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FROM STORAGE TO SERVICE: AGEING-INDUCED POLYMER NETWORK DEGRADATION IN SBS-MODIFIED ASPHALT BINDERS

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Abstract

Polymer-modified binders (PMBs) enhance pavement durability; however, their long-term performance depends largely on the ageing stability of the incorporated polymer. This study investigates the thermo-oxidative behavior of styrene–butadiene–styrene (SBS) modified binders with different molecular architectures and vinyl contents. Four commercial SBS types – linear (L-SBS), branched (B-SBS), high-vinyl linear (HV-SBS), and high-vinyl di-block (DB-SB) – were blended (4.5 wt.%) with a VG-10 binder. Non-oxidative ageing was simulated through prolonged storage at 120–180°C under limited oxygen exposure to isolate thermal degradation effects, while oxidative ageing was evaluated using RTFO and PAV. Rheological and chemical responses were assessed using Multiple Stress Creep Recovery (MSCR) and Fourier Transform Infrared (FTIR) analyses. Results indicate that storage configuration and base binder type have minimal influence under non-oxidative conditions, whereas polymer molecular structure governs stability. Low-vinyl SBS ($\leq 15\%$) showed significant softening and elongation loss due to chain scission, while high-vinyl variants ($\geq 30\%$) maintained structural and rheological integrity. Under long-term oxidative ageing, L-SBS and B-SBS exhibited higher non-recoverable creep compliance, stress–temperature susceptibility, oxidation indices, and polymer degradation index, whereas HV-SBS and DB-SB showed superior resistance. Strong correlations ($R^2 > 0.9$) between rheological susceptibility and polymer degradation confirm that long-term performance is primarily controlled by polymer network stability rather than binder oxidation alone.

Keywords: polymer-modified binders, SBS molecular architecture, High-vinyl SBS, binder ageing, thermo-oxidative durability

1 Introduction

The long-term performance of flexible pavements largely depends on the rheological stability of asphalt binders under high construction temperatures and progressive in-service ageing [1–3]. To enhance pavement durability, polymer-modified binders (PMBs) are widely used due to their improved resistance to rutting, fatigue, and thermal cracking [4–6]. Among various modifiers, styrene–butadiene–styrene (SBS) copolymers are most commonly used because they form a polymer-rich network within the bituminous matrix, enhancing elasticity and reducing temperature susceptibility [7–9]. However, SBS-modified binders are vulnerable to thermo-oxidative degradation. Exposure to elevated temperatures (120–180°C) during storage may cause polymer chain scission and morphological instability [10–12], while oxidative ageing during service leads to carbonyl and sulphoxide formation, resulting in binder stiffening and embrittlement [13–16].

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Most studies focus on polymer dosage, compatibility, and dispersion characteristics [17, 18]. Some researchers reported that SBS polymers with lower vinyl content are more vulnerable to thermal degradation, whereas higher vinyl content may improve stability due to differences in molecular configuration [19]. However, systematic comparisons of SBS molecular architectures, such as linear, branched, and diblock structures, under combined non-oxidative storage and oxidative ageing conditions remain limited. Furthermore, it is unclear whether high-temperature storage degradation is governed solely by polymer chemistry or also influenced by storage configuration and base binder type. In addition, direct correlations between chemical degradation indices and rheological susceptibility parameters are rarely established. Therefore, this study hypothesizes that ageing behavior in SBS-modified binders is primarily governed by polymer molecular architecture rather than base binder characteristics. By evaluating different SBS structures and vinyl contents under non-oxidative and oxidative ageing, this work links rheological susceptibility with chemical degradation to identify durability-controlling factors.

2 Materials and methodology

2.1 Base binder and polymer

VG-10 paving grade bitumen was used as the base binder. Four commercially available SBS polymers with different molecular architectures and vinyl contents were selected: linear (L-SBS), branched (B-SBS), high-vinyl linear (HV-SBS), and high-vinyl diblock (DB-SB). These polymers differ in butadiene block configuration and vinyl group content, representing typical commercial grades. All modified binders were prepared with 4.5 wt.% polymer, a dosage sufficient to promote continuous polymer network formation. Modification was conducted under controlled temperature and shear conditions to ensure uniform dispersion.

2.2 Non-oxidative storage ageing protocol

Non-oxidative ageing was simulated by storing SBS-modified binders at 120, 150, and 180°C in aluminium tubes and metallic containers (1, 2, and 10 L) with small vents to limit oxygen ingress. The effect of container size on property degradation was assessed through periodic conventional and mechanical testing. Based on preliminary results, 2 L containers were selected for detailed study due to practical handling and sufficient material availability.

