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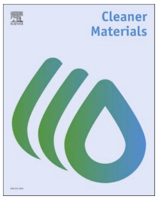

# Investigating the unique entropy-elasticity of polymer modified asphalt

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ABSTRACT

Crafting Styrene-Butadiene-Styrene (SBS) polymer into the bitumen can notably improve the elastic response of the polymer modified bitumen (PMB), which will significantly enhance the overall performance of bituminous pavement. But the molecular mechanism of the PMB's unique entropy elasticity has not been fully understood yet. The prominent entropy-elasticity of SBS polymer modified asphalt was investigated in this study. To do so, Fourier Transform Infrared (FTIR), Gel Permeation Chromatography (GPC) and Dynamic Mechanical Analysis (DMA) were conducted to investigate the molecular modification mechanism of PMB. Afterwards, polymer molecular model with a polymerization degree over 2000 is constructed and dynamic simulation is conducted to reveal the mesoscopic mechanism of SBS polymer's entropy elasticity. As for macroscopic evaluation, a series of creep and recovery tests associated with different testing temperatures (10 °C to 100 °C with a 6 °C gap), recovery times (0.01 s, 0.1 s, 1 s, 4 s and 9 s) and SBS dosages (0 %, 2.5 %, 4.2 %, 7.5 %) were carried out to characterize the elasticity of various PMBs. The results show that plain bitumen mainly shows energy-elasticity, which is small, instantaneous and highly temperature-dependent, while PMB mainly shows entropy-elasticity, which is strong, delayed and less temperature-dependent. Under the condition of low temperature and short recovery time, the bitumen molecules freeze and prevent the SBS polymer to demonstrate its entropy-elasticity, hence the energy-elasticity dominates. Higher temperatures and long recovery time render the SBS molecule more time to relax and thus the entropy-elasticity dominates. The predominant influence of entropy-elasticity in PMA leads to a unique increasing recovery rate within a specific high-temperature range. This phenomenon can be utilized as a fingerprint approach for the identification of the entropy-elasticity and polymer modification.

## Introduction

Bitumen is a complex polymeric composite of asphaltene micelles dispersed in a lower molecular weight oily medium (maltenes). Bituminous pavement has been widely used in road infrastructures due to its outstanding smoothness and surface friction (Kakar et al., 2019; Lu et al., 2023). However, plain bitumen material usually shows a mediocre aging resistance (Mousavi et al., 2016), leading to challenges to its durability (Xu et al., 2016; Yao et al., 2022; Jiang et al., 2020).

Abundant effort has been devoted in promoting the durability of bitumen material (Sun et al., 2017; Noor and Rehman, 2022; Ma et al., 2021), among which is crafting the strong and tough styrene–butadiene–styrene (SBS) polymer into plain petroleum bitumen (Yan et al., 2019). This technology can significantly improve the mechanical performance of plain bitumen and consequently extend the service life of the bituminous pavement. With the increasing traffic volumes placed on highways, the SBS polymer modified bitumen (PMB) is getting more attention (Yan et al., 2020). PMB has become one of the most used petroleum-based materials for road infrastructure (Yaro et al., 2023).

Since SBS is an elastomer, good elastic recovery is the key characteristic of PMB. Lv et al. (Lv et al., 2019) reported that bitumens with high elasticity (e.g., branched SBS or high contents of linear SBS polymer) typically showed lower rates of permanent deformation damage. Golalipour (Golalipour, 2011) successfully correlated increased elastic response of bitumen to improved service life of bitumen mixtures. Also, numerous studies indicated that high elastic recovery is beneficial to the PMB's fatigue resistance. Salim et al. (Salim et al., 2019) indicated that PMBs with higher elastic recoveries tended to demonstrate higher fatigue resistance. Zhang et al. (Zhang et al., 2016) claimed that bitumen elastic recovery is hypothesized to play a significant role in the fatigue cracking resistance.

It has been generally recognized that through SBS modification, one can alter the bitumen from the stiff and brittle state to the tough and

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elastic state, which evidently enhances the durability of the pavement (Zhang et al., 2016). Although it is well accepted that elastomer polymer like SBS notably improves the PMB elasticity, the mesoscopic mechanism of the improvement has not been fully understood yet.

Based on thermodynamics, the physical natures for elastic behavior can be divided into energy-based and entropy-based (Sperling, 2005). In stiff materials like metals or glassy state bitumen, the intermolecular bonds change in length and angle when forces are applied (energy is added to the system). When forces are removed, the bonds tend to go back to their original lower energy state, leading to energy-based elasticity. For SBS or other elastomers, when stretched, their energy remains steady while their entropy decreases. The molecules tend to wiggle back to the high entropy state and thus entropy-based elasticity is induced (Roundy and Rogers, 2013).

Since the molecular nature of elasticity differs between bitumen and SBS polymer, plain bitumen and PMB exhibit significantly different mechanical properties, especially in elastic response. Hossain et al. (Hossain et al., 2016) found that PMB shows more delayed elasticity than plain bitumen, Wang et al. (Wang et al., 2015) reported that PMB is less temperature sensitive than plain bitumen. Those differences should be properly explained by the different molecular nature of energy and entropy elasticity of plain bitumen and SBS polymer.

This study aims to investigate the unique entropy-elasticity of polymer modified asphalt. To achieve this objective, functional group characterization, molecular weight distribution characterization and rheological characterization are conducted via Fourier Transform Infrared Reflection (FTIR), Gel Permeation Chromatography (GPC) and Dynamic Mechanical Analysis (DMA), respectively, to reveal the modification mechanism of PMB. Molecular dynamic simulation is conducted to reveal the mesoscopic mechanism of SBS polymer's entropy elasticity. Afterwards, a series of creep and recovery tests are performed to macroscopically characterize the elastic recovery of PMB. A wide testing temperature range, from 10 °C to 100 °C with a 6 °C gap was adopted to mimic the varying service temperature of bituminous pavement. Different recovery times of 0.01 s, 0.1 s, 1 s, 4 s and 9 s were considered. The 0.01 s recovery time can provide a hint on the instantaneous recovery and other recovery time settings can show how the delayed elasticity emerges. Based on the aforementioned experiments, the molecular mechanism of the enhanced elasticity of PMB is discussed.

## Materials

In this study, PMB was laboratory prepared by incorporating the SBS polymers into plain petroleum bitumen through high-speed shearing. Plain bitumen was a PG 64–16 bitumen under the brand name of ESSO. SBS polymer was produced by Sinopec under the commercial name of 791-H, which is a linear polymer with an average molecule weight of 160,000 g/mol, containing 30 wt% of styrene. The properties of the petroleum plain bitumen and SBS polymer are presented in Table 1 and Table 2.

During preparation, the plain bitumen was heated to 180 °C and the SBS polymer was then added to the hot bitumen. The blend was sheared for 2 h at 4,000 rpm rate. Due to the significant difference in molecular weight and polarity, the SBS and plain bitumen are thermal-dynamically incompatible. Therefore dynamic vulcanization was performed after shearing, which was achieved by the addition of element sulfur (0.15 % by mass). Also, an aromatic-rich base oil was added as extending agent to improve the swelling of SBS polymers (2 % by mass). The properties of the base oil are shown in Table 3. After that, the blend was further stirred (500 rpm) for 4 h to cure.

