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Chemical and Oxidative Controlled Hardening of Epoxy-Modified Bitumen

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INTRODUCTION

The addition of epoxy modifier in bitumen is a relatively new modification technology (*1-4*) and the most critical epoxy polymerization-induced changes of the epoxy-bituminous materials are not fully understood. Different phenomena take place when epoxy modifiers are incorporated into bitumen and they are dependent on the material hardening conditions. Temperature is one of the most crucial parameters that influences to the development of physical, chemical and mechanical characteristics at the early life (curing or chemical hardening - CH) (*5-7*) and long-term service (oxidative hardening - OH) (*4*) of epoxy-modified binders. For this reason, in-depth exploration of epoxy chemistry in bitumen is needed to understand the evolution of the properties of these binders in time.

Within this framework, the chemical compounds and their reaction products generated under various conditions were studied to reveal the time dependency of molecular microstructures of modified binders. Special attention was given to the evaluation of physiochemical characteristics and the mechanical properties of epoxy-bituminous binders, concluding that the degree of CH and OH was dependent on the level of epoxy modification in bitumen. It was observed that the sulfoxide compounds are the most representative index for assessing the age hardening of epoxy-modified bitumens. Finally, the enhanced resistance against environmental aging in combination with the superior mechanical characteristics (i.e., higher tensile strength, flexibility and enhanced longevity) when the epoxy modification is implemented in bitumen promises a very effective technology for developing long-lasting pavement materials.

METHODOLOGY

The epoxy modifier is formulated from two liquid parts free from solvents; (i) the part A (epoxy resin formed from epichlorhydrin and bisphenol-A) and (ii) part B (fatty acid hardening agent in 70 pen bitumen). When part A and B are mixed into bitumen, the dispersion of the modifier phase inside the bitumen is achieved. All the samples were prepared by mixing part A and B at weight ratio of 20:80, according to the supplier. The epoxy modifier (i.e., Part A and B) was diluted with the unaged 70-100 pengrade bitumen with weight ratio of 20:80 (EB20) and 50:50 (EB50) of epoxy and bitumen, respectively.

The hardening of epoxy modified bitumens (EBs) was simulated in oven under atmospheric pressure over various lengths of time. The same materials were aged in a pressure-aging vessel (PAV) at 2.1-MPa pressure with oxygen (AASHTO MP1). PAV aging time for 100^{o}C was 20 hrs. After each hardening period, the physiochemical and mechanical properties were measured as function of time through Fourier Transform Infrared (FTIR) spectroscopy, modulated dynamic scanning calorimetry (MDSC) and dynamic shear rheometer (DSR).

Chemical and Physical Characteristics during Hardening

The chemical properties of the hardened EBs were determined with a FT-IR spectrometer. The FT-IR spectrometer was used to investigate the change of the molecular structure of the binders after each hardening time. Besides the chemical changes in bitumens under various conditions, the materials also undergo microstructural transformations. A parameter that describes these temperature-related transformations is the glass transition temperature (T_g). Bitumens show glassy behavior below T_g, the rubbery characteristics could be shown above T_g. In this study, the phase transition temperature T_g of EBs was measured by MDSC.

Mechanical Characteristics during Hardening

Isothermal frequency sweep measurements were performed using a DSR at different temperatures that ranged from -10 to 60^{o}C at temperature steps of 10^{o}C. The parallel plate testing geometry was used as well to evaluate the viscoelastic properties of the different binders after different hardening periods. The properties were measured at frequencies of 0.1-10 Hz. The samples of base binder were treated in the same way and master curves were constructed.

Performance under Monotonic and Cyclic Loading

The uniaxial tensile strength of these binders was determined after complete chemical reaction was evaluated under controlled isothermal temperature conditions at 0°C. Moreover, the long-term performance of EBs is assessed via a shear fatigue test, since the ultimate scope of incorporating the epoxy modifier was to increase the longevity of bituminous materials. DSR time sweep tests at a constant temperature of 0^oC and a frequency of 10 Hz were performed at three different shear stress levels. At each stress level, three fatigue tests were done for each modification. A decrease of the shear modulus to 50% of its initial value was used as criteria to determine the load repetitions till failure.