2.3 Oxidative ageing procedures

Short-term oxidative ageing was simulated using the Rolling Thin Film Oven (RTFO), wherein binders were aged at 163°C for 85 minutes under continuous airflow. Long-term ageing was subsequently performed on RTFO-aged residues using the Pressure Ageing Vessel (PAV) at 100°C and 215 kPa air pressure for 20 hours. These procedures were designed to represent ageing during construction and long-term field exposure, respectively.

2.4 Rheological and chemical characterization

The rheological behavior was evaluated under non-oxidative and oxidative ageing using the MSCR test. Non-oxidative ageing (high-temperature storage under limited oxygen) was assessed through elastic recovery (R%) to examine polymer network stability. Oxidative ageing was simulated using RTFO (short-term) and PAV (long-term). MSCR tests were conducted at 58–76°C using a 25 mm parallel plate with a 1 mm gap under three ageing conditions (Unaged, RTFOT, PAV).

Two stress levels (0.1 and 3.2 kPa) with 10 creep–recovery cycles were applied. Jnr values obtained from MSCR were used to evaluate ageing and polymer molecular structure effects on elastic response, where lower Jnr indicates lower permanent strain and better rutting resistance. Moreover, to identify the effect of different stress levels on the rheological response of the studied binders with different SBS copolymer, stress susceptibility for the Jnr value was determined as per equation 1.

$$SS_{ER,T_i} = \frac{\log\left(J_{nr\tau_1,T_i}\right) - \log\left(J_{nr\tau_2,T_i}\right)}{\tau_1 - \tau_2} \tag{1}$$

Where, $SS_{ER,\,Ti}$ is stress susceptibility with respect to elastic response at temperature T_i, $J_{nr\tau1,Ti}$ is the non-recoverable creep compliance value of the binder at stress level τ_1 and test temperature T_i and $J_{nr\tau2,Ti}$ is the non-recoverable creep compliance value of the binder at stress level τ_2 and test temperature T_i. Additionally, in order to find out the influence of ageing on the functional groups of modified binder, different indices were calculated using equations (2) to (4).

$$\text{Sulphoxide index (SI)} = \Sigma A_{1030}/A \tag{2}$$

$$\text{Carbonyl index (CI)} = \Sigma A_{1700}/A \tag{3}$$

$$\text{Polymer index (PI)} = \Sigma A_{966}/A \tag{4}$$

Where A_{1700} is the area of the spectral band around 1700 cm^{-1}, A_{1030} is the area around 1030 cm^{-1}, A_{966} is the area around 966 cm^{-1}, and A is the sum of the spectral band areas between 500 and 2000 cm^{-1}. Using these indices, the Ageing Index (AI) and Polymer Degradation Index (PDI) were calculated using equation 5 and equation 6, respectively.

$$\text{Ageing index (AI)} = (CI+SI)_{aged}/(CI+SI)_{unaged} \tag{5}$$

$$\text{Polymer degradation index (PDI)} = PI_{unaged}/PI_{aged} \tag{6}$$

3 Results and discussion

3.1 Effect of storage temperature and SBS structure on non-oxidative ageing

Figure 1a shows the influence of storage temperature (120, 150, and 180°C) on elastic recovery (ER%) using L-SBS as a representative polymer. Storage at 120°C and 150°C caused negligible changes in ER, even after 14 days. Similar trends were observed for other SBS grades, indicating that the polymer network remains thermally stable under these conditions. In contrast, storage at 180°C resulted in significant ER reductions of ~34% and ~47% after 7 and 14 days, respectively, relative to the unstored binder, suggesting accelerated thermal degradation. Figure 1b compares SBS grades at 180°C. Low-vinyl polymers (≤ 15%, L-SBS and B-SBS) exhibited rapid ER loss, particularly within the first week – an important observation given typical field storage durations (3–5 days). High-vinyl polymers (≥ 30%, HV-SBS and DB-SB) retained higher ER after prolonged exposure. This improved stability is attributed to molecular structure: low-vinyl SBS contains backbone unsaturation prone to chain scission, whereas high-vinyl SBS has greater pendant unsaturation, limiting effective backbone shortening under thermal stress.