**Table 1**
Properties of the plain petroleum bitumen.

| Item | Results | Standard |
|---|---|---|
| Performance Grade | 64–16 | ASTM D7643 |
| Penetration (25 °C 0.1 mm) | 68 | ASTM D5 |
| Ductility (10 °C cm) | 44 | ASTM D113 |
| Softening point (°C) | 47.2 | ASTM D36 |
| Brookfield viscosity (135 °C mPa.s) | 650 | ASTM D4402 |
| Flash point (°C) | 340 | ASTM D92 |
| Fire point (°C) | 362 | ASTM D92 |
| Complex modulus (64 °C Pa) | 1066 | ASTM D7175 |
| Phase angle (64 °C °) | 87.7 | ASTM D7175 |
| Rutting factor (64 °C Pa) | 1066 | ASTM D7175 |
| R3.2 (64 °C %) | 0.2 | ASTM D7405 |
| Jnr3.2 (64 °C) | 9.9 | ASTM D7405 |

**Table 2**
Properties of the SBS polymer.

| Item | Results | Standard |
|---|---|---|
| Structure | Linear | / |
| S/B ratio | 30/70 | / |
| Oil content (%) | 0 | / |
| Volatility content (%) | ≤0.7 | / |
| Ash content (%) | 0.2 | / |
| Stress at 300 % (MPa) | ≥2.2 | ASTM D3039 |
| Tensile strength (MPa) | ≥16 | ASTM D3039 |
| Elongation (%) | ≥700 | ASTM D3039 |
| Permanent deformation (%) | ≤40 | ASTM D3039 |
| Shore hardness (A) | ≥68 | ASTM D2240 |
| Melt flow rate (g/10 min) | 0.5–2.5 | ASTM D1238 |

To investigate the influence of SBS polymer content, three SBS dosages, namely 2.5 %, 4.2 % and 7.5 %, were evaluated. These dosages are selected based on common choices in the industry. 7.5 % SBS content is usually used for drainage pavement with higher air void contents in warm regions. The corresponding PMB are coded as 2.5 %SBS, 4.2 %SBS and 7.5 %SBS, respectively. The diagram of the PMB preparation process is shown in Fig. 1.

To investigate how the stiffness of the base petroleum bitumen will influence the recovery behavior of the PMB, a softened-2.5 %SBS was also produced by replacing the PG 64–16 base bitumen with PG 52–22 base bitumen. PG 52–22 has a lower apparent viscosity than PG 64–16 (480 mPa.s versus 650 mPa.s). Hence, 2.5 %SBS PMB prepared by PG 52–22 has a lower viscosity. The comparison between the original 2.5 % SBS and the softened-2.5 %SBS will show the influence of bitumen stiffness.

## Testing methods

### *Functional group characterization (FTIR)*

The infrared spectra of different modified bitumens were obtained using a Bruker TENSOR FTIR spectrometer equipped with a reflection diamond ATR accessory. 32 scans within the wavenumber range of 2000 $cm^{-1}$ to 600 $cm^{-1}$ were obtained and averaged for each sample. After scanning, spectrum baseline correction and normalization were performed by using Matlab codes (Sreeram et al., 2018). The treated spectra were reported for analysis.

**Table 3**
Properties of the extending oil.

| Item | Results | Standard |
|---|---|---|
| Density (g/$cm^3$, 25 °C) | 0.99–1.08 | / |
| Viscosity (100 °C $m^2$/s) | 35–40 | / |
| Flash point (°C) | ≥240 | ASTM D92 |
| Pour point (°C) | ≤10 | ASTM D5950 |
| Sulfur content (%) | <0.5 | / |
| Anline point (°C) | 45 | ASTM D1218 |
| Aromatic ring carbon ratio (%) | 35 | ASTM D2140 |
| Naphthenic ring carbon ratio (%) | 23 | ASTM D2140 |
| Paraffinic chain carbon ratio (%) | 42 | ASTM D2140 |

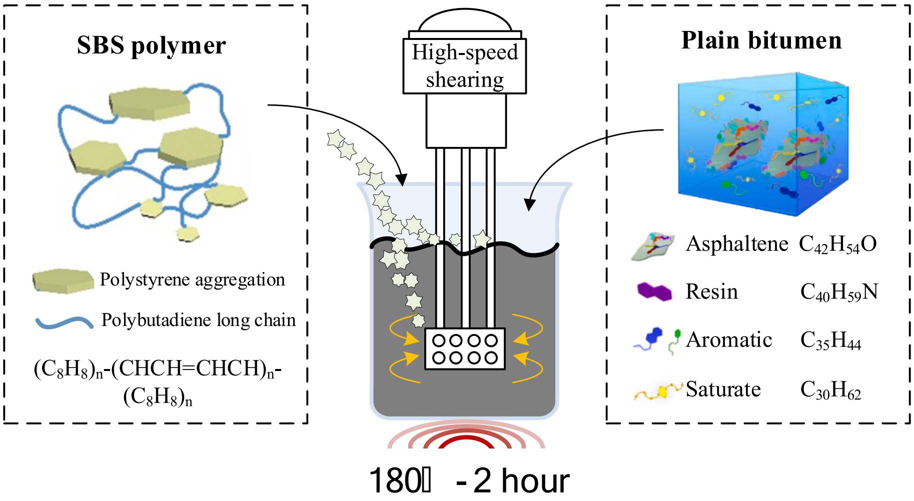

**Fig. 1.** Diagram of the PMB preparation.

### Molecular characterization (GPC)

A Waters 1515 High-Pressure Liquid Chromatography Pump and Waters 2414 Refractive Index (RI) detector were used to perform GPC tests. About 20 mg bitumen sample was dissolved in Tetrahydrofuran (HPLC grade) for testing. The solution was filtered through a PTFE filter to eliminate any insoluble components. The solution was then injected in a combination of multiple chromatographic columns for separation.

The calibration curve was built with the standard polystyrene to convert the retention time to molecular weight. The retention curve was reported, based on which, the Weight-average Molecular Weight ($M_w$) for each sample was calculated.

### Molecular dynamic simulation

The molecular nature of the entropy-elastic recovery was investigated through the molecular dynamic simulation by using Materials Studio. To do so, different of polymer long-chain molecules were constructed and subjected to shear in the simulation. The sheared molecules were then allowed to recovery and the variation in radius of gyration was recorded to quantify the molecular-level elastic recovery. The whole simulation is conducted under the Compass II force field with a cutoff distance of 15.5 Å.

The polymerization degree of the molecule model was determined based on the molecular weight derived from the GPC testing results. After the model was constructed, a 20,000-steps of geometry optimization and a 500-ps molecular dynamics equilibrium simulation was first performed to allow the long-chain polymer model to achieve an equilibrated state. The simulation was carried out at 25 °C using the NPT ensemble.

