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Evaluation of Epoxy Modification in Bitumen

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Abstract: In epoxy-bitumen systems, temperature contributes to the development of physiochemical and mechanical characteristics during curing (chemical hardening) and at the long-term service (oxidative aging) of pavement structures. Hardening (i.e., chemical or oxidative controlled) is a complex phenomenon in epoxy-modified binders and the in-depth exploration of incorporating epoxy chemistry in bitumen is needed to understand the evolution of the properties of these binders in time. Within this framework, changes in two different diluted epoxy-modified binders after oven-hardening for various time scales were analysed by means of Fourier transform infrared spectroscopy, modulated dynamic scanning calorimetry and dynamic shear rheometry. The chemical, thermal and mechanical properties of hardened binders were compared showing remarkable differences in their response under various conditions. The degree of aging was dependent on the level of epoxy modification in bitumen. It was found that the sulfoxide compounds are the most representative index for assessing the oxidative-controlled hardening of epoxy-modified bitumens. The phase angle gives useful information for assessing the long-term aging of modified binders demonstrating a linear relationship between the phase angle and sulfoxide index changes with respect to oxidative hardening. The improved performance (i.e., higher tensile strength, flexibility and enhanced longevity) of newly modified binders was demonstrated as well. Overall, the enhanced resistance against aging in combination with the superior mechanical characteristics when the epoxy modification is implemented in bitumen promises a very effective technology for developing long-lasting pavement materials.

INTRODUCTION

Studies of bitumen modification technologies have been undertaken in the past and predominantly thermoplastic polymers (i.e., block polyolefins co-polymers) are nowadays extensively used as modifiers to enhance the material durability both at low and high temperatures (1-4). Nevertheless, the exploration of new modification approaches has been at the forefront of pavement engineering research efforts due to the increasing demand on developing pavement materials with improved long-lasting characteristics.

The use of epoxy modifiers has attracted the attention of the pavement scientists and practitioners (5-10). Initially, the epoxy modifiers were utilized to minimize the permanent deformation of bituminous materials because the thermoset nature of epoxies guarantees excellent rut resistance (5). It was also suggested that use of polymeric structure of epoxy in the bituminous matrix can enhance the resistance against aging of bitumen (10). However, despite experience of practitioners on implementing epoxy modifiers in bituminous materials, a general lack of knowledge still exists about the impact of these modifiers on the physiochemical characteristics and the long-term performance of bitumen. Properties, such as tensile strength or glass transition temperature, have been evaluated in the past (11-18) but with limited studies of chemistry-related hardening phenomena, such as curing (i.e., chemical-controlled hardening - CH) or aging (i.e., oxidative-controlled hardening -OH).

The addition of epoxy modifier in bituminous binders is a relatively new modification technology and the crucial epoxy polymerization-induced changes of the epoxy-bituminous materials are not fully understood. Different phenomena take place when different amounts of epoxy are incorporated into bitumen and they are dependent on the material hardening conditions (20, 21). The concentration of epoxy resinous part in bitumen controls the microstructural characteristics of modified blends and might influence the longevity of these materials. In this paper, the chemical compounds and their reaction products generated under various hardening conditions were studied to reveal the time dependency of molecular microstructures of modified bitumen. Special attention was given to the evaluation of physiochemical characteristics and the mechanical properties of epoxy bituminous binders. Overall, the studies reported in this paper focused on establishing a testing framework specially designed for epoxy-bitumens by linking the chemistry-related phenomena with their mechanical performance.

MATERIALS AND PREPARATION

The epoxy-based modifier is a commercial product supplied by ChemCo Systems, USA and named epoxy asphalt. This 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 (blend of fatty acid hardening agent and 70 pen bitumen). When part A and B (both reacting systems) are mixed into bitumen as modifying elements, the dispersion of the modifier phase inside the bitumen is achieved. In reality, the monomers of part B react with the epoxide groups of part A to produce covalent bonds in bitumen and the molecular chains are crosslinked through the polymerization process.

