicates a binder with an absolute viscosity of 300 Pa s at 60°C and a range of 20% from the targeted viscosity is specified for the bitumen grade. The two binders were obtained from refineries following different production processes, namely air rectification and component blending. The air-blown bitumen was collected from M/s Hindustan Petroleum Corporation Ltd., Vizag refinery (VR), and the blended bitumen was from M/s Hindustan Petroleum Corporation Ltd., Mumbai refinery (MR). The binders were tested as per IS 73:2018 (2018), and the results are tabulated in Table 1. In addition, the performance grade specification as per ASTM D6373-21 (2021) is also shown in Table 1, even though such parameters are not part of IS 73:2018 (2018).

Table 1 Properties of base bitumen (VG30)

Tests (as per IS 73:2018)	Air-blown bitumen (VR)	Blended bitumen (MR)
Penetration at 25 °C, 100 g, 5 s, 0.1 mm	47	53
Absolute viscosity at 60 °C, Poises	2623	2284
Kinematic viscosity at 135 °C, cP	557	507
Softening point (R&B), °C	50	49
Complex modulus (|G|*/sin δ) as Min. 1.0 kPa, 25 mm plate, 1 mm gap at 10 rad/s, at a temperature, °C	65	64
Tests on residue from rolling thin film oven		
Viscosity ratio at 60 °C	2.0	2.1
Complex modulus (|G|*/sin δ) as Min. 2.2 kPa, 25 mm plate, 1 mm gap at 10 rad/s, at a temperature, °C	64	62
Tests on residue from pressure aging vessel		
Complex modulus (|G*|.sin δ) as Max. 5000 kPa, 8 mm plate, 2 mm gap at 10 rad/s, at a temperature, °C	22	22

2.2 Preparation of polymer modified binder

For the preparation of the polymer modified bitumen, linear triblock SB copolymer (D1192) and diblock SB copolymer (D0243) were received from M/s Kraton, India. The polymer-modified bitumen was prepared using a laboratory-scale blending unit. The initial trials of blending both blended (MR) and air-blown (VR) base bitumen with triblock SB copolymer revealed that the MR-based modified bitumen did not meet the specification criteria provided in IS 15462:2019 (2019). Hence, to meet the specification criteria, a diblock polymer was used for the blended bitumen and triblock for air-blown bitumen. It could be seen that the influence of the type of base binder, although falling under the identical grade as per IS 73-2018 (2018), is significant enough to necessitate a different modifier altogether. It is understood that SBS copolymers have a biphasic morphology of rigid polystyrene (PS) domains in the flexible polybutadiene (PB) matrix. The choice of the appropriate type of polymer for modification is based on the type of the base binder for optimum compatibility with the modifier (Zhu et al. 2014).

In this study, the polymer-modified bitumen was prepared at three dosages of polymer, namely 1, 3, and 5%. The production of polymer-modified bitumen was carried out following the protocols specified by the polymer vendors. The three blends produced using VR bitumen are designated as VR1, VR3, and VR5, and those produced using MR bitumen are denoted as MR1, MR3, and MR5, respectively, in this paper henceforth. In this case, the corresponding unmodified binders are designated as VR0 and MR0 to indicate 0% polymer. On a general note, the VR and MR bitumen-based modified binders will be denoted as VRMB and MRMB, respectively.

2.3 Tests on modified binders

All the binders were subjected to short-term aging in the laboratory using Rolling Thin Film Oven (RTFO) as per ASTM D2872-21 (2021). All the specification-based tests were carried out on the unaged/short-term aged samples as per requirement. The stress relaxation

Table 2 Test results of SBS/SB modified bitumen

Test	Air-blown bitumen (VR)			Blended bitumen (MR)		
	VR1	VR3	VR5	MR1	MR3	MR5
(A) Tests on Original Binder						
Penetration at 25 °C, 100 g, 5 s, 0.1 mm	35	34	33	41	37	29
Softening Point, (R&B), °C	54	57	83	52	56	64
Elastic recovery of half thread in ductilometer at 15 °C, percent	50	64	84	41	61	75
Viscosity at 150 °C, Poise	4	5	7	3	4	6
Complex modulus (|G|*/sin δ) as Min. 1.0 kPa at 10 rad/s, at a temperature, °C	73	77	83	69	76	81
Phase Angle (δ), degree	86	85	72	86	79	75
Separation, difference in softening point (R&B), °C	0.6	3	4	0.2	1	5
(B) Tests on Rolling Thin film Oven (RTFO) Residue						
Loss in mass, percent	0	0.2	0.03	0	0	0.5
Elastic recovery of half thread in ductilometer at 25 °C, percent	43	63	78	36	69	78
Complex modulus (|G|*/sin δ) as Min. 2.2 kPa at 10 rad/s, at a temperature, °C	72	75	76	68	70	78
(C) Tests on residue from pressure aging vessel test						
Complex modulus (|G*|.sin δ) as Max. 5000 kPa, 8 mm plate, 2 mm gap at 10 rad/s, at a temperature, °C	22	19	16	22	19	15

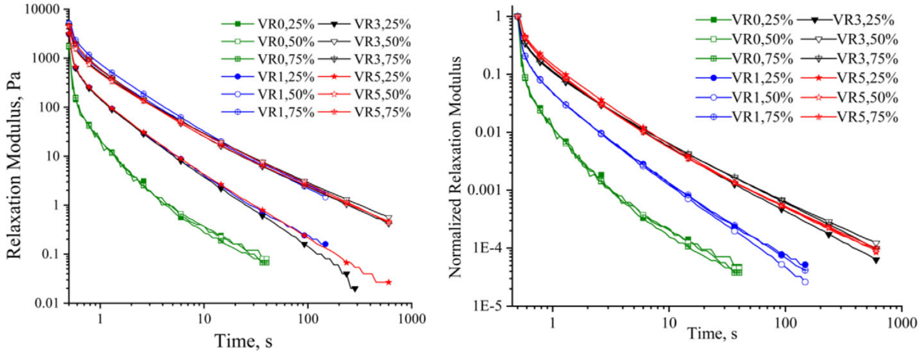
test mentioned in this study was carried out on the short-term aged samples. The modified binders were tested for the properties specified in IS: 15462-2019 and IRC SP: 53-2010 (SP:53:2010), and the test results are tabulated in Table 2. Anton-Paar Dynamic Shear Rheometer (DSR) MCR 302 was used to determine the performance grade properties specified in these codes. The performance grade properties were tested as per ASTM D7175-15 (2015).