Afterwards, a 5,000-ps shear simulation was performed with a shear rate of 1000 $s^{-1}$ using the NVT ensemble. Following the shear process, a 5,000-ps recovery session was simulated at a temperature of 725 °C. Since no chemical reaction was allowed in this simulation, the higher temperature was applied to accelerate the molecular thermal motion without altering the properties of the polymer molecules. To quantify the creep and recovery happened during the process, the change in radius of the system was recorded.

### Creep and recovery test

For macroscopic evaluation, a TA dynamic shear rheometer (DSR) DHR-3 was used to perform the creep and recovery tests. During the creep stage of the test, the bitumen sample was first sheared for 1 s, then the sample was allowed to recover for certain time. The recovery rate was calculated by dividing the recovered strain by the peak strain.

The shear stress was 0.1 kPa to ensure the linearity of the stress-strain response. To make sure the sample was stable during creep and recovery, 20 creep and recovery cycles were run. The first 10 cycles were for conditioning and the results of the last 10 cycles were averaged and reported. The stiffness was also calculated to quantify the stiffness of the bitumen sample. The stiffness was calculated by dividing the shear stress (0.1 kPa) by the peak strain ($\gamma$). The diagram of the creep and recovery test is shown in Fig. 2.

The recovery rate of 5 different recovery times were analyzed, namely 0.01 s, 0.1 s, 1 s, 4 s and 9 s. 0.01 s recovery time can provide a hint on the instantaneous elasticity while the other recovery times can show how the delayed elasticity emerges. A wide testing temperature range of 10 °C-100 °C with a 6 °C gap was adopted to understand the behaviors at different environment temperatures. A summary of the testing plan and associated bitumens are shown in Table 4.

## Results and discussion

### General microstructure and mechanical properties of PMB

PMB as a composite material are heterogeneous at the microscopic scale, although macroscopic inspection indicates homogeneity. It has a typical two-phase microstructure that vastly differs from the plain bitumen (Fu et al., 2007). The results of fluorescence microscopy are shown in Fig. 3, which allow the observation of the dispersed polymer phase in the bitumen, showing the areas containing polymer in yellow color and bitumen in black color. The combination of these two phases makes PMB show signficantly different mechanical properties from the plain bitumen.

A temperature sweep (20 °C-140 °C) oscillation test can show the overall mechanical properties of PMB, as presented in Fig. 4. The plain bitumen is a complex of relatively small molecular-weight aliphatic and aromantic hydrocarbons. Thus, it shows very strong temperature-sensitivity and a fast-decreasing modulus with rising temperature. Polymer modification amends this temperature-sensitivity as PMB shows a slower decrease in modulus as the temperature rises. This is more obvious for the elastic fraction (storage modulus). Also, a distinct rubbery plateau can be observed in Fig. 4. The presence of a rubbery plateau is usually considered as the sign of a crosslinked elastic polymer network (Airey, 2003), which can translate to exceptional entropy elasticity (Sperling, 2005).

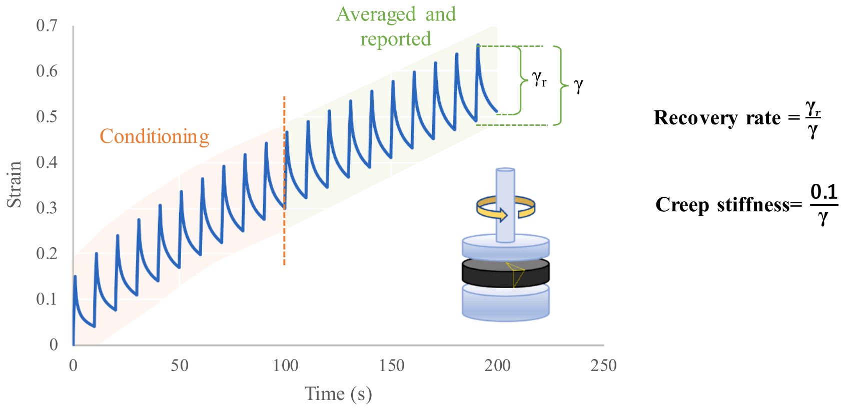

**Fig. 2.** Diagram of the creep and recovery testing.

**Table 4**
Summary of the testing plan.

| Interested variable | Levels | Tested sample |
|---|---|---|
| Temperature (°C) | 10, 16 … 100 | Plain bitumen, 4.2 %SBS |
| Recovery time (s) | 0.01, 0.1, 1, 4, 9 | Plain bitumen, 4.2 %SBS |
| SBS content (%) | 0, 2.5, 4.2, 7.5 | Plain bitumen, 2.5 %SBS, 4.2 %SBS, 7.5 % SBS |
| Bitumen stiffness | Original, Softened | 2.5 %SBS, softened-2.5 %SBS |

### *Molecular mechanism of the entropy elasticity of PMB*

#### *Functional group*

Fig. 5 presents the infrared spectra of PMB with different SBS dosages. The introduction of SBS can be detected by a series of functional groups from 700 $cm^{-1}$ to 1,100 $cm^{-1}$. The peak at 700 $cm^{-1}$ is associated with –CH of monoalkylated benzene ring (Canto et al., 2006), which is the sign of polystyrene (PS) blocks. The introduction of PS blocks imparts the PMB with strength. Also, they serve as physical-crosslink joints for the rubbery polybutadiene (PB) matrix. As PS blocks quickly de-aggregates when the temperature is above 100 °C and reform at cooler environment (Airey, 2003), this structure is thermoplastic and of great significance to the convenient construction of bituminous pavement.

