Chemical and Morphological Evolution of Polymer Networks in Bitumen during Aging: Insights from FTIR and Fluorescence Microscopy

V.T. Thushara[1], Athira Mangalath Shine[2], Sabine Leischner[2], Erik Kamratowsky[2], Thomas Köberle[2], and J. Murali Krishnan[3]

[1] College of Engineering Trivandrum, Kerala, 695016, India
[2] Technische Universität Dresden, Dresden,01069, Germany
[3]Indian Institute of Technology Madras, Chennai, 600 036, India
`thusharavt@cet.ac.in`

Abstract.
Modified binders are evaluated for rutting and fatigue resistance after short and long-term aging. While short-term aged tests such as the Multiple Stress Creep and Recovery (MSCR) test, can indicate polymer network integrity through parameters like percent recovery and Jnr_{diff}, the persistence of these networks after long-term aging remains unclear. This uncertainty is critical when reclaimed asphalt pavement (RAP) contains residual polymer-modified binders. Since conventional rheological tests cannot quantify polymer degradation, advanced techniques are required. In this study, an unmodified binder, three SBS-modified binders (with dosages of 3.5% and 6.5% both produced at the laboratory, and a commercial one), and three RAP binders were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) and Fluorescence Microscopy (FM). FTIR showed butadiene loss with aging and strong oxidation in RAP binders, while FM revealed dispersed domains (PMB-3.5%), crosslinked networks (PMB-6.5%), and degraded remnants in RAP. Together, FTIR and FM confirm the loss of functional polymer networks in RAP, highlighting the need for improved rejuvenation strategies.

Keywords: Polymer Modified Bitumen (PMB), Reclaimed Asphalt Pavement (RAP), Fourier Transform Infrared Spectroscopy (FTIR), Fluorescence microscopy (FM)

1 Introduction

Bitumen is a complex colloidal material whose mechanical responses are strongly influenced by its composition, modification, and aging. Modification of bitumen using Styrene-Butadiene-Styrene (SBS) polymers is widely used to enhance the rheological performance of bitumen, achieved through the formation of networks within the bitumen matrix. These networks are responsible for characteristic rheological features, such as the plateau in the phase angle master curve, which is indicative of a stable polymer connectivity (Silva et al., 2004). However, during service, oxidative aging affects both the bitumen matrix and the polymer network, causing network degradation, phase separation, and chemical transformations, which are reflected in the loss of the plateau region in the phase angle master curve (Lin et al., 2019; Cappello et al., 2021; Kokken et al., 2025). Understanding this evolution is essential for the effective utilization of reclaimed asphalt pavement (RAP), particularly when the RAP binder is known to be SBS-modified. To take advantage of the potential residual activity of the aged SBS polymer, it is crucial to assess its current condition and reactivity. Moreover, understanding how the existing SBS network interacts with the added virgin binder is important for determining whether its effectiveness will be enhanced or diminished.

Though conventional rheological tests provide macroscopic performance indicators, they cannot directly reveal the microstructural and chemical changes underlying these property shifts, such as polymer chain scission, oxidation, and phase separation. Therefore, evaluating the condition and reactivity of aged polymers remains a significant challenge. Advanced characterization methods such as fluorescence microscopy (FM) and Fourier Transform Infrared Spectroscopy (FTIR) can help bridge this gap, with each technique providing insight into a specific aspect. For instance, FM reveals polymer morphology, whereas FTIR detects chemical and oxidation-related changes. FM enables direct visualization of the spatial distribution and morphological evolution of polymers within the bitumen matrix (Sun et al., 2021; Wu et al., 2024), while FTIR provides insights into chemical functional group changes associated with oxidation, polymer degradation, and aging (Nivitha et al., 2015; Primerano et al., 2023).

The present study investigates how polymer networks in bitumen evolve chemically and morphologically during aging, a topic of particular relevance for RAP binders originally containing polymers, as the structural integrity and effectiveness of aged polymer constituents remain uncertain. To address this, two laboratory-produced polymer-modified bitumens (PMBs) with different polymer dosages were examined in the unaged state, while a commercial PMB was evaluated under two aging conditions using Fourier-transform infrared spectroscopy (FTIR) and fluorescence microscopy (FM). Additionally, three binders extracted from reclaimed asphalt materials were analyzed to relate laboratory and field aging. Together, these investigations aim to assess whether the diagnostic capabilities of FTIR and FM can reliably capture the degradation of polymer structures in aged binders, leading to an understanding of RAP containing polymer-modified bitumen.