In this study, all the samples were prepared by mixing part A and B at weight ratio of 20:80, according to the supplier. Unless otherwise stated the two components, part A and B, were oven-heated separately for 1 hour, to 85°C and 110°C, respectively. After that one hour, they were mixed together for approximately 10 to 20 seconds and this epoxy modifier was mixed further with an already pre-heated unaged 70-100 pengrade bitumen at 120°C, on the basis of the supplier's recommendations. Two epoxy modification levels of bitumen were studied; by adding 20 and 50 %wt. of modifier with replacing equivalent amount of bitumen. In other words, two epoxy-modified bituminous binders were formed with weight ratio of 20:80 (EB20) and 50:50 (EB50) of epoxy and bitumen, respectively. The study of these two

modification levels is linked also with an effort to generate economically feasible and long-lasting paving materials since the initial price of supplied system, named epoxy modifier, is high. Finally, all the prepared samples were placed in a refrigerator at -10°C to prevent any further reaction.

The hardening of the binders was simulated in a draft oven under atmospheric pressure over various lengths of time. At a temperature of 130°C and at 1.0-kPa hardening times of 0, 2, 5, 8, 24, 120, 240 and 480 hrs, were compared. The same materials were aged in a pressure-aging vessel (PAV) on pans with 140-mm in diameter and 3-mm film thickness at 2.1-MPa pressure with oxygen (AASHTO MP1). PAV aging time for 100°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). The testing methods used for this research are presented in the following sub-sections.

EXPERIMENTAL METHODS

Chemical and Physical Characteristics during Hardening

The chemical properties of the hardened epoxy modified bitumens (EBs) were determined with a Perkin–Elmer Spectrum FT-IR spectrometer equipped with an Attenuated Total Reflectance (ATR) fixture. The hardening of materials was analysed after the time intervals used. The FTIR spectrometer was used to investigate the change of the molecular structure of the binders after each hardening time and to provide information about CH and OH of EBs. The FT-IR spectra with wavenumber from $4,000$ to 600 cm^{-1} were recorded and collected for all the samples. A certain amount of material was placed directly on the ATR crystal pedestal and pressed with a constant force to ensure proper contact to the surface. A minimum of three sub-samples were investigated for each sample and 20 scans per sub-sample were performed with a fixed instrument resolution of 4 cm^{-1} (22, 23). **Fig. 1(a)** shows the FT-IR spectra of base (EB0) and epoxy modified bitumen (EB50) recorded after 480 hrs at 130°C .

For OH of bitumen, the carbonyl ($1753\text{--}1660\text{ cm}^{-1}$) and sulfoxide index ($1047\text{--}995\text{ cm}^{-1}$) are normally used to follow the aging in bitumen (24, 25). Their values were calculated by using the area method representing the extent of age. The calculation is performed by dividing the area under a specific location of the spectrum by the sum of other specific areas. However, carbonyl groups ($\text{C}=\text{O}$) play an important role in the CH hardening of EBs as well. During CH, oxirane groups ($\text{C}_2\text{H}_4\text{O}$) (at 917 cm^{-1}) react with the carbonyl acid group (RCOOH) (at 1709 cm^{-1}) resulting into ester (RCOOR'') (at 1735 cm^{-1}) and ether (ROR') (at 1040 cm^{-1}). The potential contribution of methylene (H_2C) (3050 cm^{-1}) is not considered in these cases. Fundamental analysis was performed using the absorbance intensity method of peak difference (**Fig. 1(b)**) after the CH and OH hardening times.

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 . Previous studies have shown a range of T_g values for epoxy-bitumens from -8 to 50°C (11–16), with neat binders to show a range between -40 to 0°C (19).

In this study, in addition to chemical evaluation of involving compounds through CH, also the phase transition temperature T_g of EBs was measured by MDSC under a nitrogen atmosphere with $40^{\circ}\text{C}/\text{min}$ heating rate from -50 to 200°C . When the temperature of 200°C was reached the samples were kept at this temperature for 2 min. MDSC is a thermal analysis technique to determine the temperature and the heat flow associated with material transitions as function of temperature and time. After the preparation and hardening of samples, they

were sealed in aluminum pans, and the CH behaviour was assessed by non-isothermal experiments. The peak and mid-point of the heat flow shift denotes the T_g of materials. At least two measurements were performed in each sample. Samples were hardening at different hardening times from 0 to 180 min of 60 min time step. The MDSC curves of the studied EBs during the heating processes are shown in **Fig. 2**, where T_g was characterised as the temperature at which the first slope alteration took place, which coincides to an endothermic peak in the first derivative plots.

Mechanical Characteristics during Hardening

To investigate the evolution of mechanical characteristics during curing (i.e., CH), the complex modulus at 10 Hz was measured for a time window between 0 to 180 min at the chosen hardening temperature of 130°C under isothermal conditions. DSR measurements were performed using the parallel plate test configuration with disposable plates of 25-mm diameter, and 1-mm sample thickness.