The stress relaxation test was performed on all the modified binder samples along with the base binders at three different strain levels, namely, 25, 50, and 75% strain. All the samples were tested at three temperatures, namely 50, 60, and 70 °C. The test protocol for the stress relaxation test discussed in Nivitha et al. (2018) was followed in this study. The constant strain value was maintained for 600 s. The stress relaxation data was monitored through 100 points varying in a logarithmic scale with data collection intervals varying from 0.001 s to 53 s. The repeatability of results for two trials was within 10%.

3 Analysis and discussion

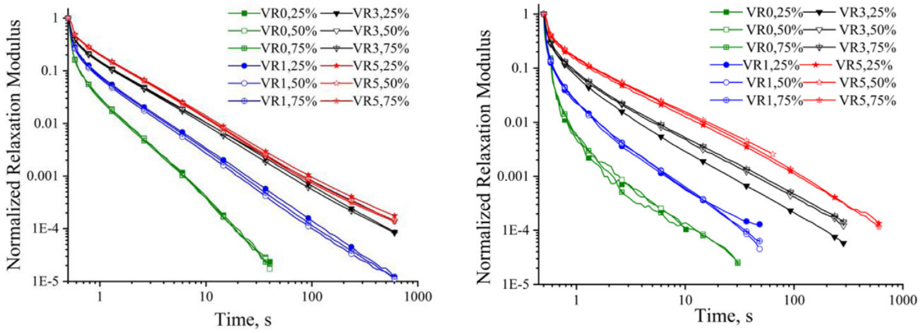
3.1 Relaxation modulus

Figure 1(a) shows sample data of the relaxation modulus at 60 °C for the base binder and all the three modified blends of the VR binder at three strain levels, namely 25, 50, and 75%. Relaxation modulus is defined as the ratio of σ_t to ε_0. Here σ_t is the time-dependent stress and ε_0 is the imposed step strain. It is understood that the relaxation modulus is independent



(a) Relaxation Modulus **(b) Normalised relaxation modulus**

Fig. 1 Variation of relaxation modulus at 60 °C for modified air-blown (VR) bitumen



(a) 50ºC **(b) 70ºC**

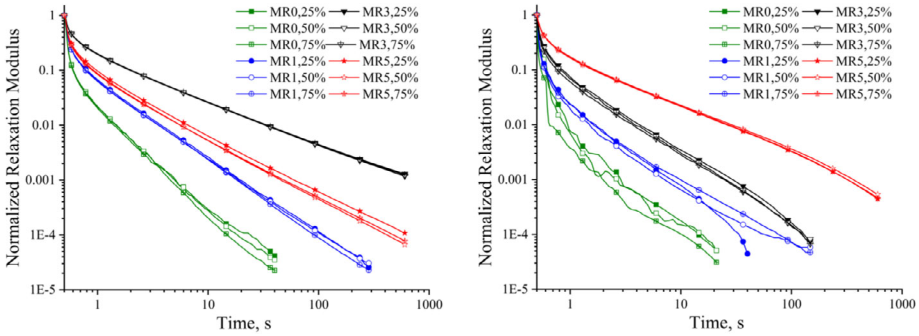
Fig. 2 Variation of relaxation modulus for modified air-blown (VR) bitumen

of the strain magnitude for linear response. All the computations in this study are based on relaxation modulus, and hence the linearity of the response is ensured by scaling. The absolute value of relaxation modulus varies significantly with the type of bitumen and the test temperature. To compare how at different temperatures the stresses relax for the two types of binders, it is convenient to normalize the data. The normalization here is carried out with respect to the magnitude of stress at its maximum value, and a sample plot is shown in Fig. 1(b).

The normalized relaxation modulus will henceforth be used for all analyses and discussions carried out in this study. In the following, the influence of polymer dosage, test temperature, and the type of base binder on the relaxation behavior is discussed in detail for the unmodified and polymer-modified bitumen at different dosages.

3.1.1 Influence of polymer dosage on the relaxation modulus

Figures 2 and 3 show the variation of the normalized relaxation modulus at a constant temperature for different blends prepared using VR and MR bitumen as the base binder, respectively. At 50 °C (Fig. 2(a)), it can be seen that the plots are separated into groups only based on the dosage. From Fig. 3, it can be seen that the relaxation behavior for the MR base bitumen and the three modified binders are distinct at both temperatures. For MRMB at 50 °C