2 Materials

Three binder sets were evaluated to study the morphological and chemical evolution of polymer networks in bitumen during aging using FM and FTIR. The first set comprised laboratory-produced SBS-modified binders and their base binder (penetration grade 70/100, UB) according to DIN EN 12591 (2009). A linear SBS copolymer (Kraton D1101, 31% styrene) was incorporated into the base bitumen (UB) at two concentrations: 3.5 wt% (designated as PMB-3.5, representing conventional modification) and 6.5 wt% (designated as PMB-6.5, representing highly modified binder). Modification was carried out at 170 °C with high-shear mixing (3,500 rpm, 7 h) after preheating UB at 160 °C for 1 h to enable polymer swelling and network formation. The second set consisted of a commercial SBS-modified binder (25/55-55A, PMB-C) and PMB-C aged for 12 h and 20 h (PMB-C-12h and PMB-C-20h) at 100 °C in the Rolling Thin Film Oven (RTFO), with the lower temperature chosen to simulate oxidative aging (Bonaquist et al., 2021). Rheological parameters T_{BTSV} (temperature at $|G^*|=15$ kPa, 1.59 Hz) and δ_{BTSV} (phase angle) were determined according to TP Bitumen-StB Part 3 (FGSV 720). The third set included binders recovered from three reclaimed asphalt pavement (RAP) sources (RAP1–RAP3), analyzed to assess their degree of polymer modification and polymer network evolution. The T_{BTSV} values (°C) of UB, PMB-3.5, PMB-6.5, PMB-C, PMB-C-12h aged, PMB-C-20h aged, RAP1, RAP2, and RAP3 were 48.8, 56.1, 67.0, 52.9, 56.3, 57.7, 60.3, 71.8, and 77.9, respectively. The T_{BTSV} value indicates that the aging level of the RAP binders follows the order RAP3 > RAP2 > RAP1. It should also be noted that the T_{BTSV} of PMB-6.5 is higher than that of RAP1.

3 Methodology

Fourier-transform infrared spectroscopy (FTIR) was employed to probe chemical functional groups and molecular structural changes in the bitumen samples. FTIR identifies chemical bonds by measuring the absorption of infrared radiation, which occurs when molecular vibrations induce changes in the dipole moment. The resulting spectra display absorbance or transmittance as a function of wavenumber. Characteristic absorption bands, particularly in the fingerprint region (1500–600 cm^{-1}), provide information about specific functional groups and molecular structures for bitumen. FTIR spectroscopy was performed on the binders using a Perkin Elmer FTIR spectrometer using Attenuated Total Reflectance (ATR) mode. The specimen preparation and testing were carried out in accordance with AASHTO T 302-22 (2022). The spectra were acquired in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}, using 32 scans for each measurement. A total of four samples were analyzed, with four replicates per sample. Only prominent bands with sufficient intensity were considered for qualitative analysis [Weigel, 2018].

FM was used to visualize and quantify the polymer network within the bitumen. The polymer components, such as SBS, fluoresce under excitation, allowing their distribution and morphology to be clearly observed within the bitumen matrix. Images were processed into binary form to analyze polymer dispersion, size distribution, and particle shape (circularity and aspect ratio). Comparisons across differently aged samples were carried out to provide insights into the evolution and activity of the polymer network. FM was performed using a Zeiss Axiotech reflected-light microscope equipped with a 50 W mercury (Hg) lamp and an EpiPlan 50×/0.70 HD objective. A small drop of the test material was placed on a glass slide, heated in an oven at 120 °C for one hour to form a thin film, then covered with another glass slide and immediately stored at –20 °C until testing. FM was performed under blue light excitation using a Zeiss S09 filter set, and images were captured with a Canon EOS 250D (ISO 800, 2 s exposure time).