Additionally, viscoelastic characteristics, such as complex modulus and phase angle, were used as reliable indicators for describing the aging behaviour (i.e., OH) of crosslinked epoxy within the bitumen. Isothermal frequency sweep measurements were performed using a dynamic shear rheometer (DSR, Anton Paar, EC Twist 502) at different temperatures that ranged from -10 to 60°C. The parallel plate testing geometry was used as well to evaluate the viscoelastic properties of the different binders after different hardening periods. Plates of 8-mm diameter with a 2-mm gap were used at temperatures below of 20°C, while at temperature above 30°C plates of 25-mm diameter with a 1-mm sample gap were used. The properties were measured at frequencies of 0.1-10 Hz at temperature steps of 10°C from -10 to 60°C. Sample was placed onto the bottom plate at the desired test temperature ($\pm 0.1^\circ\text{C}$). The samples of base binder were treated in the same way and master curves were constructed. For the master curves, the time-temperature superposition model was used to shift all temperatures to a reference temperature of 30°C.

Performance under Monotonic and Cyclic Loading

The tensile strength has been investigated in the past showing various strength values from 1.25 to 9.90 MPa at standard test conditions (11, 13-18). In this paper, after curing, the strength of these binders was determined under controlled isothermal temperature conditions at 0°C. The samples were prepared, poured into a Teflon mould, and taken out of the storage container any excess material was trimmed off and fixed with clamps in the DSR. The cylindrical sample (height 10-mm, diameter 6-mm) was loaded in tension with a displacement speed of 0.05 mm/s. The tensile strength was calculated on the base of the sample geometric configuration and the calculated value can be used to compare the results of different modifications with bitumen.

Finally, the DSR was used to assess the long-term performance of epoxy binders via a shear fatigue test, since the ultimate scope of incorporating this type of modifier is to increase the longevity of bituminous materials. The DSR testing geometry of 8-mm diameter was used with 2-mm gap and time sweep tests at a constant temperature of 0°C and a frequency of 10 Hz were performed at three different shear stress levels (i.e., 0.4, 0.5 and 0.6 MPa). 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.

RESULTS AND DISCUSSION

Oxidative controlled Hardening

In general, the properties of EBs are linked to specific changes in their chemical structure. Initially, the transition borders from CH to OH phenomena, and the initiation of aging, were identified by measuring the carbonyl and sulfoxide components.

Fig. 3(a) shows the carbonyl content calculated with area method as a function of oven-hardening time at 130°C for the studied binders. Along with the carbonyl content, the change of sulfoxide due to age hardening was evaluated with the same method as well, and the results depicting the relationship of sulfoxide over different times for EB0, EB20 and EB50 are shown in **Fig. 3(b)**. At high time lengths, both sulfoxide and carbonyls can indicate OH. 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, see **Fig. 3(b)**. 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. According to the PAV results, despite the inconsistencies of carbonyls generated from oven and PAV hardening (**Fig. 3(a)**), the sulfoxide compounds are equivalent to oven hardening at 130°C for 480 hrs (**Fig. 3(b)**). The patterns generated from the two methods demonstrate that the sulfoxide index gives an effective way to describe the OH in EBs.

The viscoelasticity behaviour is determined by exploring the frequency-dependent material properties (i.e., complex shear modulus and phase angle) of the binders. Due to the fact that EBs consist of a wide range of temperature-dependent molecular structures with various polarities, the viscoelasticity of these binders is related completely on the interactions between the different structures and their chemistry.

Fig. 4 shows the complex modulus master curves for the binders after oven hardening at 130°C. These curves demonstrated the influence of OH on the viscoelastic behaviour of the different EBs. It can be observed that the complex modulus increases slowly over the first 24 hrs of hardening, in which the network formation has been formed and the material hardens due to curing, and then increases substantially as time increases up to 480 hrs. At relatively low frequencies, the complex modulus increases continuously at all time lengths. The modulus tends to merge together to the same value at higher frequencies for both EB20 and EB50. The performance is clearly dominated by the inclusion of epoxy modifier into the bitumen. The slight difference between the modulus at EB20 and EB50 is due to that fact that epoxy molecules need more time to link with each other at low modification levels.