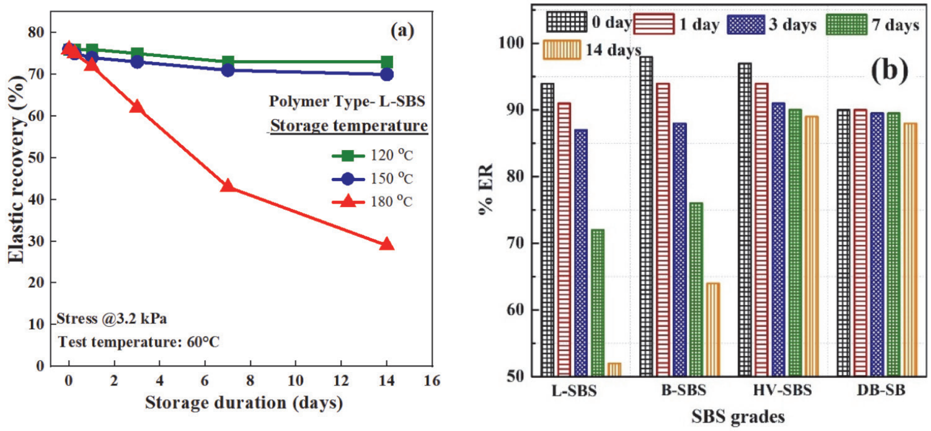

Figure 1 a) Change in %ER value along with different storage temp, b) Variation of %ER of the four SBS modified binders during 180°C storage

3.2 Influence of storage configuration under non-oxidative ageing

To evaluate the influence of storage configuration and oxygen availability on the property deterioration of SBS-modified binders, the binders were stored at 180°C in aluminium tubes as well as in 1, 2, and 10 L metallic containers and the change in property is depicted in figure 2 a and 2b. If oxidative ageing were dominant, larger containers with greater headspace would show higher deterioration. However, softening point trends with storage time were nearly identical across all volumes, indicating comparable degradation rates.

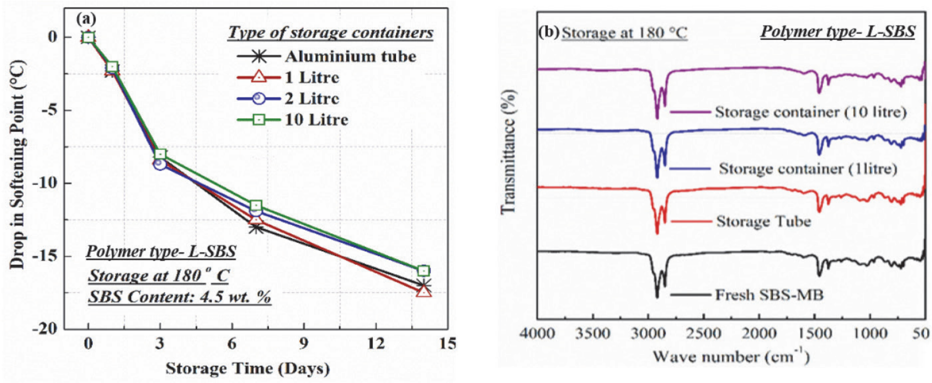

Figure 2 a) Effect of storage container on the variation of SP value, b) FTIR test result for binder at different container during storage at 180°C

FTIR analysis further supported this finding (figure 2b), showing no measurable increase in carbonyl (~1700 cm^{-1}) or sulphoxide (~1030 cm^{-1}) bands relative to the fresh binder. As these are established markers of oxidation, their absence confirms negligible oxidative ageing. The combined rheological and spectroscopic evidence demonstrates that degradation at 180°C is primarily thermally driven, resulting from polymer chain scission and network disruption. The mechanism is therefore intrinsic to polymer stability and independent of container size or oxygen exposure.

3.3 Rheological response under oxidative ageing

3.3.1 Stress–temperature susceptibility and SBS molecular structure

Table 1 summarizes Jnr (3.2 kPa) for all binders under unaged, RTFO-, and PAV-aged conditions across temperatures. Jnr indicates rutting resistance and polymer network effectiveness, where higher values reflect greater non-recoverable strain due to polymer degradation. RTFO ageing reduced Jnr at all temperatures, indicating oxidation-induced stiffening and improved rutting resistance. In unaged and RTFO states, B-SBS exhibited the lowest Jnr, followed by HV-SBS, L-SBS, and DB-SB, suggesting stronger network integrity. After PAV ageing, behavior became temperature-dependent: at lower temperatures Jnr remained below RTFO values due to binder-phase stiffening, whereas at ≥ 64°C, L-SBS and B-SBS showed significant Jnr increases while HV-SBS and DB-SB maintained lower compliance. This indicates that under severe ageing and high temperature, degradation of low-vinyl polymer networks governs the rheological response. Table 2 shows that SS increased with temperature, reflecting binder softening. Ageing generally reduced SS due to oxidation-induced stiffening. In the unaged state, B-SBS showed the lowest SS, indicating a stiffer and less stress-sensitive network, while DB-SB exhibited higher stress dependence. After RTFO ageing, binder differences became marginal, suggesting limited polymer disruption. However, after PAV ageing, L-SBS and B-SBS displayed higher SS than HV-SBS and DB-SB, indicating greater degradation in low-vinyl systems.