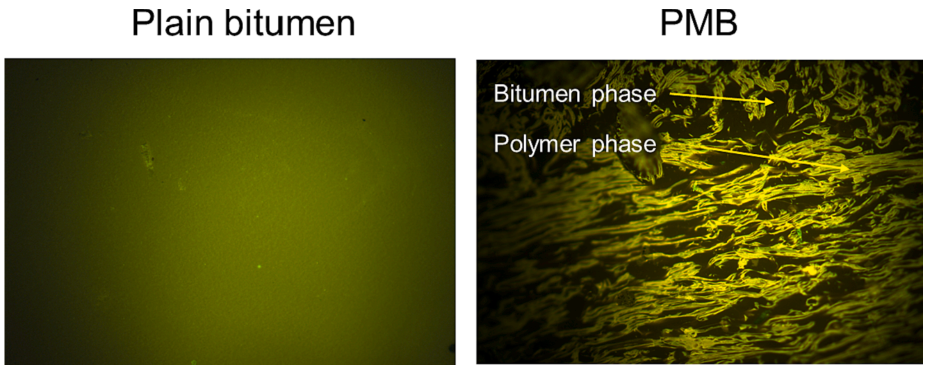

**Fig. 3.** The fluorescence microscopy results of plain bitumen and 7.5 %SBS.

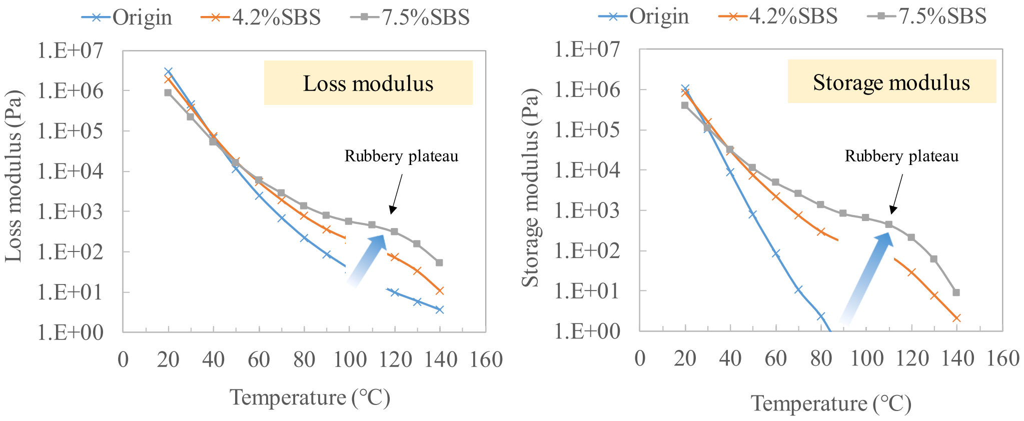

**Fig. 4.** The results of oscillation test for plain bitumen and PMB.

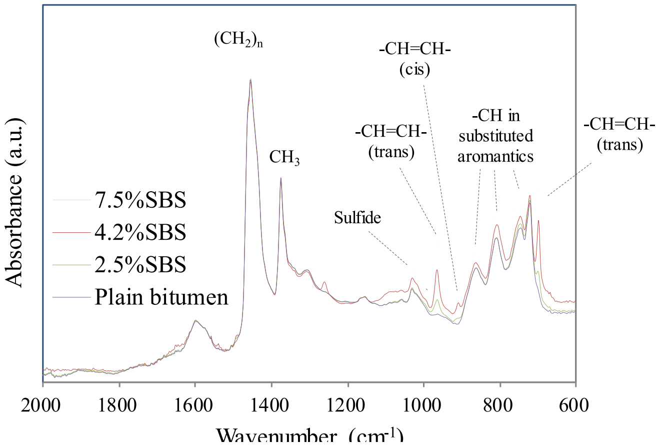

**Fig. 5.** The infrared spectra of plain bitumen and PMB of various SBS contents.

The peaks from 700 $cm^{-1}$ to 900 $cm^{-1}$ are induced by the –CH in substituted aromantics. They may also be attributed to the addition of PS block as a higher SBS content shows more absorption in this region. The peak at 966 $cm^{-1}$ and 912 $cm^{-1}$ are attributed to trans- and terminal-PB, respectively (Yan et al., 2018; Yan et al., 2017). The isolated double carbon bonds of PB segments result in less steric hindrance effect and excellent flexibility of the polymer long chain. These are key characteristics that lead to the outstanding entropy elasticity of SBS polymer.

The growth of $S = O$ is likely due to the dynamic vulcanization during the preparation of PMB. Due to the large difference in molecular weight and polarity, plain bitumen is a poor solvent for SBS polymer. The addition of sulfur can bridge PB segment and some of the asphaltene/resin molecules, resulting in lowered surface energy and better compatibility (de Carcer et al., 2014).

### *Molecular weight*

To perform the molecular dynamic simulation on the SBS entropy elasticity, the GPC test was first carried out to determine the actual molecular weight. Fig. 6 shows the GPC molecular weight distribution curves obtained for the plain bitumen and PMB relative to the polystyrene standards. Chromatography curves show that there are more than one peaks for each sample, which are associated to the polymer phase and bitumen phase with different molecular weights. The most intense peak corresponds to the maltene fraction of the plain bitumen. The existence of SBS can be detected by the peak around 17 min. A relatively short retention time suggests that SBS has a higher molecular weight and polymerization degree than the plain bitumen, which allows the SBS molecule to exhibit a wider range of conformations and demonstrate entropy elasticity.

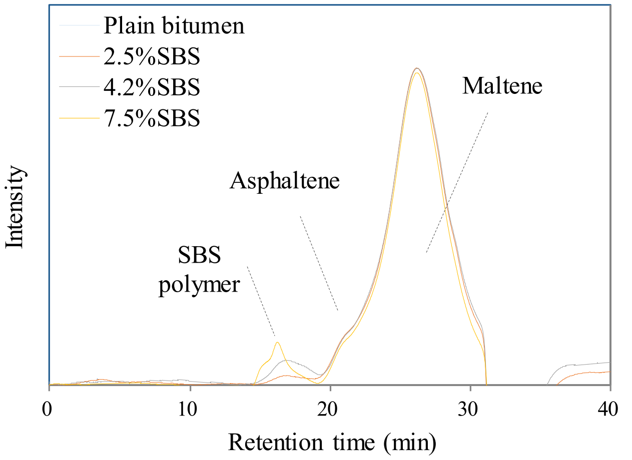

**Fig. 6.** The gel permeation chromatography of plain bitumen and PMB of various polymer contents.

The weight-average molecular weights ($M_w$) of the plain bitumen and PMB are calculated via integration of the chromatography curves. The results are summarized in Table 5. It can be seen that polymer modification caused slightly improvement in the $M_w$ of the plain bitumen from 2,070 to 2,300-ish. The $M_w$ of the SBS phase is also higher than that reported by the SBS manufacture (160,000). The growth in $M_w$ is likely associated with the dynamic vulcanization during the PMB preparation. Based on the molecular weight, the polymerization degree used for molecular dynamic simulation was set at 2,000.

### *Molecular dynamic simulation*

In this section, the molecular nature of SBS polymer's entropy-elasticity is investigated using molecular dynamic simulation. Because SBS is a block polymer composed of both PB and PS segments, the PB and PS segments were investigated separately in the molecular dynamic simulation. For more reference, the behavior of commonly used SBR polymer was also assessed. SBR shares the same chemical nature with SBS but has a different molecular structure. While SBS is a block polymer, SBR is the product of the random copolymerization of PB and PS, and thus is also named as random copolymer.

A sufficient polymerization degree is necessary for the molecules to exhibit entropy elasticity. Based on the GPC testing results, the polymerization degree used for the molecular dynamic simulation was set at 2,000. The PB segment, PS segment and SBR, which is an isomer of SBS, were evaluated. The simulated molecular shear-recovery behavior and the calculated radius of gyration are shown in Fig. 7.

From Fig. 7, it can be seen that the polymer chain first stretches towards the direction of shear and then shrinks back a little bit due to the molecular thermal motion. The changes in polymer conformation do not immediately demonstrate how much the polymer shrinks/recoveries, therefore the radius of gyration, which is the internal radius of rotation of the molecule chain around the center of mass, was calculated. It can be used to describe the size/volume/tightness of the molecule chain. The radius of gyration shows a drastic increase during the shear process due to the chain extension, and then it gradually decreases during the following recovery session. The difference of the radius before and after recovery session can be used to quantify the entropy-elastic recovery of polymer molecules.

The results show that the PB segment exhibits the most prominent recovery due to its highest chain-flexibility. The PS segment shows the least recovery due to its rigid backbone structure. This is consistent with the fact that the SBS polymer mainly derives its excellent elasticity from the PB matrix. SBR shows a relatively lower recovery than PB as a result of the introduction of randomly distributed PS functional groups on the backbone.