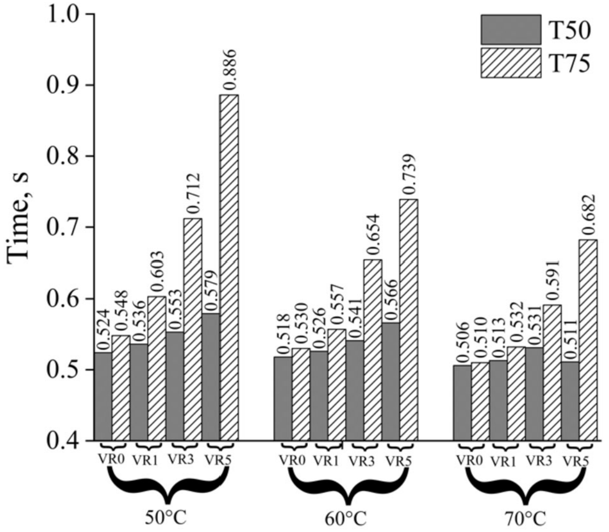


(a) 50ºC

(b) 70ºC

Fig. 3 Variation of relaxation modulus for modified blended (MR) bitumen

Fig. 4 Relaxation time for the base and modified air-blown (VR) bitumen at 25% strain

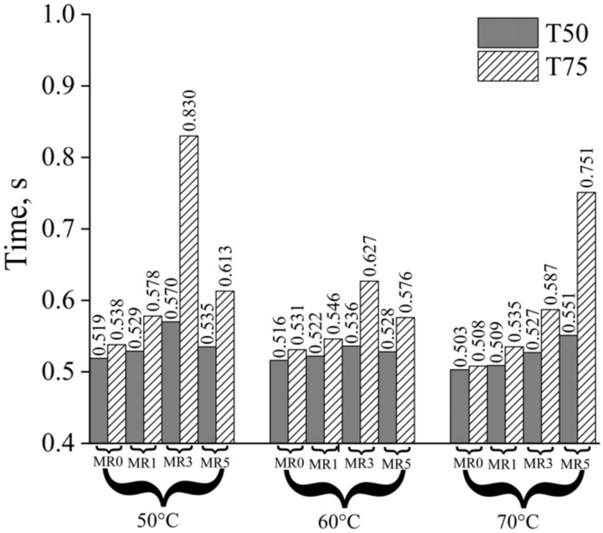


(Fig. 3(a)), it can be seen that the relaxation modulus is higher for 3% dosage as compared to 5% dosage. However, as the test temperature is increased to 70 °C (Fig. 3(b)), it is seen that the dosage of 5% exhibits a higher modulus as compared to 3%. On comparing Figs. 2 and 3, it can be seen that no such variability was observed in the case of VRMB though the 3 and 5% dosages exhibited closer relaxation modulus values at 50 °C.

To quantify the variability in the relaxation behavior exhibited by different binders, stress relaxation time corresponding to 50% and 75% reduction in initial modulus was calculated and denoted as T50 and T75, respectively (Wineman and Rajagopal 2000). The relaxation time obtained for different materials is shown in Figs. 4 and 5. Since the response at different strain levels is similar, the results at 25% strain are reported here.

It is first necessary to analyze the effect of base binder on the response of polymer-modified binders. For this purpose, the T50 and T75 values at 25% strain levels and 50 °C of the base binders (VR0 and MR0) are compared, and it can be seen that, on a marginal scale, the MR binders relax stresses at a faster rate compared to the VR binders. This behavior

Fig. 5 Relaxation time for the base and modified blended (MR) bitumen at 25% strain



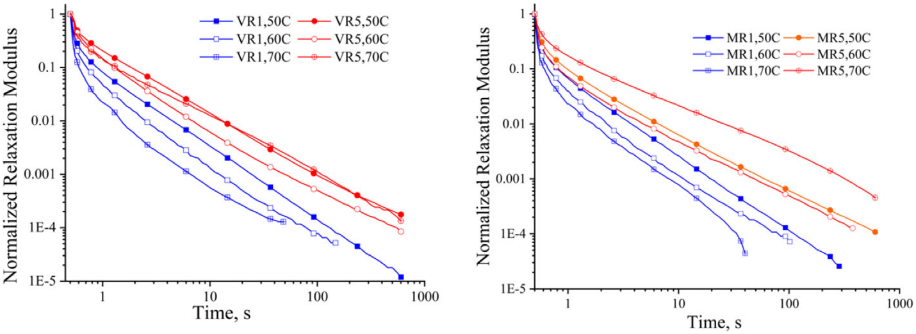
could be attributed to the air rectification process of the VR binders, wherein subjecting the material to a continuous supply of oxygen generally increases the carbonyl and sulfoxide compounds (Nivitha et al. 2016). The formation of these carbonyl and sulfoxide compounds has been observed to increase the stiffness of the material (Herrington et al. 1994; Petersen 2009). The higher ‘stiffness’ of the VR base binders as compared to the MR base binders could also be observed from the penetration at 25 °C and absolute viscosity at 60 °C as given in Table 1.

In the case of modified binders with VR, it is observed that with the addition of polymer, the relaxation times, both T50 and T75, increase with an increase in dosage at 25% strain, except for a slight reduction in T50 observed for VR5 compared to VR3. However, a distinct difference in the behavior of the material can be observed in the case of MRMB, wherein MR5 exhibited a lesser relaxation time than MR3, both at 50 and 60 °C. However, again at 70 °C, the response of the material with dosage is identical to that of VRMB.

3.1.2 Influence of temperature on the relaxation modulus

Figure 6 shows the relaxation behavior of 1 and 5% polymer modified bitumen prepared using the two different base binders at the three temperatures considered in this study. With 1% modification, both VR and MR exhibited slower relaxation rates with an increase in temperature. However, as the dosage is increased to 5%, the MR binder relaxed slower at 70 °C than MR5 at 60 °C. For 3% polymer dosage, results identical to 1% dosage were observed.

