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Evaluation of Aging Effects in Polymer-Modified Bitumen Using Rheological, Chemical, and Morphological Analyses

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Abstract

The growing use of reclaimed asphalt pavement (RAP) in sustainable pavement construction raises important challenges related to the presence and activity of polymers in aged binders. In particular, the long-term performance of mixtures depends on whether polymer-modified binders in RAP retain their functionality after aging. This study investigates the evolution of styrene–butadiene–styrene (SBS) modified binders during aging, with comparisons to a RAP binder and an unmodified binder. The SBS binders were subjected to laboratory aging, and their response was evaluated using a combination of rheological, chemical, and morphological analyses. Dynamic Shear Rheometry (DSR) assessed changes in dynamic modulus, phase angle, and creep-recovery behavior, while Fourier Transform Infrared Spectroscopy (FTIR) provided insights into chemical modifications in the polymer–bitumen matrix. Fluorescence Microscopy (FM) enabled quantitative evaluation of the polymer network, including particle density, size distribution, and morphology. The results demonstrate that aging causes significant restructuring in PMBs, as evidenced by reduced polymer peak magnitudes in FTIR, disintegration of the polymer network observed in FM, and diminished polymer network activity in the phase angle master curve.

Keywords: Bitumen; Polymer; RAP; Aging; FTIR spectroscopy; Fluorescence Microscopy; Rheology

1. Introduction

Polymer Modified Binders (PMB) are extensively used across the globe for surface and binder course layers in asphalt pavements. With the increasing demand to reuse Reclaimed Asphalt Pavement (RAP) in new pavements, it is important to assess whether the RAP still contains polymers and to what extent their presence influences the blend

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design during recycling. This necessitates a better understanding of the aged PMBs to capture the presence of polymers in aged RAP binders.

When RAP binders contains polymers, there are uncertainties related to whether the polymer in RAP binders remains active, how it interacts with virgin polymer-modified binders during recycling, and how its functionality evolves over time. Addressing these challenges requires reliable methods to quantify the chemical, rheological, and morphological evolution of polymers in aged binders. In this context, Fourier Transform Infrared Spectroscopy (FTIR), and Fluorescence Microscopy (FM) can serve as effective tools. FTIR enables the identification of the functional groups of bitumen, which can be directly linked to changes in its chemical composition during aging (Nivitha et al., 2016). In the case of SBS-modified bitumen, the absorption band at 966 cm^{-1} is attributed to polybutadiene (PB), whereas the band at 699 cm^{-1} corresponds to polystyrene (PS) (Lin et al., 2019). Furthermore, FM can confirm the presence of polymers and visualize the spatial distribution of polymer particles within the polymer–bitumen matrix. Monitoring changes in parameters such as particle density, size distribution, and morphology of polymer particles during aging offers valuable insights into the effects of aging on PMBs.

The complexities associated with PMB aging arise from two main processes: the hardening of the base bitumen and the degradation of polymers and their network (Petersen, 2009; Cuciniello et al., 2018; Wu et al., 2024). To better understand these processes, it is essential to characterize the rheological response of PMBs. Careful analysis of the dynamic modulus and phase angle master curves can provide valuable insights into the role of the polymer network. Changes in the dynamic modulus with aging primarily reflect the hardening of the base binder, whereas the phase angle master curve offers information on the activity of the polymer network. The plateau observed in the phase angle master curve is a widely accepted indicator of an active polymer network, as it reflects reduced thermal (or frequency) susceptibility (Socal da Silva et al., 2004).

With this background, the present study evaluates the properties of a RAP binder in comparison with a laboratory-aged SBS-based commercial PMB, with an unmodified, unaged binder included as a reference. Laboratory aging of PMB is essential to reproduce, under controlled conditions, the progressive changes in polymer network structure that occur in the field, thereby enabling comparison with RAP binders. Advanced testing techniques were employed, including FTIR to confirm polymer presence and characterize chemical composition and aging status, FM to identify polymer structures and their distribution, and DSR to assess rheological properties and the activity of the polymer network. Together, these methods provide deeper insights into the behavior of aged PMBs, including RAP binders.