Fig. 7 clearly shows how the variation of polymer-chain conformation results into elastic recovery. This section will further elaborate the molecular basis of this entropy-based elasticity. According to thermodynamics, the elastic behavior of materials is in general governed by the Helmholtz's free energy (Sperling, 2005), which is expressed as Equation (1) and has two parts: energy term and entropy term.

$F = U - TS$(1)

where F is free energy, U is (internal) energy, T is temperature and S is

**Table 5**
Molecular weight of the plain bitumen and PMB.

| Sample | $M_w$ of bitumen phase | $M_w$ of SBS polymer phase |
|---|---|---|
| Plain bitumen | 2,070 | / |
| 2.5 %SBS | 2,293 | 170,141 |
| 4.2 %SBS | 2,316 | 186,993 |
| 7.5 %SBS | 2,249 | 203,295 |

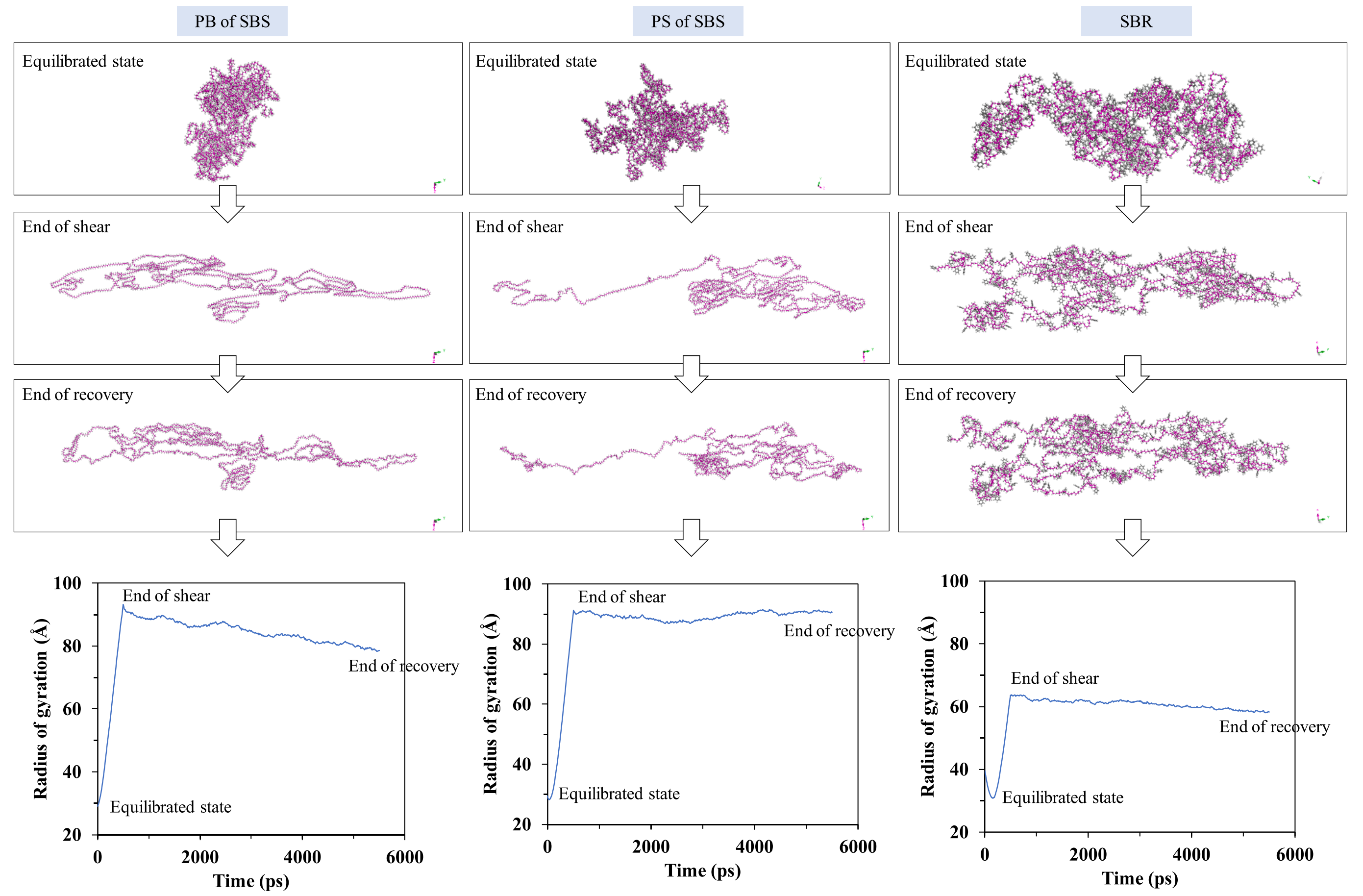

**Fig. 7.** Molecular shear-recovery behavior and calculated radius of gyration for PB, PS and SBR.

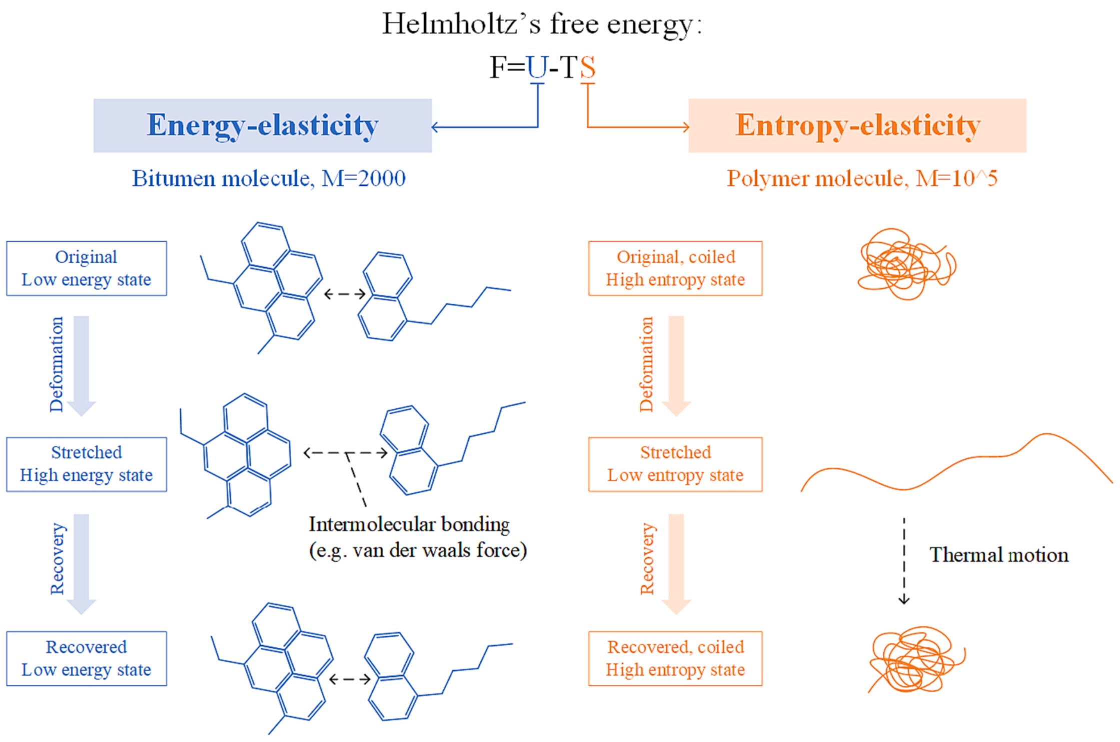

**Fig. 8.** Molecular mechanism of energy-elasticity and entropy-elasticity.

entropy.