To compare the relaxation response variation with temperature, the T50 values between 50 and 70 °C are compared for the VR and MR base binders at 25% strain (Figs. 4 and 5). It is seen that this value reduces by 3.4% for the VR binder and 3.08% for the MR binder, as the temperature is increased from 50 to 70 °C. The reduction in T50 values with temperature is seen to be identical for both the base binders. If the same values are compared for polymer modified binders, say at 3% dosage, it is seen that the reduction is nearly 4% for VRMB and 7.5% for the MRMB. It is seen that with an increase in temperature, the absolute value of both T50 and T75 reduces for all cases except for MR5. If one compares the ratio of T50 or



(a) Air-blown bitumen (VR)

(b) Blended bitumen (MR)

Fig. 6 Variation of relaxation modulus for 1% and 5% polymer modified binders at different temperatures, at 25% strain

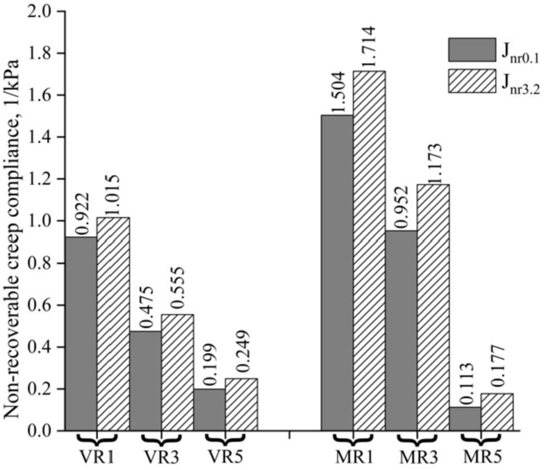


Fig. 7 Non-recoverable creep compliance from multiple stress creep and recovery test at 64 °C for air-blown (VR) and blended (MR) bitumen

T75 between 50 and 70 °C for the base binders, 1% and 3% VRMB/MRMB, it is seen that the values remain identical for all cases.

If the fundamental characterization tests conducted on unaged modified binders (Table 2) are relooked at this juncture, the difference in the performance of VR1 and MR1 is scarcely captured by the penetration test at 25 °C or the dynamic modulus test performed on the unaged samples. It is also seen that for a given dosage, Table 2 shows that both binders can be considered to fall under the same grade. Only the tests that capture the recovery properties of the binder, such as the elastic recovery test and the Multiple Stress Creep and Recovery (MSCR) test, could capture the effect of different types of bitumen, especially at 5% dosage. The MSCR test was carried out as per ASTM D 7405-20 (2020) at a temperature of 64 °C at two stress levels of 0.1 kPa and 3.2 kPa. The non-recoverable creep compliance (J_{nr}) at the two stress levels is shown in Fig. 7. Figure 8 shows the percent recovery at 3.2 kPa stress level ($R_{3.2}$) and the percentage difference in J_{nr} at the two stress levels (J_{nrdiff}).

It can be seen from Fig. 7 that the non-recoverable creep compliance decreases with the polymer dosage, and such response is found to be similar to both the base binders. However, the stress sensitivity of this response is not prominent as noted from J_{nr} at the two

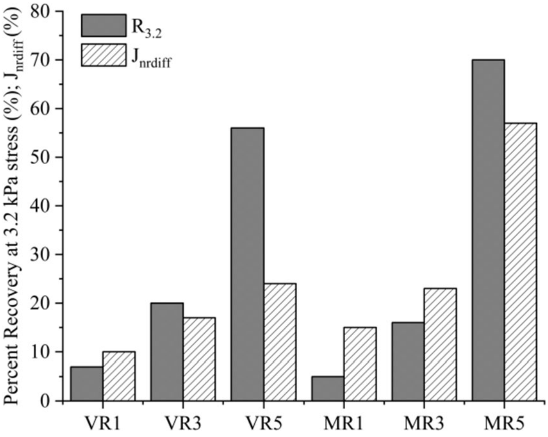


Fig. 8 Percent recovery at 3.2 kPa stress level and J_{nrdiff} from MSCR test at 64 °C for air-blown (VR) and blended (MR) bitumen

stress levels of 0.1 and 3.2 kPa. The J_{nrdiff} (Fig. 8) is in the range of 10 to 25%, except for MRMB with 5% dosage, where the J_{nrdiff} is more than 50%. Figure 8 shows that the percent recovery is higher in the case of MRMB as compared to VRMB at 5% dosage, whereas at lower dosages of modifier, the percent recovery is more or less identical. This could be attributed to the architecture of the two different modifiers. In triblock SBS, both the ends are restrained through the polystyrene component, whereas, in the case of diblock SBS, only one end is restrained. The unrestrained dangling free chains in the case of diblock SBS could relax stresses at a faster rate for MRMB compared to VRMB. While such behavior is captured by the MSCR test, the temperature-dependent effect of dosage could not be captured by any of the standard tests.

Further, even if parameters such as the relaxation modulus and time for relaxation to different percentages of the initial stress are considered, they do not provide any insights into the possible reasons behind such variability exhibited by different modified bitumen considered here. Analysing the number of relaxation modes in each case, the relaxation times associated with such modes, and how they vary with the polymer architecture and dosage can provide a better understanding of the relaxation behavior of modified bitumen prepared using VR+SBS and MR+SB. The relaxation spectrum is calculated for this purpose, and a detailed discussion about the same is provided in the following.