The phase angle master curves are not as straight forward as the complex modulus mastercurves and the epoxy modifications in the bitumen showed considerable reductions in phase angle. The phase angle is measured of the time lag between an applied stress and the resulting strain and indicates whether a binder will behave as elastic-, visco-elastic or viscous-dominated material. When the phase angle is low, the material is more elastic. For EB20 and EB50, it can be seen that the modulus is higher at longer hardening times but the slope of the phase angle of EB50 is different than of EB20. From the results it can be seen also that the modifier had insignificant effects on the phase angle at relatively low frequencies. The presence of phase angle plateaus at intermediate frequencies for EBs indicates the epoxy molecular networks in binders. The modifier enhanced the elasticity of bituminous material. The material behaves more glassy when the hardening process has been

completed, due to the dominance of modifier in EB50. Measurements of phase angle are more sensitive to chemical changes and thus the modification of bitumen than modulus.

The above findings have suggested that it could be interesting to link the evolution of viscoelastic properties to the chemical characteristics of the binders during OH. **Fig. 5(a)** and **Fig. 5(b)** show the relationship between the sulfoxide index and the changes in complex modulus and phase angle at 10 Hz, respectively, indicating a linear relationship for all binders over the OH extent. This performance indicates that the sulfoxide formation tends to correlate with increased modulus and reduced phase angle as the binders harden. In addition to this observation, the viscoelastic response of binders subjected to PAV hardening provided almost identical hardening with the oven hardening for 480hrs, with the EB50 and EB0 showing the highest modulus and lowest phase angle, respectively. Finally, since the level of OH is of primary concern when comparing hardened binders, it is reasonable to conclude that addition of epoxy modifier generates more resistant binders against oxidative aging. However, the lower the phase angle at the same stiffness, probably the more susceptible a binder becomes to monotonic and cyclic fracture. For this reason, the tensile strength characteristics and the fatigue life of studied binders were assessed as well, and the results are given in a later subsection.

Chemical controlled Hardening

According to the previous observation (see **Fig. 2(a)**), the initial fluctuation of carbonyl indices at the beginning of hardening (from 0 to 8 hrs) may be related with the possible contribution of these compounds to CH. For this reason, the time between 0 to 8 hrs is assumed to be the time window for CH.

Fig. 6(a) demonstrates that the intensity of oxirane reduces with prolonged hardening time for both EBs tending to converge as time increases. The epoxide rings (C_2H_4O) are opening through the consumption of oxirane and new compounds are formed. The hardener is considered to be an acid-type since the carbonyl acid group decreased over time similarly with the oxirane group. This performance indicates that the carbonyl acid and oxirane precursors (the reactive groups) were consumed almost completely after approximately 5 hrs at $130^\circ C$. Ester ($RCOOR'$) and ether (ROR') compounds increase initially while remaining constant after a time period indicating that esterification and etherification reactions take place during the CH. Therefore, it is assumed that oxirane and carbonyl acid groups reacted together to create the crosslinked network into the bituminous phase and formed the ester and ether groups (**Fig. 6(b)**). Moreover, the level of epoxy modification affects the CH accelerating the reactions when higher epoxy amounts were used. The network of epoxy modifier (as resulted from the polymerization of epoxy resin in part A of modifier with the assistance of hydroxyl functionalities of hardener in part B) is formed slightly faster when higher modification levels are applied, mainly because there is less bitumen available to prevent the network evolution. Moreover, it can be seen that longer hardening times produces a higher curing increment. This can be seen from the steeper curve shape at the higher modification level (EB50) than at a lower (EB20).

FTIR spectrometer, MDSC and DSR analyses were conducted to explore the increase of T_g and modulus of crosslinking epoxy binders within the CH window. As shown in **Fig. 7**, the presence of the epoxy modifier in the bitumen causes an increase of modulus and T_g whereas longer hardening times also increase both parameters. On the one hand, the increase of mechanical and physical parameters as depicted in **Fig. 7** is related to the increase of crosslinking density until a point that represents the ultimate value corresponding to the completion of CH. Also, these results show that both material parameters are very sensitive to small changes in the microstructure of bitumen at a constant (high) temperature, and consequently of the crosslinking network of the reacting modifier.