When deformed, molecules tend to settle back into the state with the minimal free energy, that is, to minimize its internal energy but maximize its entropy. Depending on whether the energy or the entropy term dominates the free energy, the elasticity can be classified as energy-elasticity and entropy-elasticity. The generation mechanism of these two kinds of elasticities is shown in Fig. 8.

For relatively low molecular weight materials such as plain bitumen ($M_w = 2070$), the energy-elasticity dominates and it is mainly attributed to the intermolecular bonding (e.g. van der waals forces, dipolar, hydrogen bond and ionic) (Cerrada, 2005). Energy-elasticity is usually instantaneous and highly stiffness-dependent. When the environmental temperature is raised, molecules are mobilized, which in turn reduces the material stiffness. Therefore, the elasticity of the plain bitumen rapidly decreases with increased temperature.

PMB on the other hand, as a consequence of polymer modification, exhibits considerable entropy-elasticity. Due to thermal motion, the PB segment of SBS polymer behaves like wriggling worms, constantly changing their conformations by rotating their carbon-carbon single bonds, ranging from a fully stretched chain to a randomly coiled sphere (see Fig. 7). Statistically, the coiled shape is much more likely to be seen than the stretched one, simply because there are many more ways for the chain to be coiled than to be fully stretched (Roylance, 2000).

In thermodynamic terms, the entropy of the coiled conformation is very high (many possible microstates) while the entropy of the stretched conformation is very low (only one possible microstate). If the chain is stretched, the entropy is reduced and the molecule would tend to wriggle back to its most-possible/highest-entropy state (coiled sphere), resulting in an elastic force, which is the entropy-elasticity.

PMB's entropy-elasticity is much stronger and less temperature-sensitive than the plain bitumen's energy-elasticity because it depends on covalent bond within the polymer molecule instead of van der waals forces between molecules. These merits are of great significance to the performance of PMB. A greater entropy-elasticity can notably improve the fatigue/deformation resistance of materials, especially at high strain levels. It also reduces the temperature-sensitivity of the material. On the other hand, energy-elasticity may benefit the fatigue resistance of the material at relatively lower strain level. But when strain accumulates, the material may yield sudden fracture. The following sections will discuss how the elastic response of plain bitumen and PMB differs at the macro-level creep and recovery experiments.

### *Elastic recovery behavior*

In this section, the macroscopic elastic responses of the plain bitumen and PMB are compared through a series of creep and recovery tests.

It should be mentioned that the difference between “elastic recovery rate” and “elasticity” is usually ambiguous in terms of characterizing bitumen materials. In solid physics (Kittel et al., 1996), elasticity is the ability of a body to resist deformation under forces. For pure elastic material, its elasticity is quantified by Young's modulus or elastic modulus instead of “elastic recovery rate” because pure elastic materials always show a 100 % recovery rate when the force is removed. A solid body is only considered more elastic when its elastic modulus is higher.

On the other hand, bitumen is viscoelastic (Sun et al., 2020) and does not always show 100 % recovery rate. Therefore, the “elasticity” from solid physics is not suitable for bitumen and the elasticity for bitumen is indeed a performance-related parameter, which shall be measured with elastic recovery rate (e.g., AASHTO T301) instead of elastic modulus (or storage modulus/complex modulus). For bitumen, modulus related parameters should be viewed as stiffness indicators rather than elasticity indicators. In this study, the bitumen elasticity is quantified using the recovery rate derived from the creep and recovery test, and the bitumen stiffness is quantified using the creep stiffness. These two parameters are rather independent. It will be exhibited that it is possible for some bitumen samples (e.g. softened-2.5 %SBS) to show high elastic recovery rate associated with low stiffness.

#### *The influence of temperature on the elasticity*

First, the influence of different testing temperatures is discussed. The recovery time was fixed at 1 s. The results of recovery rate at different temperatures are shown in Fig. 9. Plain bitumen shows a clear and simple decreasing trend with increasing temperature, which is expected due to the reduction of stiffness and van der waals forces. Meanwhile, the variation in elastic recovery rate for 4.2 %SBS is quite interesting. It is not monotonic and shows three stages, with a unique increasing stage inserted between two decreasing stages.

This non-monotonic behavior of 4.2 %SBS is believed to be a combined result of the interplay between bitumen phase and SBS polymer phase. At low temperatures (10 °C-22 °C), the bitumen molecules freeze (in a viscoelastic manner) and prevent the SBS polymer from exerting any influence. The sample behavior is governed by the plain bitumen and energy-elasticity and therefore shows a decreasing trend.

With temperature being raised and the bitumen molecules unfrozen (22 °C −82 °C), SBS polymer and entropy-elasticity start to play a role. Entropy-elasticity shows much less temperature-sensitivity and will not decrease with increasing temperature. In contrast, it may even increase with temperature due to the intensified molecular thermal motion (Roundy and Rogers, 2013). Also, as the bitumen phase getting softer, the SBS phase is able to exert more influence and thus increased elasticity is seen.

Many have observed similar phenomenon in oscillation tests. Lu et al. (Isacsson and Lu, 1999) and Airey (Airey, 2003) reported that PMB showed decreased phase angle with increasing temperatures. Their results are consistent with what is seen in this paper, which is the first time an increased elasticity is characterized in a creep and recovery test.

With the temperature further increased (82 °C – 100 °C), a second decreasing stage is seen. This might be because the polystyrene segment of SBS polymer gradually de-aggregate at high temperatures, leading to the diminishing of the polymer network. Or, it could be because the stiffness of bitumen phase being so low that too much un-recoverable viscous strain accumulates. This matter will be further discussed in section 4.3.4.

#### *The influence of SBS content on the elasticity*

This section further discusses how the SBS polymer network alters the behavior of plain bitumen by examining different SBS polymer dosages (0 %, 2.5 %, 4.2 %, 7.5 %). The testing results are shown in Fig. 10.

With an increasing SBS polymer content, the unique recovery growth of PMB at high temperatures becomes more evident. 7.5 %SBS exhibits a 23.2 % recovery growth when the temperature is increased from 28 °C to 82 °C. This growth is quite unique and differs from the plain bitumen, it might be used as a fingerprint technique to identify the existence of elastomer modifier.

For more detailed information, the actual creep and recovery curves of these bitumens are shown in Fig. 11. The black arrow points the direction of increasing temperature, and a lighter color of the curve represents a higher testing temperature. Fig. 11 clearly shows how the SBS modification reverses the relation between recovery rate and temperature.