3.2 Relaxation spectrum

3.2.1 Characteristics of the relaxation spectrum

The relaxation behavior for the polymer-modified bitumen is simulated considering n-Maxwell elements in parallel, and the relaxation modulus can be explained as shown in Eq. (1).

$$G(t) = \frac{\sigma(t)}{\gamma_0} = \sum_{i=1}^{n} G_i e^{-t/\tau}, \tag{1}$$

where G_i is the elastic modulus of the spring, τ_i is the time of relaxation for discrete Maxwell elements. On replacing summation with integral and $G_i(\tau_i)$ with $g(\tau)d\tau$, Eq. (1)

is rewritten as shown in Eq. (2).

$$G(t)=\int_{0}^{\infty} g(\tau)e^{-t/\tau}d\tau. \tag{2}$$

When the relaxation modulus extends over a wide range, it is preferred to use a logarithmic scale. $G(t)$ on a logarithmic scale is shown as follows (Eq. (3)).

$$G(t)=\int_{-\infty}^{\infty} H(\tau)\, e^{-\frac{t}{\tau}} d\ln\tau. \tag{3}$$

Different statistical parameters have to be calculated to compare the shape of the spectra and quantify the changes with polymer dosage and temperature. Considering the normalized form for the spectra, the α^{th} moment is calculated using the following equation as defined in Tschoegl (1989), Zorn (2002), and Bhattacharjee et al. (2011).

$$\langle\ln\tau\rangle^{\alpha}=K^{-1}\int_{-\infty}^{\infty} \tau^{\alpha} H(\tau)\, d\ln\tau. \tag{4}$$

The zeroth moment of the relaxation time spectrum is called $E_g - E_e$, where E_g is the initial modulus, and E_e is the equilibrium modulus. In the literature, few other statistical parameters are reported, including the mean relaxation time, the width of the relaxation spectrum, and its asymmetry (Bhattacharjee et al. 2011). The mean relaxation time $\langle\ln\tau\rangle$ is the first moment about the origin, and it is obtained by setting $\alpha = 1$ in Eq. (4). The second moment about the mean is called variance, and it is calculated as shown in Eq. (5).

$$\sigma^{2}_{\ln\tau}=(K^{-1}\int_{-\infty}^{\infty} \tau^{2} H(\tau)\, d\ln\tau)-\langle\ln\tau\rangle^{2}. \tag{5}$$

In this study, the continuous relaxation spectrum is obtained by using the ReSpect code (Takeh and Shanbhag 2013). A discrete or a continuous relaxation spectrum could be used here, and studies on polymers have used both. However, Malkin (2006) suggest the use of a continuous relaxation spectrum in place of discrete relaxation spectrum as a large number of independent parameters are required to describe a discrete relaxation spectrum while a few parameters would suffice for a continuous relaxation spectrum. Because of this fact, many studies have used the continuous relaxation spectrum to describe the viscoelastic properties of polymeric materials, including bituminous mixture (Bhattacharjee et al. 2011). The continuous relaxation modes are determined by dividing $\tau_{\min}$ to $\tau_{\max}$ into equally spaced points. For the function $\mathrm{V}(\lambda)=\rho^{2}+\lambda\eta^{2}$, the η vs. ρ curve is generated, and the optimum λ is determined using the point of intersection of the two slopes. For a given λ, the $\mathrm{H}_{\lambda}(\tau)$ that minimizes $\mathrm{V}(\lambda)$ is determined using the Levenberg-Marquardt method (Takeh and Shanbhag 2013).

3.2.2 Effect of polymer dosage and temperature on relaxation spectrum

Figure 9 shows the effect of strain on the relaxation spectrum for the two base binders. Two relaxation modes are seen to be present here for both the base binders, though the second mode is not very prominent. While such bimodal relaxation is common for SBS modified bitumen, the reasons contributing to the same for the base bitumen have to be analyzed in detail. Figure 10 shows the same for polymer-modified bitumen at 3% dosage, both at 50 °C. For the sake of analysis, the relaxation spectrum for 25% strain alone will be considered

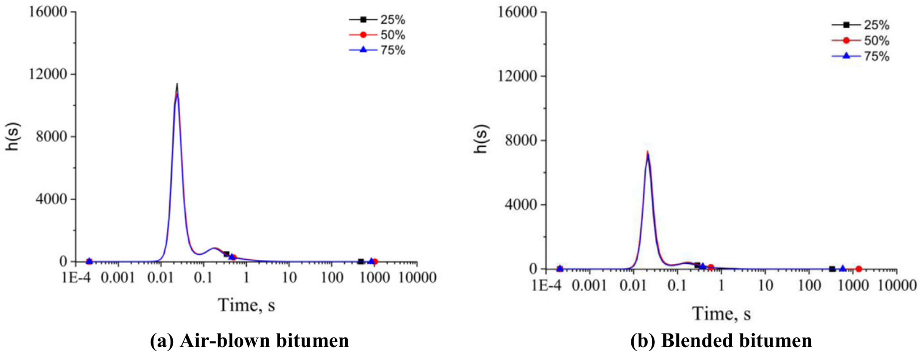


Fig. 9 Effect of strain on base binders at 50 °C

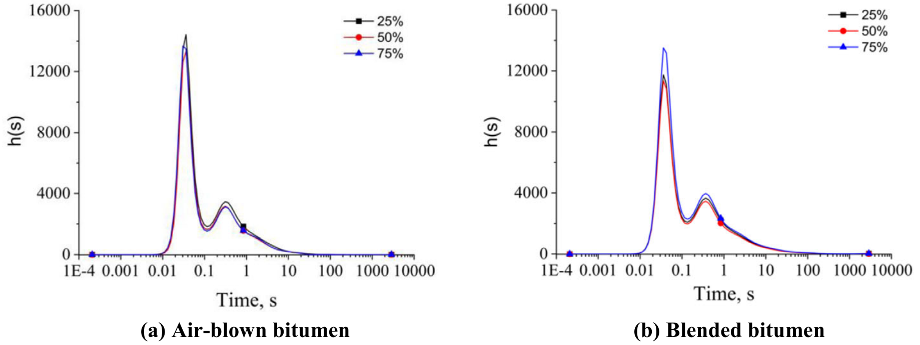
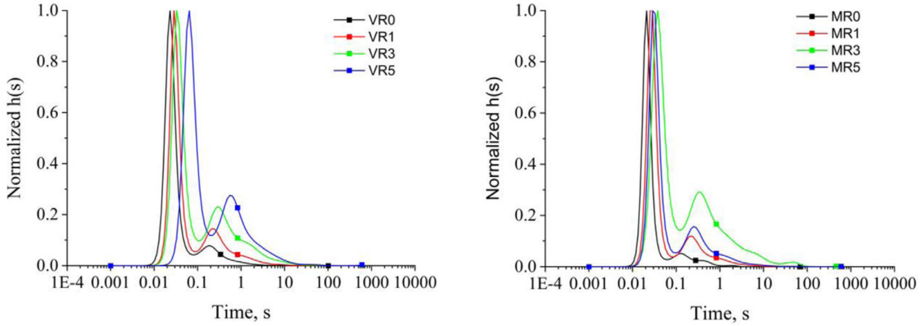