Nomenclature

ATR	Attenuated Total Reflectance
DSR	Dynamic Shear Rheometer
FM	Fluorescence Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
PB	Polybutadiene
PMB	Polymer Modified Bitumen
PS	Polystyrene
RAP	Reclaimed Asphalt Pavement
RTFO	Rolling Thin Film Oven
MSCR	Multiple Stress Creep Recovery

2. Materials tested

In this study, an unmodified binder of penetration grade 50/70 (DIN EN 12591, 2009), hereafter referred to as UB, which is commonly used in asphalt pavements in Germany, was selected as the reference bitumen. To assess the effect of aging on the properties of PMB, a commercial PMB 25/55-55A (DIN EN 14023, 2013), hereafter referred to as PMB, was investigated. To evaluate the presence of polymers in RAP binder, material was collected from a RAP stockpile at an asphalt mixing plant in Dresden/Germany. The RAP binder is hereafter referred to as RAPb. Aging of the PMB was simulated in the laboratory using the RTFO procedure according to DIN EN 12607-1(2014), with the exception that the temperature was set to $100\text{ }^{\circ}\text{C}$ in order to simulate aging more gradually and to restrict it only to

the oxidative aging. Samples were collected after 12 and 20 hours to analyse the evolution of the chemical and rheological properties of the binder during aging.

Table 1. Materials tested and basic properties.

Materials	T_{BTSV} (°C)	δ_{BTSV} (°)
UB - unaged	49.4	80.5
PMB - unaged	52.9	67.3
PMB - 12h aged	56.3	66.2
PMB - 20h aged	57.7	65.4
RAPb	77.9	73.0

Following TP Bitumen-StB Part 3 (2012), the temperature and phase angle corresponding to an absolute complex shear modulus of 15 kPa at a frequency of 1.59 Hz were determined for all binders, denoted as T_{BTSV} and δ_{BTSV} , respectively, and are provided in Table 1. The T_{BTSV} is an indicator of the softening point, which characterizes the thermal resistance of bitumen. It can be observed that even after 20 h of RTFO aging at 100°C, the T_{BTSV} of the PMB-20h aged remains considerably lower than that of the RAP binder, indicating that the RAPb has a high aging level.

3. Laboratory tests

3.1 FTIR Tests

To assess the chemical composition of the UB, RAPb, and PMB at different aging levels, FTIR spectroscopy was performed using a Perkin Elmer FTIR spectrometer with ATR mode. The test samples were prepared and tests were carried out in accordance with AASHTO T 302-22 (2022). Spectra were collected over a wavenumber range from 4000 cm^{-1} to 400 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans per measurement. Four samples, each with four repetitions, were measured.

3.2 FM

FM was performed using a Zeiss Axiotech reflected light microscope equipped with a 50 W Hg lamp and an EpiPlan 50 \times , 0.70 HD objective. A drop of the test material was placed on a glass slide, heated in an oven maintained at 120 °C for one hour to form a thin film, then covered with a glass slide and immediately stored in a freezer at –20 °C until testing. FM was conducted using blue light excitation with a Zeiss S09 filter combination. Images were captured using a Canon EOS 250D camera at ISO 800 with a 2 s exposure time.

3.3 DSR Tests

Frequency sweep tests were performed to evaluate the rheological properties of the binders over a temperature range of 80 to –20 °C in 10 °C intervals and frequencies of 0.1 to 25 Hz, except for RAPb, which was tested from 80 to 0 °C with frequencies of 0.1 to 15 Hz. The tests were performed using an Anton Paar DSR, MCR 702e, with a 25 mm plate and 1 mm gap for the temperature range of 50 to 80 °C, and an 8 mm plate with 2 mm gap for the range of 40 to –20 °C. The tests were performed in a strain-controlled mode within the linear viscoelastic regime of the materials. Using the collected data, master curves were generated, with reference temperature 20°C, employing the 2S2P1D rheological model in combination with the Williams-Landel-Ferry equation for the shift factors (Di Benedetto et al., 2007).

4. Results and Discussion

4.1 Chemical Aspects: FTIR Test Results

Figure 1 shows the FTIR spectra collected for the UB, RAPb, and PMB at their different aging levels, and Table 2 presents the integrated peak areas for the Sulfoxide, Styrene, and Butadiene functional groups. The key aging-related

peaks, Carbonyl (1700 cm^{-1}) and Sulfoxide (1030 cm^{-1}), are significantly higher in the RAPb than in the PMB-20h aged sample, indicating that the applied laboratory aging procedure is not sufficient to reach the aging extent of the RAPb. Elastomeric-specific peaks associated with SBS modification, 966, 911, and 699 cm^{-1} , are marked in Figure 1. Although small in magnitude, the RAPb exhibits detectable peaks at 699 and 966 cm^{-1} , confirming the presence of polymeric components. The effect of aging is further illustrated by the integrated peak (Table 2). It is observed that the adopted aging procedure has no influence on the Styrene component, whereas the Butadiene component decreases with aging. The RAPb shows very low areas for both Styrene and Butadiene peaks, confirming the low polymer presence, as discussed in the following pages.