#### *The influence of extended recovery time on the elasticity*

The influence of different recovery time is demonstrated in Fig. 12. It is immediately apparent that the difference between plain bitumen and PMB grows more noticeable as the recovery time increases. This confirms the notion that SBS polymer mainly improves the delayed elasticity. This is because entropy-elasticity is usually delayed as it relies on time-sensitive relaxation behavior of polymer molecules.

The non-monotonic evolution and unique increasement of recovery rate can be seen for different recovery times except for the 0.01 s

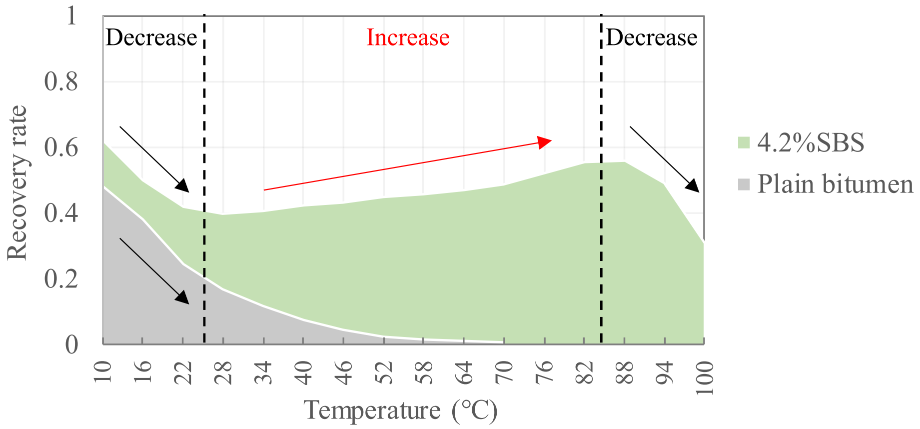

**Fig. 9.** The recovery rate of 4.2 %SBS at different temperatures.

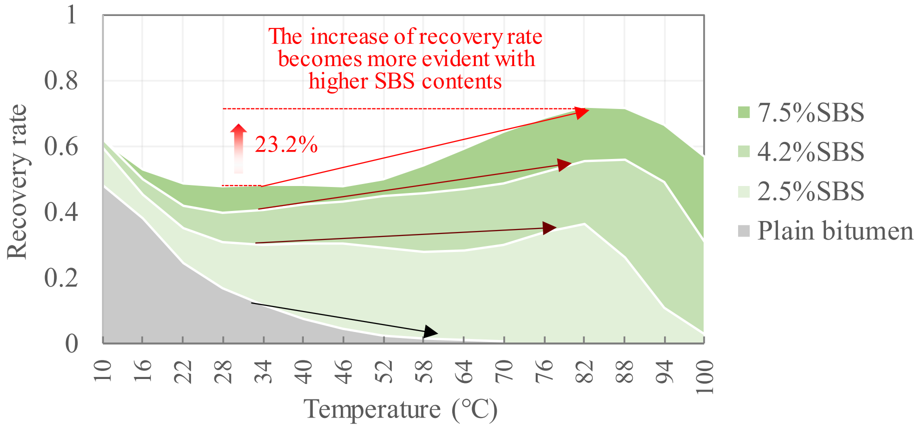

**Fig. 10.** The recovery rate of PMB with various SBS dosages (recovery time = 1 s).

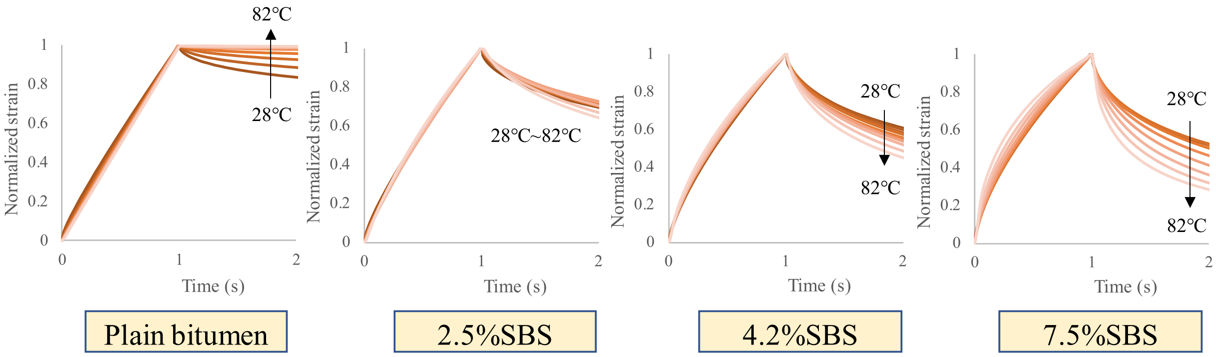

**Fig. 11.** The actual creep and recovery curve of PMB with various SBS dosages.

interval. Under 0.01 s interval, plain bitumen and PMB show almost overlapped results, and even highly-dosed 7.5 %SBS shows little improvement regarding 0.01 s recovery time. Meaningful recoveries are only observed at low temperature ranges (10 °C – 22 °C). These recoveries come from the frozen bitumen phase, which means they are energy-based, instantaneous and will quickly diminish upon increasing temperatures. Once again, these results point out that PMB mainly improves the delayed entropy-elasticity.

*The influence of the bitumen stiffness on the elasticity*

Based on previous results, it can be deduced that the stiffness of the bitumen phase plays a role in the recovery behavior of PMB. This section will provide a more detailed discussion of this influence, which is achieved by comparing the recovery behavior of the original 2.5 %SBS and softened-2.5 %SBS. The results are shown in Fig. 13. In first row of Fig. 13, recovery rates are plotted against testing temperature, while in second row of Fig. 13, recovery rates are plotted against the corresponding stiffness of the PMB measured at the testing temperature.

By plotting the recovery rate against testing temperature (first row of Fig. 13), it is seen that the general trends of 2.5 %SBS and softened-2.5 % SBS are quite similar except that reduced bitumen stiffness has “shifted” the curve of softened-2.5 %SBS to the lower temperature end. But this does not imply that softened samples always show smaller recovery rate, as illustrated by the comparison at 34 °C depicted in Fig. 13.