4 Results and Discussion

4.1. FTIR Results

Figure 1 shows the FTIR spectral regions associated with oxidative aging, carbonyl (1700 cm^{-1}) and sulfoxide (1030 cm^{-1}), and SBS polymer, styrene (699 cm^{-1}) and butadiene (966 cm^{-1}), for the different binders. Table 1 presents the corresponding peak areas, with oxidative aging peaks calculated by baseline integration and SBS-related peaks by reference line integration, as described in Kamratowsky et al. (2025). The Aging Index (AI_{FTIR}) is computed as the ratio of the sum of carbonyl and sulfoxide areas to the aliphatic area (Kamratowsky et al., 2025).

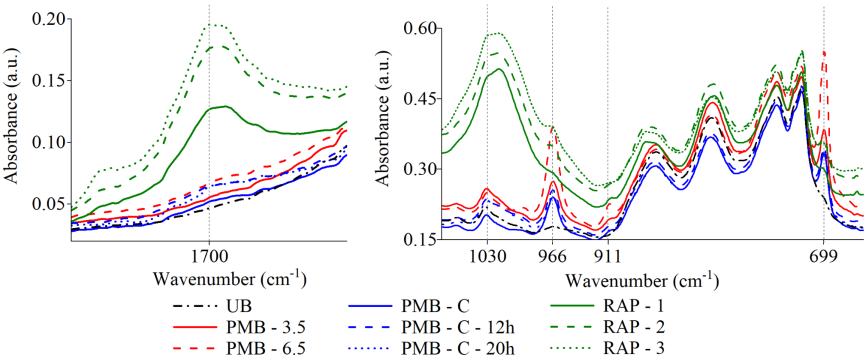


Fig. 1 Representative FTIR spectra of different binders

Table 1. FTIR spectral values

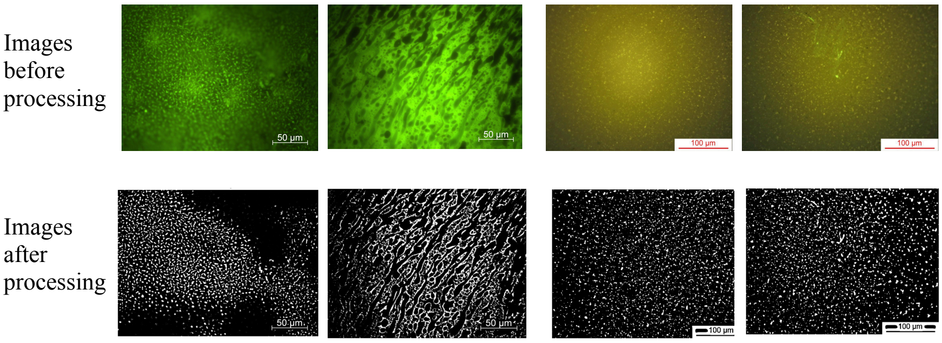
Materials	**Carbonyl Area (-)**	**Sulfoxide Area (-)**	**AI$_{FTIR}$ (-)**	**Styrene Area (-)**	**Butadiene Area (-)**
UB	5.0	17.4	0.33	-	-
PMB-3.5	5.5	20.7	0.36	0.73	1.07
PMB-6.5	6.1	20.1	0.38	1.57	2.38
PMB-C	5.1	16.7	0.33	0.63	1.01
PMB-C-12h	5.6	18.9	0.37	0.63	0.97
PMB-C-20h	5.7	18.6	0.37	0.63	0.95
RAP-1	9.3	39.5	0.65	0.12	0.01
RAP-2	12.2	43.5	0.7	0.26	0.17
RAP-3	13.3	43.7	0.74	0.16	0.18

It can be observed that PMB-6.5 exhibits nearly twice the Butadiene and Styrene peak areas when compared to PMB-3.5. The polymer content of PMB-C is estimated as 3.36%, by comparing it with the polymer contents of PMB-3.5 and PMB-6.5, in accordance with AASHTO T 302-22 (2022). Furthermore, RTFO aging up to 20 h at 100 °C has no effect on the Styrene peak area; however, a slight reduction is observed in the Butadiene peak area. Although significantly lower compared to PMB-3.5 and PMB-C-20h binders, the RAP binders also indicate the presence of polymers. However, FTIR analysis alone cannot confirm how much polymer is present or whether it is still active in RAP binders. The original binder may have been only slightly modified, or the polymer network may have broken down over time. In addition, because RAP binders are highly variable, small extracted samples may not contain any visible traces of polymer.