On the other hand and from the molecular viewpoint, bitumen consists of a plethora of molecules classified into asphaltene and maltene fractions. Asphaltenes (polar compounds) are dissolved into the maltenes medium of various in terms of polarity compounds. In addition to the fact that at very low temperatures, the T_g of bitumen correlates mainly to the non-polar compounds of maltene medium (T_g) (26), the polar epoxy chains-asphaltene interactions could result increase of mobility of non-polar moieties leading to T_g decrease. However, from **Fig. 7**, the T_g 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. In general, differences in polymer crosslinking structures in fully hardened modified binders are related also to the polarization and orientation of reacted molecules and the reaction pathways.

Mechanical Performance of CH Hardened Binders

The tensile characteristics of fully chemically hardened samples (i.e., at 130°C after 5 hrs) under monotonic direct tensile load was examined as well. In general, 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 characteristics than the base bitumen (**Fig. 8(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 (**Fig. 8(b)**).

Finally, the fully hardened samples (i.e., at 130°C after 5 hrs) were exposed to cyclic loading at three different shear stress levels in the DSR to assess the fatigue properties of these newly developed binders. As shown in **Fig. 9**, the fatigue life at all three stress levels is higher for the epoxy modified binders than for the unmodified bitumen (EB0). The difference at lower stress levels is huge. In conclusion, not only the toughness of the modified bituminous also improved the fatigue performance. Combination of these properties with low temperature behaviour can strongly increase cracking resistance at all temperatures.

SUMMARY AND 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 (i.e., the first 5 hrs) indicate that the esterification and etherification (CH) are taking place due to the reaction of hardener (part B of modifier) with the epoxy resin (part A of modifier). Second, the inconsistency of carbonyls for the short and long time intervals in the oven- and PAV-hardening leads to the conclusion of termination of chemical and the initiation of age hardening after 5 hrs, 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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REFERENCES

1. Ait-Kadi, A., H. Brahimi, M. Bousmina. Polymer Blends for Enhanced Asphalt Binders. *Polymer Engineering and Science* 36, 1996, pp. 1724-33.
2. Lu, X., U. Isacsson. Chemical and Rheological Characteristics of Styrene-Butadiene-Styrene Polymer-Modified Bitumens. In *Transportation Research Record, No. 1661*, National Research Council, Washington, D.C., 1999, pp. 83-92.
3. Fawcett, A.H., T. McNally. Blends of Bitumen with Polymers having a Styrene Component. *Polymer Engineering and Science* 41, 2001, pp. 1251-64.
4. Airey, G.D. Styrene-butadiene-styrene Polymer Modification of Road Bitumens. *Journal Material Science* 39(3), 2004, pp. 951-959.
5. Simpson, W.C., H.J. Sommer, R.L. Griffin, T.K. Miles. Epoxy Asphalt Concrete for Airfield Pavements. *Journal of the Air Transport Division, Proceedings of the American Society of Civil Engineer* 86, 1960, pp. 57-71.
6. Widyatmoko, I., B. Zhao, R.C. Elliott, W.G. Lloyd. Curing Characteristics and the Performance of Epoxy Asphalts. *Presented at Tenth International Conference on Asphalt Pavements*, Quebec, Canada, 2006.
7. Herrington, P., D. Alabaster. Epoxy Modified Open-graded Porous Asphalt. *Road Materials and Pavement Design* 9(3), 2008, pp. 481-498.
8. Xiao, Y., M.F.C. van de Ven, A.A.A. Molenaar, Z. Su, F. Zandvoort. Characteristics of Two-component Epoxy Modified Bitumen. *Materials and Structures* 44(3), 2010, pp. 611-622.
9. Lu, Q., J. Bors. Alternate Uses of Epoxy Asphalt on Bridge Decks and Roadways. *Construction and Building Materials* 78, 2015, pp. 18-25.
10. International Transport Forum. *Long-life Surfacing for Roads: Field Test Results*. ITF Research Reports, OECD, Paris, France, 2017.
11. Li, S., K. Huang, X. Yang, M. Li, J. Xia. Design, Preparation and Characterization of Novel Toughened Epoxy Asphalt Based on a Vegetable Oil Derivative for Bridge Deck Paving. *Royal Society of Chemistry* 4, 2014, pp. 44741-49.
12. Yin, H. H. Jin, C. Wang, Y. Sun, Z. Yuan, H. Xie, Z. Wang, R. Cheng. Thermal, Damping, and Mechanical Properties of Thermosetting Epoxy-modified Asphalts. *Journal of Thermal Analysis and Calorimetry* 115, 2014, pp. 1073-1080.
13. Zhang, Y., X. Pan, Y. Sun, W. Xu, Y. Pan, H. Xie, R. Cheng. Flame Retardancy, Thermal and Mechanical Properties of Mixed Flame Retardant Modified Epoxy Asphalt Binders. *Construction and Building Materials* 68, 2014, pp. 62-67.
14. Sun, Y., Y. Zhang, K. Xu, D. Yu, L. Zhu, H. Xie, R. Cheng. Thermal, Mechanical Properties, and Low-temperature Performance of Fibrous Nanoclay-reinforced Epoxy Asphalt Composites and their Concrete. *Journal of Applied Polymer Science*, 2015, pp. 41694 (1-9).
15. Cong, P., Y. Tian, N. Liu, P. Xu. Investigation of Epoxy-resin-modified Asphalt Binder. *Construction and Building Materials* 122, 2016, pp. 473-477.
16. Zhou, W., Y. Xia, F.-C. Tsai, T. Jiang, H. Zhao, J. Wen. Effects of Compound Curing Agent on the Thermo-mechanical Properties and Structure of Epoxy Asphalt. *International Journal of Pavement Engineering* 18(10), 2017, pp. 928-936.
17. Yu, J.Y., P.L. Cong, S.P. Wu. Laboratory Investigation of the Properties of Asphalt Modified with Epoxy Resin. *Journal of Applied Polymer Science* 113, 2009, pp. 3557-3563.
18. Kang, Y., Q. Wu, R. Jin, P. Yu, J. Cheng. Rubber-like Quasi-thermosetting Polyetheramine-cured Epoxy Asphalt Composites Capable of Being Opened to Traffic Immediately. *Scientific Report* 6, 2016, 18882.
19. Cheung, C.Y., D. Cebon. Deformation Mechanisms of Pure Bitumen. *Journal of Materials in Civil Engineering*, Volume 9, Issue 3, 1997, pp. 117-129.
20. Apostolidis, P., X. Liu, C. Kasbergen, M.F.C. van de Ven, G. Pipintakos, A. Scarpas. Chemo-rheological Study of Hardening of Epoxy Modified Bituminous Binders with the Finite Element