Fig. 10 Effect of strain on 3% dosage samples at 50 °C

henceforth for analysis. Also, to understand the effect of the shift in relaxation spectrum due to the polymer dosage and the type of base binder, the normalized relaxation spectrum is considered for analysis. Figure 10 shows that the bimodal relaxation is prominent in the case of modified bitumen when compared to the base binder (Fig. 9). For instance, the height of peak2 is in the range of 400 to 800 for the base binder, whereas it is in the range of 3700-3900 in the case of 3% modified bitumen at 50 °C.

Polacco et al. (2006) showed that similar to most polymeric systems, SBS modified bitumen exhibited two relaxation modes, an initial fast relaxation corresponding to the chain retraction and the second phase of slow relaxation corresponding to reptation of the chains. It has also been shown that for the application of small strains, conformational changes of the polybutadiene blocks and rigid movements of the polystyrene blocks could be expected. These are hypothesized to be completely reversible once the stresses begin to relax. At higher strains, the polystyrene blocks could jump domains that cannot recover once the stresses begin to relax. This is specified to be a reason for the incomplete relaxation observed in the case of SBS modified binders at high strain levels even after sufficient time of observation. The effect of temperature is considered to alter only the Brownian dynamics of the molecules, and hence only a change in the absolute value of the relaxation times was observed without altering the relaxation function.

Figure 11 shows the effect of dosage on the relaxation spectrum for the two materials at 50 °C and 25% strain. For both VRMB (Fig. 11(a)) and MRMB (Fig. 11(b)), it was seen



(a) Air-blown bitumen (VR) **(b) Blended bitumen (MR)**

Fig. 11 Effect of dosage at 50 °C and 25% strain

Table 3 Parameters calculated from relaxation spectrum

Sample	Air-blown bitumen (VR)				Blended bitumen (MR)			
	Location of peak1 (s)	Location of peak2 (s)	Mean (s)	SD (s)	Location of peak1 (s)	Location of peak2 (s)	Mean (s)	SD (s)
0,50C,25%	0.023	0.212	2.3	8.4	0.021	0.142	2.2	5.7
1,50C,25%	0.029	0.247	42.7	118.2	0.029	0.247	50.5	141.9
3,50C,25%	0.033	0.324	106.3	192.2	0.038	0.370	352.1	267.5
5,50C,25%	0.064	0.634	142.0	223.1	0.029	0.283	166.9	232.6
0,60C,25%	0.015	0.056	12.9	34.5	0.015	0.045	0.7	1.8
1,60C,25%	0.022	0.216	84.1	194.2	0.019	0.165	87.8	187.1
3,60C,25%	0.025	0.247	116.2	204.4	0.025	0.247	75.7	148.1
5,60C,25%	0.056	0.484	123.7	209.7	0.025	0.216	156.3	223.3
0,70C,25%	0.006	0.089	0.2	1.0	0.004	0.011	3.0	4.8
1,70C,25%	0.011	0.074	210.9	276.3	0.008	0.099	3.8	6.9
3,70C,25%	0.022	0.216	83.5	179.4	0.015	0.161	19.6	41.5
5,70C,25%	0.043	0.484	139.6	210.3	0.019	0.165	205.0	215.6

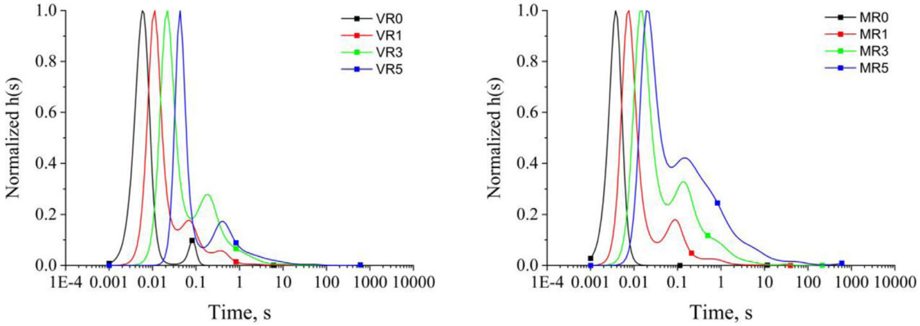
that the relaxation spectrum shifted to the right with the increase in dosage. The shift is more prominent in the case of VRMB, which has triblock SBS compared to MRMB with diblock SB as can be seen from Fig. 11. In triblock polymers, all the end blocks are involved in the formation of the polystyrene domain, and the entanglements are physically trapped. However, in the case of SB polymers, the polybutadiene ends are not anchored, and they are considered to be a dangling free chain (McKay et al. 1995). In addition, for polymer-modified bitumen, a broader relaxation spectrum has been observed compared to their base bitumen (Bouldin et al. 1991; Gahvari 1997; Glover et al. 2001; Ruan et al. 2003; Rojas et al. 2010). Gahvari (1997) showed that the addition of polymers led to a larger dispersion of the relaxation modes resulting in a broad relaxation spectrum. Gahvari (1997) also indicated that SB exhibited the broadest relaxation spectrum compared to other modifiers.