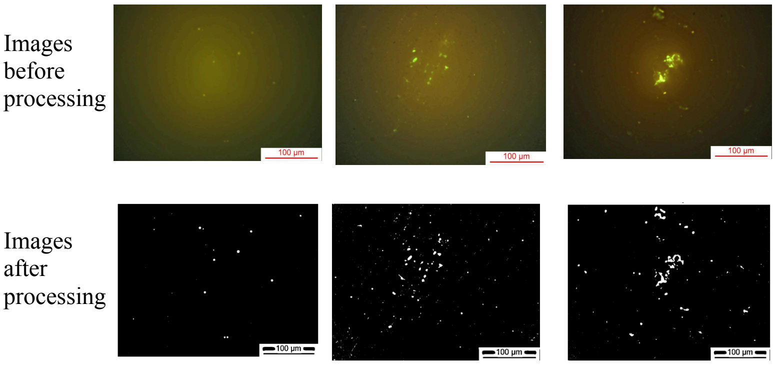
The peak area associated with oxidative aging, the Carbonyl and Sulfoxide peaks, indicate that the aging level of PMB-3.5 and PMB-6.5 is slightly higher than that of their base binder, UB. This can be attributed to the aging that occurred during the modification process. The aging level of PMB-C-20h is lower than that of RAP binders, indicating that a prolonged laboratory aging procedure is required to simulate RAP. The RAP binders can be ranked in terms of aging severity as RAP3 > RAP2 > RAP1, which is also consistent with the stiffness indicated by the T_{BTSV} values.

4.2. FM results

FM images were analyzed to quantify polymer dispersion and its network characteristics. Original and processed FM images for the binders are shown in Fig. 2.



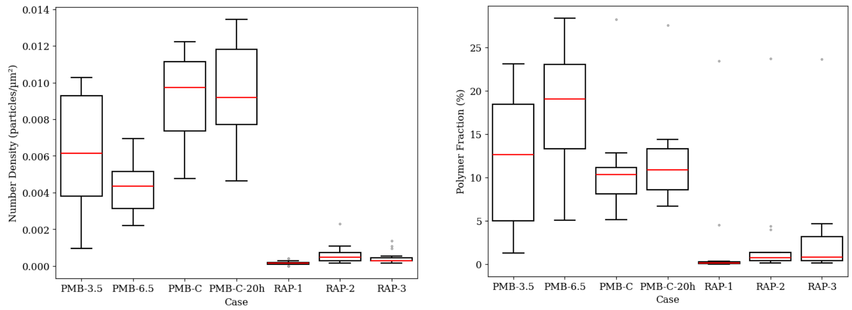
(a) PMB- 3.5 (b) PMB-6.5 (c)PMB-C (d)PMB-C-20h