Table 1 Creep compliance values of the studied modified binders with ageing type

SBS grades	Temperature [°C]	Creep compliance			
		L-SBS	B-SBS	HV-SBS	DB-SB
Fresh	64	0.8	0.63	0.73	0.95
	70	1.4	1.05	1.22	1.6
	76	2.58	1.85	2.23	2.75
RTFO	64	0.3	0.22	0.28	0.4
	70	0.6	0.42	0.52	0.75
	76	1.33	0.88	1.05	1.55
PAV	64	0.09	0.07	0.06	0.07
	70	0.25	0.22	0.13	0.16
	76	0.8	0.7	0.35	0.39

Temperature susceptibility (TS) was determined similarly to equation 2, with temperature considered as the variable parameter. TS increased with both temperature and ageing, as elevated temperature softens the binder matrix and long-term ageing weakens the polymer network. After PAV ageing, L-SBS and B-SB exhibited the highest TS, while HV-SBS and DB-SB remained comparatively stable, likely due to higher vinyl content and more thermally resistant molecular architecture. Due to brevity, the detailed TS values are not presented here but mentioned in table 2.

Table 2 Stress susceptibility of the studied modified binders with ageing type

SBS grades	Temperature [°C]	Stress susceptibility		
		Unaged	RTFO	PAV
L-SBS	64	2.929	2.78	2.62
	70	4.137	3.783	4.447
	76	5.68	5.209	6.307
B-SBS	64	2.739	2.656	2.594
	70	3.67	3.464	4.227
	76	4.729	4.638	5.965
HV-SBS	64	2.888	2.756	2.336
	70	3.798	3.536	3.073
	76	4.947	4.714	4.057
DB-SB	64	3.237	3.039	2.597
	70	3.984	3.8	3.354
	76	5.403	5.323	4.385

3.4 Correlation between rheological susceptibility and ageing indices

Chemical changes due to oxidative ageing of SBS-modified binders were evaluated using FTIR test. Spectra are not presented due to space limitations table 3 summarizes the ageing index (AI) and polymer degradation index (PDI) with respect to polymer architecture and ageing type. RTFO ageing caused only minor changes, indicating adequate short-term stability. In contrast, PAV ageing significantly increased oxidation, particularly in L-SBS and B-SBS, while HV-SBS and DB-SB exhibited lower AI values and improved resistance. To link rheological susceptibility with chemical ageing, stress and temperature susceptibility (76°C) were correlated with polymer degradation index (PDI) and ageing index (AI). Linear regression and Pearson analysis showed stronger correlations for PAV-aged binders than RTFO-aged ones. Under PAV conditions, susceptibility strongly correlated with PDI (r ≈ 0.98, 0.96) and moderately with AI (r ≈ 0.91, 0.80), indicating that long-term ageing affects rheology primarily through polymer degradation. Correlation coefficients were calculated using equation 7 and are listed in table 3.

$$r = \frac{n\left(\sum xy\right) - \left(\sum x\right)\left(\sum y\right)}{\sqrt{\left[n\sum x^2 - \left(\sum x\right)^2\right]\left[n\sum y^2 - \left(\sum y\right)^2\right]}} \tag{7}$$

Table 3 Correlation of stress and temperature susceptibility (76°C) with PDI and AI under RTFO and PAV ageing

Ageing type	SBS grades	SS	TS	PDI	AI	Pearson correlation coefficient			
						SS_{PDI}	TS_{PDI}	SS_{AI}	TS_{AI}
RTFO	L-SBS	5.209	0.058	1.12	1.19	0.713	0.678	0.565	0.701
	B-SBS	4.638	0.054	1.05	1.05				
	HV-SBS	4.714	0.051	1.07	1.1				
	DB-SB	5.323	0.053	1.08	1.09				
PAV	L-SBS	6.307	0.084	2.28	2.63	0.984	0.962	0.912	0.801
	B-SBS	5.965	0.085	2.03	2.04				
	HV-SBS	4.057	0.07	1.31	1.61				
	DB-SB	4.385	0.066	1.26	1.68				

4 Conclusion

This study examined the influence of SBS molecular architecture and vinyl content on the non-oxidative and oxidative ageing behavior of polymer-modified binders. Results show that degradation during high-temperature storage under limited oxygen is mainly governed by polymer molecular structure. High-vinyl SBS exhibited greater thermal stability, whereas low-vinyl polymers were more prone to chain scission and structural degradation. Short-term oxidative ageing mainly affected the binder phase, while long-term ageing significantly degraded low-vinyl polymer networks. Strong correlations between rheological susceptibility and polymer degradation indices confirm that long-term performance is primarily controlled by polymer network integrity rather than binder oxidation alone. These findings highlight the importance of polymer molecular architecture in ageing resistance. Practically, selecting SBS modifiers with higher vinyl content and stable molecular structures can improve the durability and rutting resistance of polymer-modified binders in high-temperature pavement applications.

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