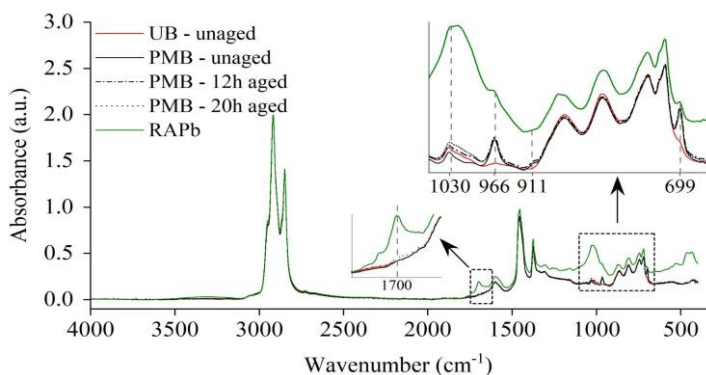


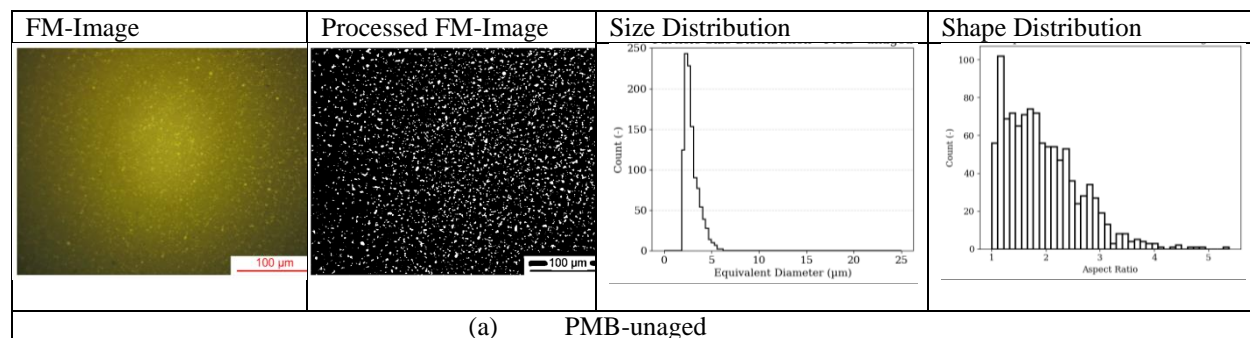
Figure 1: FTIR spectra.

Table 2: FTIR spectral values.

Materials	Carbonyl Area (-)	Sulfoxide Area (-)	Styrene Area (-)	Butadiene Area (-)
UB - unaged	5.7	17.8	-	-
PMB - unaged	5.1	16.7	0.63	1.01
PMB - 12h aged	5.6	18.9	0.63	0.97
PMB - 20h aged	5.7	18.6	0.63	0.95
RAPb	13.3	43.7	0.16	0.18

4.2 Polymer Network Aspects: FM images

FM was used to examine the presence of polymers, the network structure, and the effect of laboratory aging on network integrity. FM images of PMB-unaged, PMB-20h aged, and RAPb were captured. Only the two extreme cases of laboratory aging are presented, while the FM results for PMB-12h aged were omitted. The FM images were processed using Python into binary representations to enable quantitative analysis of the polymer network, including particle dispersion, size distribution, and their morphological characteristics. Representative original and processed FM images, along with particle size and shape distribution of detected polymer particles, are shown in Figure 2.