To quantify the characteristics of the relaxation spectrum, the parameters such as the location of peak1 (first from left-hand side corresponding to the lower relaxation time) and peak2 (second prominent one from left-hand side corresponding to the higher relaxation time), mean relaxation time, standard deviation, and skewness are calculated and shown in Table 3. For VR samples at 50 °C and 25% strain, it is seen that both the peaks shift to longer relaxation time with an increase in dosage. For instance, the location of peak1 shifted from 0.023 s in the case of base binder to 0.064 s in the case of 5% modified sample (178%), and this is evident from Fig. 11(a). A similar trend is also observed for the location of peak2 wherein the peak shifts from 0.212 s to 0.634 s. This is also clearly evident from Fig. 11, wherein the peak2 of the VR5 sample is shifted to the right. It is also seen here that with an increase in dosage, an increase in the spread of the relaxation spectrum is observed, especially towards the longer relaxation times. The spread is indicated in terms of the larger Standard Deviation (SD) value for VR5 (223.1 s) as compared to VR0 (8.4 s). Hence it can be concluded that the addition of polymer to the base binder does not result in the formation of any new peak in the relaxation spectrum and rather shifts the existing peaks of the base bitumen to longer relaxation times.

In the case of MR samples at 50 °C and 25% strain, the shift in the location of peak1 is from 0.021 s to 0.038 s (81%) as the maximum shift is observed here for the case of 3% modified sample. Similarly, for the peak2 also, the location has shifted from 0.142 s for the base binder to 0.370 s for the 3% sample and 0.283 s for the 5% sample. Table 3 shows that the mean relaxation time and the standard deviation values are also higher for MR3 samples when compared to MR5 samples. While one reason that could be attributed to such behavior of MR binders is the nature of the post-processing method adopted for the base binder, the major factor could be associated with the type of modifier. Kumar et al. (2020) compared the properties of triblock SB (Kraton D1192) and diblock SB (Kraton D0243) polymers identical to that used in this study. The viscosity of diblock polymer over a range of temperatures was observed to be lower when compared to linear and other branched triblock SB polymers. The molecular weight of these two polymers was measured in their study, and it was seen that diblock polymers exhibited a lower molecular weight when compared to triblock polymers.

In addition to these factors, the ability of the triblock polymers to form a network-like structure is said to be a major factor contributing to its higher viscosity and elasticity compared to diblock polymers. In the case of diblock polymers, it is the formation of star-like clusters due to the absence of a second polystyrene unit. The entanglement density is considered to be lower for diblock polymers, and it has been directly related to the modulus and elasticity of the polymer-modified system (Kumar et al. 2020). Hence, increasing the percentage of diblock SB by 50% is said to reduce the stiffness by about 50% (Stroup-Gardiner and Newcomb 1995). As dosage is increased from 3 to 5% in the case of MRMB, the increase in the concentration of polybutadiene units could result in a faster relaxation of stresses as compared to 3% samples (Fig. 3(a)). Such effect of dosage is also seen in the case of VRMB wherein the shift in the location of peak1 is from 0.029 to 0.033 s for 1 to 3% dosage while it is from 0.033 to 0.064 s for an increase in dosage from 3 to 5%.

If the desired behavior is to be specified for the polymer-modified bitumen, a longer relaxation time is desirable as it corresponds to an ‘elastic’ response having lesser irrecoverable strain. Based on the analysis carried out, it can be seen that the choice of dosage for the desired behavior will depend upon the combined influence of the type of the base binder and polymer architecture. However, the sensitivity of this combined influence depends on the temperature. For VRMB, the relaxation time increases with an increase in dosage for all three temperatures considered here. For MRMB, the relaxation time increases with dosage for 50 and 60 °C, whereas for 70 °C, MR3 exhibited a longer relaxation time compared to MR5. It can thus be said that temperature plays a critical role in the choice of polymer dosage.



(a) Air-blown bitumen (VR) **(b) Blended bitumen (MR)**

Fig. 12 Effect of dosage at 70 °C and 25% strain

As the temperature increases, at 70 °C, the nature of peaks, especially the second peak, is different for the modified bitumen with different base binders. The second peak is of very low intensity such that it looks as though it is almost absent in the normalized spectrum of the MR base binder while it is relatively prominent for the VR base binder. At 70 °C, the effect of dosage is more prominent as seen from Fig. 12. Here, the shift in peaks towards longer relaxation time with an increase in dosage is seen. If the spectrum parameters listed in Table 3 are compared for the VR base binder, the location of the peak1 is 0.023 s at 50 °C while it is 0.003 s at 70 °C. A similar shift in the position of peak1 is also observed in the case of MR base binder (0.021 to 0.004 s) as temperature increases from 50 to 70 °C. If the effect of temperature is compared for VRMB, the location of peak1 and peak2 increases with an increase in dosage and reduces with an increase in temperature for all dosages. However, for MRMB, the location of peak1 and peak2, especially for 3 and 5% dosages, are dependent on temperature. At 50 °C, the location of peak1 and peak2 is higher for 3% MRMB compared to 5% MRMB, and as temperature increases, at 70 °C, it can be seen that the location of peaks for 5% MRMB is higher when compared to 3% MRMB.