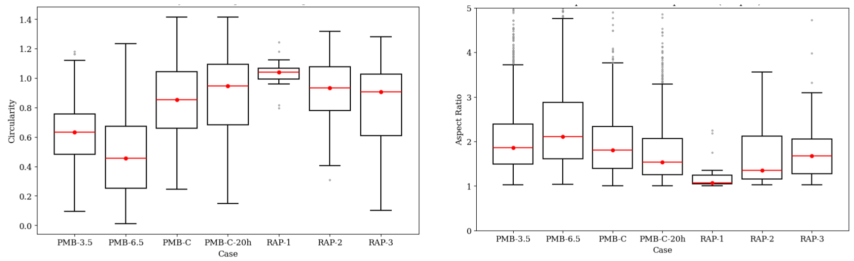
(e) RAP -1 (f) RAP- 2 (g) RAP-3

Fig. 2. FM images: original and processed for all binders

This enabled assessment of variations due to polymer dosage and aging, and comparison with RAP binders. Image analysis was performed in Python using adaptive thresholding and morphological cleaning, followed by the extraction of morphological features, including area, circularity, aspect ratio, equivalent diameter, and Feret diameter. Area measures the total number of pixels contained within a feature, while circularity quantifies how close the shape is to a perfect circle. Aspect ratio is the ratio of the major to minor axis lengths, equivalent diameter represents the diameter of a circle with the same area as the feature, and Feret diameter is the longest distance between any two points along the feature boundary. These descriptors were used to compare binders and evaluate polymer network behavior. FM confirmed the presence of polymer in all RAP binders by detecting characteristic fluorescence emission. However, the evidence indicates that only a small amount of polymer is present in these RAP binders.



(a) Number Density per subimage (b) Polymer Fraction (%)



(c) Circularity (d) Aspect Ratio

Fig. 3. Dispersion and shape characteristics

To quantify the uniformity of dispersion of polymer strands, each FM image was divided into nine subimages, and polymer descriptors such as number density and polymer fraction were extracted for each subimage. Number density is the number of polymer strands detected in each unit micrometer area, and polymer fraction is the percentage coverage of polymer strands in the subimage. The variability across subimages was represented using box plots in Fig. 3a and Fig. 3b. Among the fresh binders, PMB-3.5 showed a higher density of finely dispersed polymer strands, whereas PMB-6.5 exhibited greater polymer coverage, indicative of a more continuous and interconnected network. The commercial PMB exhibited the highest number density, indicating the possibility of better polymer dispersion during commercial production, which can be attributed to the presence of added crosslinkers. Laboratory aging reduced the mean number density in commercial PMB, which can be considered indicative of polymer degradation and network loss. However, more insights can be gained only after subjecting the material to prolonged aging protocols. RAP binders showed a much lower number density and polymer fraction than fresh PMBs, indicating that their polymers might have degraded during service or might have been produced with a low dosage of polymer modification. Among the RAP binders, the polymer fraction ranked RAP1 < RAP2 < RAP3, suggesting RAP3 might have a relatively higher polymer dosage when compared to the other RAP binders.

Shape analysis was performed using circularity and aspect ratio as descriptors for each binder (Fig.3c and Fig.3d). Circularity measures how closely a particle resembles a perfect circle, while aspect ratio describes the degree of elongation. Fresh binders showed a clear trend: circularity decreased with polymer dosage—reflecting more irregular shapes due to network formation—but increased with aging as networks degraded into rounded fragments. RAP binders exhibited nearly circular particles with low aspect ratios, indicating degraded and inactive polymer remnants. The widest spread in aspect ratio values occurred in PMB-6.5%, suggesting phase separation and crosslinked networks, whereas PMB-3.5% and the commercial PMB showed narrower distributions, consistent with dispersed polymer domains. Among RAP binders, higher circularity and lower aspect ratio variability confirm the loss of active network structures, with degradation severity following RAP1 < RAP2 < RAP3, consistent with polymer fraction analysis.

5 Summary and Conclusions

FTIR analysis confirmed that PMB-6.5 had nearly twice the Styrene and Butadiene content of PMB-3.5, while the commercial PMB was closer to PMB-3.5. With RTFO aging, Butadiene decreased slightly, whereas Styrene remained stable. RAP binders exhibited very low polymeric peak areas, making polymer presence difficult to confirm by FTIR alone. Oxidative aging indices (Carbonyl, Sulfoxide) ranked severity as RAP3 > RAP2 > RAP1, consistent with their higher stiffness, as indicated by their T_{BTSV} values. FM revealed clear morphological differences: PMB-3.5 contained dispersed polymer domains, PMB-6.5 formed a crosslinked network, and the commercial PMB showed more polymeric dispersion. Aging reduced polymer number density and connectivity, while RAP binders exhibited very low polymer fraction and nearly circular particles, confirming more degradation of polymer networks and polymer agglomeration. Based on dispersion and shape descriptors, RAP polymer activity and presence ranked RAP1 < RAP2 < RAP3. Together, FM and FTIR provide complementary insights: FTIR quantifies polymer content and the degree of aging in binders, but cannot capture degraded polymers in RAP, whereas FM directly visualizes polymer morphology and network loss.

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