This “shift” is further investigated by plotting the recovery rate against stiffness (second row of Fig. 13). This helps eliminate the

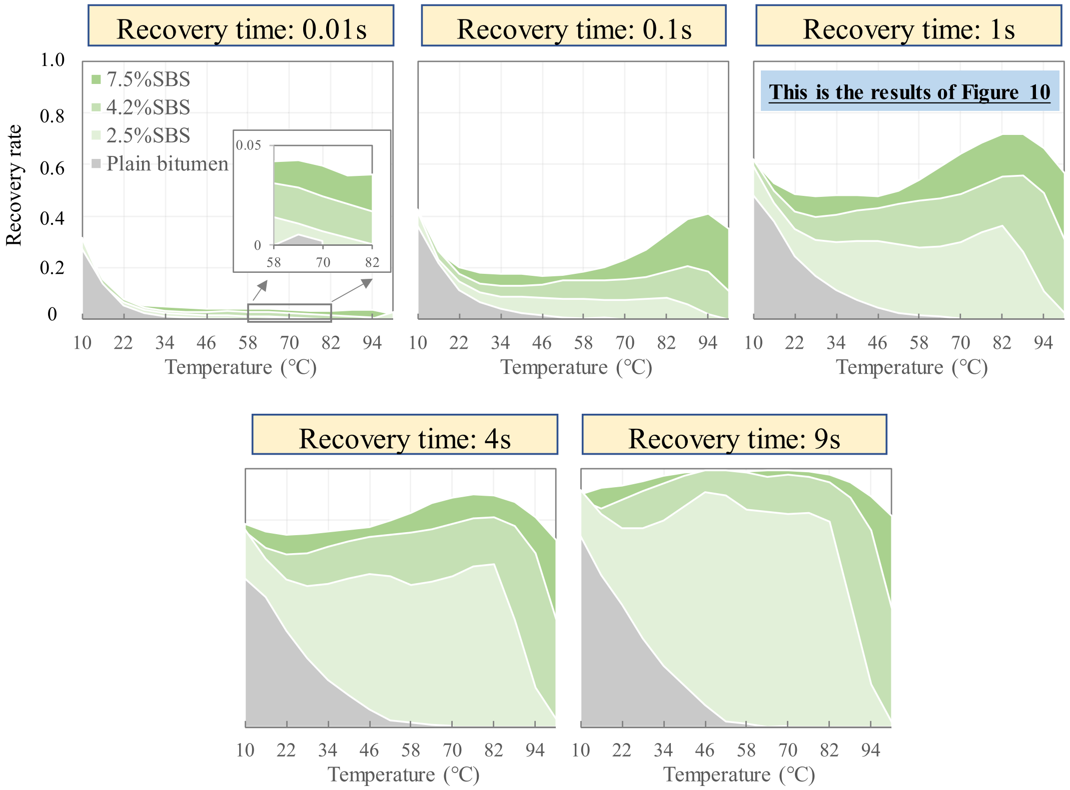

**Fig. 12.** The recovery rate of PMB with various SBS dosages for different recovery time.

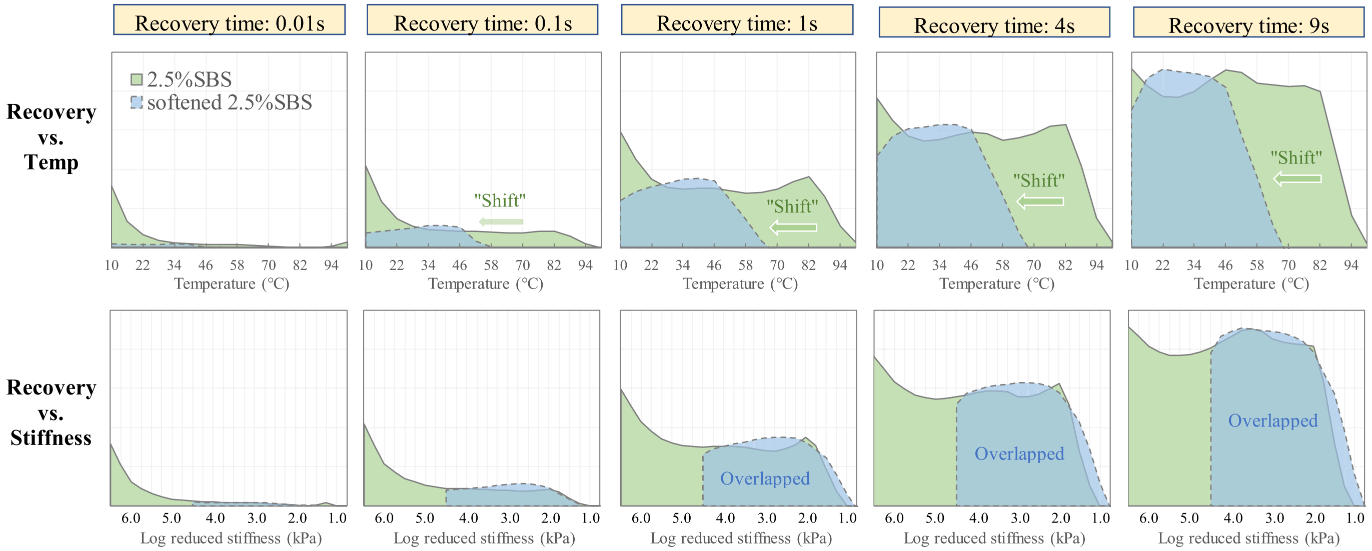

**Fig. 13.** The comparison between 2.5 %SBS and softened-2.5 %SBS.

influence of different bitumen stiffness. Notably, when stiffness is used as the x-axis, the “shift” disappears, as the curves of 2.5 % SBS and softened-2.5 % SBS overlap. These results point out bitumen stiffness plays a crucial role in the creep and recovery behavior of bitumen, the temperature-sensitivity of PMB’s elasticity is indeed stiffness-sensitivity.

In section 4.3.1, we speculated the second decreasing stage from 82 °C to 100 °C might be due to the de-aggregation of the PS block at high temperatures. However, Fig. 13 disproves this speculation, given softened-2.5 %SBS starts to shows a second decreasing trend at 52 °C which is way lower than the PS de-aggregation temperature (around 100 °C). Hence, the reduced stiffness and resultant viscous strain accumulation is the primary cause of the second decreasing stage.

This observation is important as it indicates that PMB with an intact polymer network may also show insufficient elastic recovery if its bitumen phase is not stiff enough (elastomer polymer such as SBS does not notably improve the bitumen stiffness). A good recovery rate, which is essential for the rutting and fatigue resistance, is a combined result of a strong polymer network and sufficient bitumen stiffness.

## Conclusions

In this study, FTIR and GPC tests, and molecular dynamic simulation were first conducted to investigate the molecular mechanism of the elasticity of PMB. Afterwards, a series of elastic recovery tests are conducted to show how the elastic response of PMB differs from the plain bitumen at a macro-level. Detailed conclusions are as follows.

- Based on the Helmholtz free energy theory. Plain bitumen mainly shows energy-elasticity, which is instantaneous and highly temperature-dependent. PMB mainly shows entropy-elasticity, which is strong and less temperature-dependent.
- Under low temperature and short recovery time, the bitumen molecules freeze (in a viscoelastic manner) and prevent the SBS polymer to demonstrate its entropy-elasticity. Hence the energy-elasticity dominates. Under high temperatures and long recovery time, the entropy-elasticity derived from the polymer network dominates.
- As temperature increases, the PMB recovery rate shows three stages, with a unique increasing stage (22 °C – 82 °C) inserted between two decreasing stages. This can be utilized as a fingerprint technique for the identification of bitumen modification.
- PMB with an intact polymer network may also show insufficient elastic recovery if the bitumen phase is not stiff enough (elastomer polymer such as SBS does not notably improve the bitumen stiffness). A good recovery rate is a combined result of a strong polymer network and sufficient bitumen stiffness.

## CRediT authorship contribution statement

**Chuanqi Yan:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Jiang Xi:** . **Changfa Ai:** Project administration, Supervision, Writing – review & editing. **Zhen Leng:** .

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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