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Insights into Polymerization-induced Phase Separation of Epoxy-Bitumen Systems and Strategies to Tailor High-Performance Bituminous Materials

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INTRODUCTION

The utilization of epoxy-based polymers as bituminous modifiers in developing durable and long-lasting pavement structures have gained increasing interest over the last years showing evidence of high performing materials (1-8). It has been noticed that the addition of epoxy-based modifier into bitumen lead to materials with superior characteristics against oxidative aging (1, 3, 8). Next to aging resistance, the incorporation of epoxy modifiers in bituminous materials has added functional benefits, such as improved resistance to moisture damage and fatigue cracking (5, 6). Despite the evidence of aging resistance in epoxy-asphalt concrete mixes, the influence of the epoxy-based polymers on the bitumen aging and the microstructure morphology of newly formed systems have not been fundamentally evaluated yet. Within the scope of this research, the aging susceptibility of epoxy modified bitumen has been investigated. The extent of aging has been probed by using a Fourier Transform Infrared spectrometer and also rheologically evaluated using a dynamic shear rheometer. Furthermore, an improved compatibility between epoxy and bitumen at the microstructural level defines the long-term chemo-mechanical performance of EB systems in a controlled manner. Thus, another aspect of this study was to investigate the morphological and interfacial characteristics of EB microstructure.

IMPLEMENTATION OF EPOXY MODIFICATION FOR IMPROVING AGING RESISTANCE

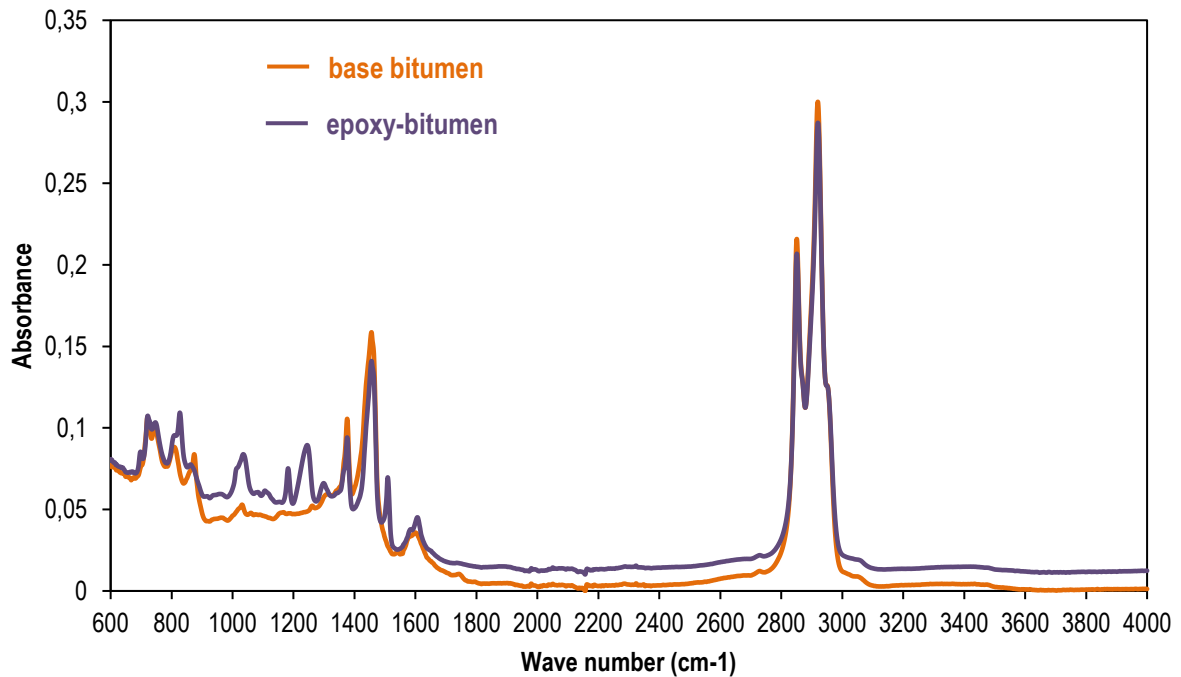
Materials and Preparation

The studied epoxy modifier was formulated by two liquid components; (i) the epoxy monomer and (ii) the hardener. In general, this modifier is an epoxide system in which the epoxide rings can open up when certain energy conditions are available and react with each other forming crosslinks (9, 10). Herein, the epoxy monomer consist of three elements; bisphenol-A-(epichlorhydrin) epoxy resin ($M_w = 700 \text{ g mol}^{-1}$), bisphenol-F-epichlorhydrin-Harze ($M_w < 700 \text{ g mol}^{-1}$) and benzyl alcohol, which used as solvent. Moreover, the same solvent was used in the mix of amine-type agents forming the hardener. A 70/100 pen bitumen (paraffinic) was epoxy modified forming the studied systems and the following preparation process was taken place. The two components of modifier were oven-heated for 1 hr at 70°C, and then stirred together for approximately 1 minute. The epoxy modifier was produced ready to be diluted with the already pre-heated bitumen at 150°C. Two different dilution ratios by mass (1:17 – EB17 and 1:24 – EB24) were studied. All samples were placed in a refrigerator at -10°C to prevent any further reaction.