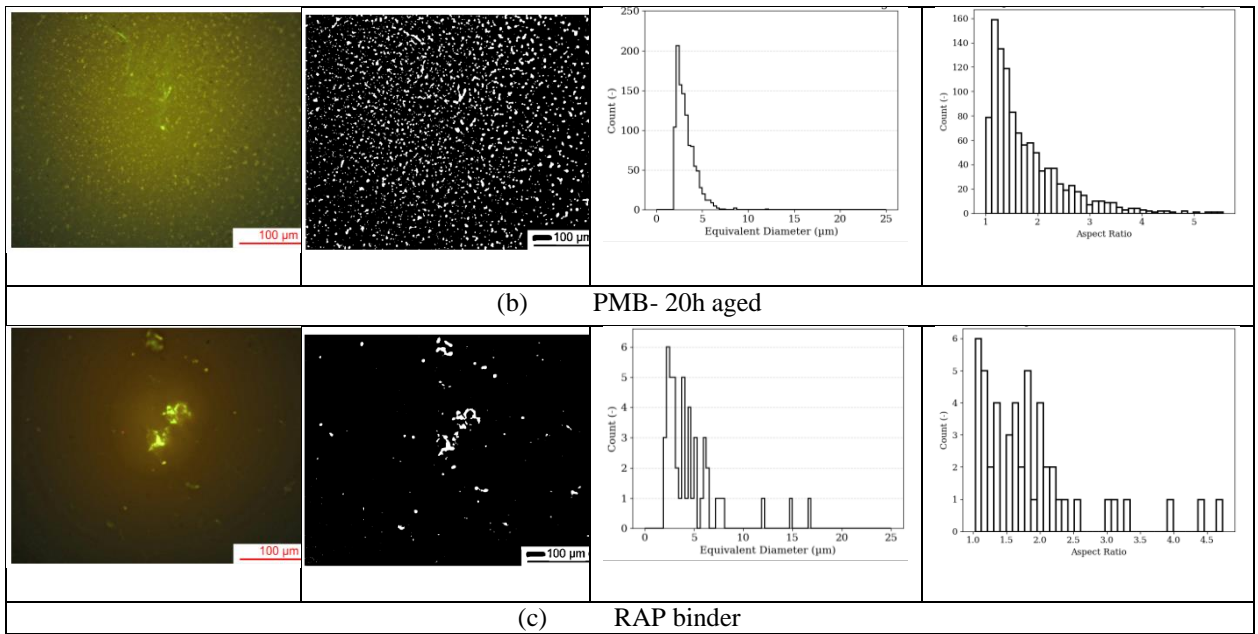


Figure 2: FM images of PMB - unaged, PMB - 20h aged, and RAPb.

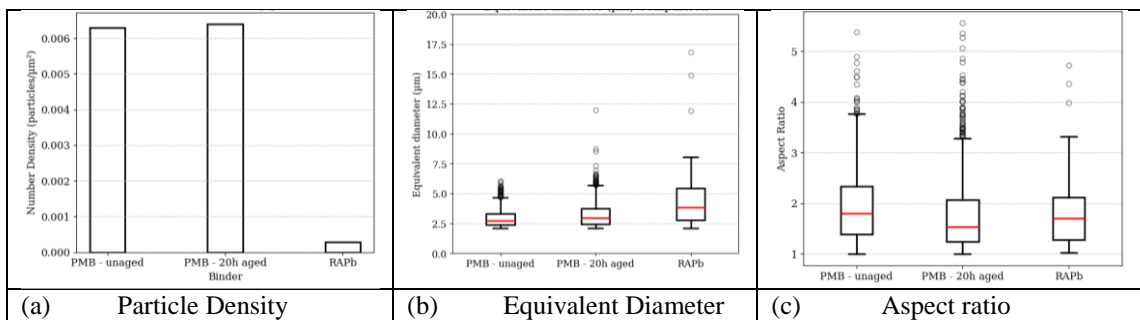


Figure 3. Comparison of dispersion, size and shape metrics among the binders.

The analysis focused on three aspects of the polymer strands: dispersion, quantified by particle density; size characteristics, quantified by the distribution of equivalent diameter; and shape characteristics, quantified by the distribution of aspect ratio. Comparison of these metrics for the binders is shown in Figure 3. As shown in Figure 2 and Figure 3, the virgin PMB exhibits a continuous, crosslinked SBS polymer network that is uniformly dispersed within the bitumen. After 20 hours of aging, signs of SBS degradation and agglomeration are apparent, as reflected by an increase in particle size and a higher proportion of polymer strands with elevated aspect ratios. Comparison with the RAP binder further supports this trend, showing greater agglomeration, reduced dispersion, and higher aspect ratios. Overall, aging induces notable changes in the polymer network, reflected in the dispersion characteristics as well as particle size and shape distributions. Specifically, aging results in a lower particle count, reduced dispersion, increased agglomeration, and decreased circularity of the polymer strands.