The reason that could be attributed to such behavior is the orientation of the block copolymers. Studies have shown that how the molecules orient themselves under shear for triblock polymers will differ significantly from that of diblock polymers (Riise et al. 1995). This is attributed to the variability in response observed at different temperatures for the two types of modifiers. However, such differences could not be observed for variation in strain level at a given temperature. This is said to be more valid at low temperatures considering the increase in molecular dynamics with an increase in temperature. At temperatures of about 100 °C, which is the glass transition temperature of the polystyrene, the association of polystyrene end domains cannot hold any further, and they dissociate into individual molecules. Such dissociation is expected to be relatively easier in the case of diblock polymers due to the absence of network structure when compared to triblock polymers with significant entanglement and network structure.

To compare the effect of base binder and dosage on temperature, the variation in the location of peak1 is normalized to the values at 50 °C as shown in Fig. 13. It can be seen that among the base binders, the VR binder is observed to be more sensitive to variation in temperature while the sensitivity of the MR binder increases beyond 60 °C. With the addition of modifier, it can be seen that for 1% dosage, the normalized peak locations for VRMB have increased while that of MRMB is comparable to that of its base binder. As the dosage increased to 3%, it can be seen that MR3 exhibited higher sensitivity to temperature

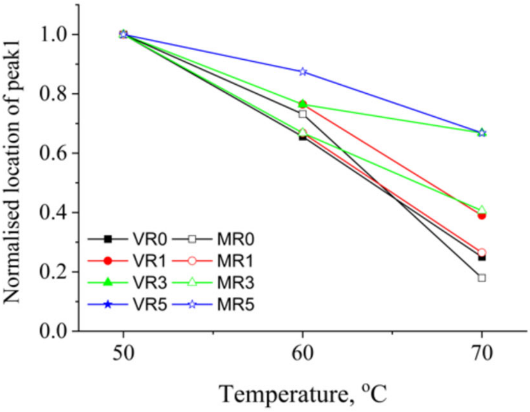


Fig. 13 Normalized location of peak1 with temperature

(higher slope) when compared to VR3. However, at 5% dosage, the normalized plots for VRMB and MRMB lie on top of each other. This is different from the observations obtained from T50 and T75 values wherein the temperature sensitivity of the base binders and the polymer modified binders, especially 1 and 3%, were observed to be identical. This shows that though relaxation modulus is sensitive to many parameters considered in this study, the parameters calculated from the relaxation spectrum could be considered to be more sensitive, especially to the temperature-dependent behavior.

4 Conclusion

In this paper, a study was conducted to evaluate the influence of polymer dosage and temperature on the relaxation behavior of polymer-modified bitumen prepared using two different processes. The base bitumen chosen in the study was produced using two different processes, namely, air rectification and component blending. The choice of the modifier was dictated by the bitumen type, even though they belong to the same performance grade. It was seen that a triblock SB polymer was compatible with the VR base binder while a diblock SB polymer was appropriate for the MR base binder. The two polymer-modified bitumen with different base binders and polymers were subjected to stress relaxation tests and different temperatures and strain levels. The following are the observations based on the analysis of relaxation modulus and the continuous relaxation spectra at the linear regime of response.

- It was seen that the specification test parameters are unable to capture the changes in the high-temperature rheological response of the material at different temperatures and strain levels. The MSCR test was sensitive to the polymer architecture to a certain extent, but it could not capture the effect of interaction.
- The relaxation times, T50 and T75, calculated from the stress relaxation data, could capture the variation in response of the modified binders to the type of base binder, polymer architecture, test temperature, and strain level. For the unmodified bitumen, the MR binders relaxed stresses at a faster rate compared to the VR binders. This is attributed to the air rectification process adopted for the VR binders increasing the oxidation products and thereby leading to an increase in stiffness over the MR binders.
- For the polymer-modified bitumen, it was seen that VRMB took a longer time to relax the stresses when compared to MRMB. The VRMB contains triblock SBS polymer resulting

in a physically entangled network, while the diblock SB polymer forms a star-like cluster in MR binder. The dangling ends of the polybutadiene component can relax stresses at a faster rate in the case of diblock polymer-modified bitumen. In addition to these factors, the ability of the triblock polymers to form a network-like structure is said to be a major factor contributing to its higher viscosity and elasticity compared to diblock polymers.

- The bimodal relaxation is observed for both unmodified and modified bitumen, but it was prominent in the case of modified bitumen. Also, the addition of polymer to the base binder did not result in the formation of any new peak in the relaxation spectrum and rather shifted the existing peaks of the base bitumen to longer relaxation times.
- For MRMB samples, T50/T75 were higher for 3% dosage when compared to 5% dosage at 50 °C while at 70 °C, the order was seen to reverse. No such behavior was seen in the case of VRMB samples. This behavior of MRMB samples is attributed to the dissociation of the polystyrene domains, which is considered to be easier in the case of diblock polymers when compared to triblock polymers with a higher degree of entanglement. Hence the desired dosage could only be selected based on the polymer architecture and the temperature range of interest.
- The temperature sensitivity of the polymer-modified bitumen improved significantly when compared to the base binders. The magnitude, however, depended on the base binder and the dosage of polymer. While this was seen through the parameters calculated from the relaxation spectrum, no such distinct differences were observed from the T50/T75 values calculated using the relaxation modulus data or the specification-based parameters.

Author Contribution All authors contributed to the study's conception and design. Material preparation, data collection, and analysis were performed by Devika R., Nivitha M. R., and Neethu Roy. The first draft of the manuscript was written by Nivitha M. R. and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code Availability The codes used in this study are available from the corresponding author on reasonable request.

Declarations

Conflicts of interest/Competing interests The authors have no relevant financial or non-financial interests to disclose.

Ethics approval Authors declare that the manuscript in part or in full has not been submitted or published anywhere.

Consent for publication The authors hereby give the consent for the publication of identifiable details, the details within the text, figures, and tables in the manuscript submitted, to be published in the Mechanics of Time-Dependent Materials Journal.

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