FINDINGS

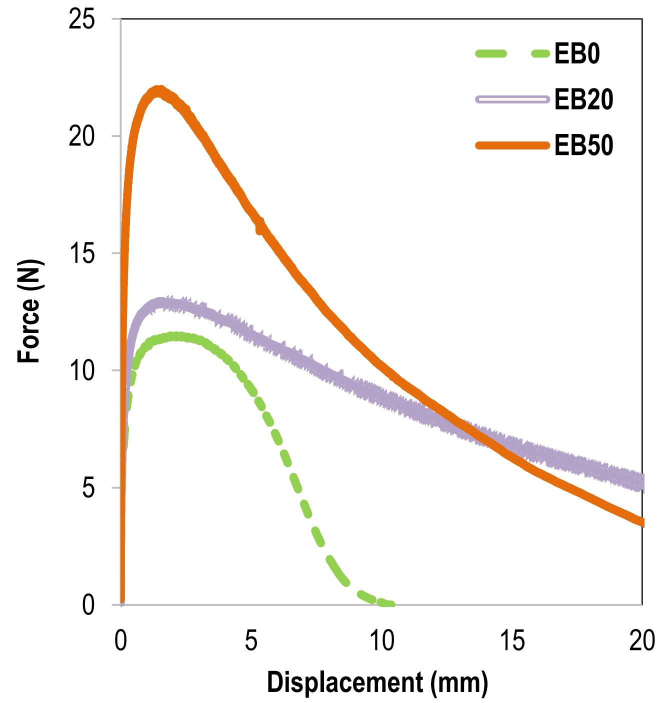
Oxidative controlled Hardening

In general, the mechanical properties of EBs are linked to specific changes in their chemical structure. Thus, the initiation of aging was identified by measuring the carbonyl and sulfoxide components. These compounds increase as hardening time increases and the results gave a similar tendency for all samples with a lower hardening effect for the modified binders. Therefore, it seems that the modified binders are more resistant against aging with EB50 showing the lowest OH sensitivity. EB50 shows a lower sulfoxide index than the base bitumen (EB0). The carbonyl and sulfoxide compounds of EB0 increase more rapidly than EB20 and EB50, and as consequence, higher epoxy modification levels provide lower aging indices. In addition to oven-hardening simulations, the long-term performance of EBs after the PAV test seems promising as well when the sulfoxide index is used.

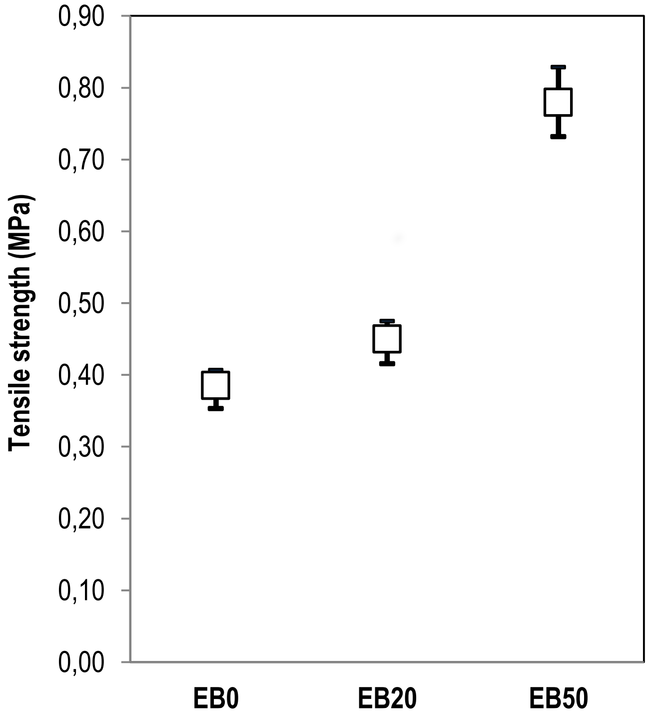
Additionally, the *Tg* increases over time during CH showing that the bitumen almost does not participate and the epoxy-asphaltene interaction is limited in CH. It is assumed that bitumen reduces the contact opportunities between unreacted parts of modifier still available in the matrix and hence EBs release less heat. In other words, bitumen inhibited the polymerization reactions between the two epoxy parts leading to reduction of maltenes mobility and subsequently to T_g increase.

Mechanical Performance of CH Hardened Binders

The tensile strength of the samples depends on the extent of the hardening reaction, the ratio of the unlinked molecules to crosslinked molecules and the internal chemical structures. The modified binders experienced ductile behavior, and thus exhibited higher flexibility than the base bitumen (see **Figure-a**). Modifier enhances greater toughness in the bituminous system forming materials of high tensile failure resistance (i.e., high tensile strength), and this strength increased with the content of modifier into the bitumen (see **Figure-b**). Finally, the fully hardened samples were exposed to cyclic loading at three different shear stress levels in the DSR to assess the fatigue properties of these newly developed binders. The fatigue life at all three stress levels is higher for the EB20 and EB50 than for the unmodified bitumen.



(a)



(b)

FIGURE Monotonic tensile test results : (a) representative tensile force versus displacement curves and (b) tensile strength of fully chemically hardened binders at temperature of 0^{o}C and 0.05 mm/s of displacement rate

CONCLUSIONS

In this paper, epoxy polymerization-induced physiochemical phenomena have been related to the mechanical properties, and two corollaries to the chemical analysis were made helping to understand the behaviour of EBs. Firstly, the increase and the decrease of certain carbonyl compounds (increase of carbonyl ether and ester, decrease of carbonyl acid) at the beginning of hardening indicate that the esterification and etherification (CH) are taking place due to the reaction of hardener with the epoxy resin. Second, the inconsistency of carbonyls for the short and long time intervals in the oven- and PAV-hardening leads to the conclusion of CH termination and the OH initiation, respectively. The sulfoxide index is proposed to be an efficient indicator for evaluating the aging extent of epoxy modified binders. With regards the mechanical performance of EBs, the complex modulus of EBs is similar to base bitumen, and EBs provide higher tensile strength, flexibility and enhanced fatigue performance.

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Author Contribution Statement
The authors confirm contribution to the paper as follows: study conception and design: P. Apostolidis, A. Scarpas; data collection: P. Apostolidis, M. Zhang; analysis and interpretation of results: P. Apostolidis, X. Liu, M.F.C. van de Ven, S. Erkens, A. Scarpas; draft manuscript preparation: P. Apostolidis. All authors reviewed the results and approved the final version of the manuscript.

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