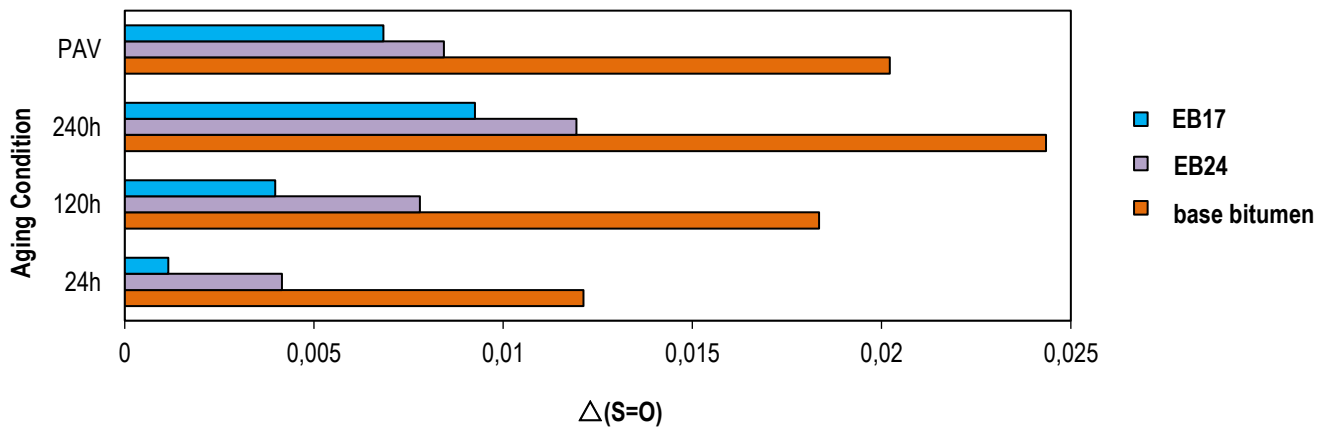
Aging Performance

The age hardening of studied binders was performed in an oven under free-atmospheric air pressure over 24, 120 and 240 hrs at 130°C. Also, materials of 3-mm film thickness were aged on pressure-aging vessel (PAV) pans 140-mm in diameter and hardened for 20 hrs at 2.1-MPa pressure, and at 100°C temperature. After aging, a Perkin–Elmer Spectrum Fourier Transform Infrared (FT-IR) spectrometer equipped with an Attenuated Total Reflectance (ATR) fixture was used to measure the incremental sulfoxide $\Delta(\text{S=O})$ indices, which are normally used with carbonyl $\Delta(\text{C=O})$ (11-13) to evaluate the aging extent of the studied systems. As noticed from a previous research (8), carbonyl groups, such as carbonyl acid, carbonyl ether and ester, play important role in polymerization phenomena of EBs, they were not taken into account in the study. The amounts of sulfoxide compounds were calculated using the area method. By definition, the incremental value of $\Delta(\text{S=O})$ was obtained by subtracting the sulfoxide index at time $t > 5$ hrs $[(\text{S=O})_t]$ from the same index at 5 hrs $[(\text{S=O})_{5h}]$. The absorbance of base and modified bitumen is shown in **Fig. A(a)**. It can be

observed that, comparing with base bitumen, the new binder has three new functional groups appeared in the wavenumber range within 1170 and 1290 cm^{-1} .



(a)



(b)

FIGURE A FTIR test results; (a) representative graph, (b) incremental sulfoxide $\Delta(\text{S}=\text{O})$ index after oven- and PAV-aging

Fig. A(b) demonstrates that the sulfoxide content as a function of oven-aging time at 130°C for base bitumen, EB24, and EB17, showing increase of sulfoxides over time. $\Delta(\text{S}=\text{O})$ index increases with increasing the aging time but decreases with increasing the amount of epoxy diluted in bitumen. The results show similar tendency for all samples with less aging when epoxy is added, especially at the highest dilution ratio. The reacting modifier can reduce the amount of oxygen reacted sulphur compounds in bitumen and generates a durable material against the aggressive environmental conditions. Taking into account that sulfur is more reactive than carbon in bitumen (13), or sulfoxides are formed earlier than carbonyls, the current results shows that the proposed modifier is able to block the most oxygen-sensitive compounds of bitumen. Along the oven-aging studies, the long-term aging performance of

studied systems seems promising as well when they were PAV-aged depicting similar aging extent as the oven-aging for 120 hrs.

FUTURE WORK

In this research, the epoxy modifier was added in bitumen to develop a binder with improved anti-aging characteristics. The newly formed systems were aged and the results demonstrated that the extent of sulfoxide index over time showing that modifier can prevent sulphur to react with oxygen. Further studies should include relationship of in-lab- with in-field-aged materials and how these systems perform under various cycles of aging simulating their reusability after the end of their life. Another purpose of this study was to evaluate the microstructural characteristics generated through polymerization of reactive epoxy in bitumen. The assessment of microstructure morphologies of EB systems was carried out and suggestions toward enhancement of synergy between thermoset and thermoplastic incorporated phases were discussed.

Author Contribution Statement

The authors confirm contribution to the paper as follows: study conception and design: P. Apostolidis; data collection: P. Apostolidis, S. Nahar; analysis and interpretation of results: P. Apostolidis, S. Nahar, X. Liu, B.-J. Lommerts, S. Erkens, A. Scarpas; draft manuscript preparation: P. Apostolidis, S. Nahar. All authors reviewed the results and approved the final version of the manuscript.

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