4.3 Rheological Aspects: DSR Test Results

Figure 4 compares the dynamic modulus and phase angle master curves of the PMB at different aging stages with those of the UB and RAPb. The results show that the dynamic modulus of the PMB, already higher than that of the UB, increases more significantly during the first 12 hours of aging. The dynamic modulus of the RAPb is greater than that of the PMB-20h aged across the entire frequency range, confirming that the RAPb is heavily aged. Regarding the

phase angle master curves, the presence of a plateau region is a widely acknowledged indication of polymer activity, a feature not observed in unmodified binders (Socal da Silva et al., 2004; Lu & Isacsson, 1996). Such a plateau indicates that the proportion of storage and loss modulus, i.e., the elastic and viscous components respectively, remains independent of frequency (or temperature) within this region (Socal da Silva et al., 2004). Compared to an unmodified binder, this response in PMBs indicates reduced thermal susceptibility as it retains elasticity over the corresponding temperature (or frequency) range, resembling a rubbery-state, which is a well-recognized contribution of elastomeric modifiers such as the SBS polymers (Socal da Silva et al., 2004). The phase angle master curve of the UB exhibits no such plateau, whereas the PMB-unaged shows a clear plateau region, indicating the presence of an active polymer network (Lin et al., 2019). With progressive aging, although the PMB-12h aged and PMB-20h aged show a plateau, the width of the plateau diminishes, most notably during the first 12 hours. This narrowing reflects a reduction in temperature/frequency range and can be attributed to the diminishing of the polymer network activity. In the case of RAPb, no plateau region is evident in the phase angle master curve, indicating the absence of polymer activity.

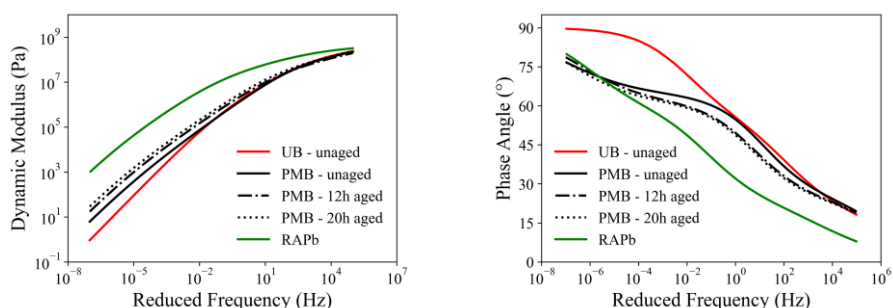


Figure 4: Dynamic modulus (left) and phase angle (right) master curves (Reference temperature 20°C).

5. Summary and Conclusions

This study evaluated polymer-modified binders at various aging stages using Fourier-transform infrared spectroscopy (FTIR), fluorescence microscopy (FM), and rheology. The results showed that 20 hours of RTFO aging of PMBs at 100°C did not reach the extent of aging observed in field RAP binders notwithstanding the fact that the origin and prior history of the RAP binder itself remain uncertain.

Different methods provided differing pictures of whether the aging state of the laboratory-aged PMB matched that of the field-aged RAP binder, underscoring the need to identify the most reliable indicators of polymer effectiveness. FTIR spectra confirmed the presence of SBS polymers in the RAP binder through the characteristic polybutadiene and polystyrene peaks, with a consistent reduction in peak magnitudes observed with the aging of the PMB. FM further verified the presence of polymers in both the PMB and the RAP binder and offered detailed insights into the polymer network structure, and hence on polymer morphology. Parameters such as aspect ratio, equivalent diameter, and particle density allowed quantification of aging effects on the polymer network. Reduction of polymer network activity with aging in the PMB is indicated by a narrowing of the plateau region in its phase-angle master curve, while the RAP binder showed no evidence of polymer network activity. Among the rheological results, the absence of a plateau in the phase-angle master curve emerged as a clear marker of polymer network degradation.

In the subsequent work, the key challenge is to define test methods, or combinations thereof, that best simulate aging and allow meaningful comparison between laboratory-aged PMBs and RAP binders.

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