- Method. In *Transportation Research Record*, 2446-18, 2018, TRB, National Research Council, Washington, D.C.
21. Apostolidis, P., X. Liu, M.F.C. van de Ven, S. Erkens, A. Scarpas. Kinetic Viscoelasticity of Crosslinking Epoxy Asphalt. In *Transportation Research Record*, 2019, TRB, National Research Council, Washington, D.C.
 22. Hofko, B., M.Z. Alavi, H. Grothe, D. Jones, J. Harvey. Repeatability and Sensitivity of FTIR ATR Spectral Analysis Methods for Bituminous Binders. *Materials and Structures* 50, 2017, pp. 187:1-15.
 23. Hofko, B., L. Porot, A. Falchetto Cannone, L. Poulikakos, L. Huber, X. Lu, K. Mollenhauer, H. Grothe. FTIR Spectral Analysis of Bituminous Binders: Reproducibility and Impact of Ageing Temperature. *Materials and Structures* 51, 2018, pp. 45:1-16.
 24. Petersen, J. C., J. F. Branthaver, R. E. Robertson, P. M. Harnsberger, J. J. Duvall, E. K. Ensley. Effects of Physicochemical Factors on Asphalt Oxidation Kinetics. In *Transportation Research Record* 1391, TRB, National Research Council, Washington, D.C., 1993, pp. 1–10.
 25. Petersen, J. C., P. M. Harnsberger. Asphalt Aging: Dual Oxidation Mechanism and Its Interrelationships with Asphalt Composition and Oxidative Age Hardening. In *Transportation Research Record* 1638, TRB, National Research Council, Washington, D.C., 1998, pp. 47–55.
 26. Masson, J.F., G.M. Polomark, P. Collins. Time-dependent Microstructure of Bitumen and its Fractions by Modulated Differential Scanning Calorimetry. *Energy Fuels*, 16, 2002, pp. 470–476.

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(a)

(b)

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FIGURE 2 MDSC scans at 40°C/min from -50 to 200°C of base and epoxy modified bitumen (EB50)

(a)

(b)

FIGURE 3 Relationship of (a) carbonyl (C=O) and (b) sulfoxide (S-O) and time in oven at 130°C

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463

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(c)

FIGURE 4 Master curves of complex modulus and phase angle of studied binders after OH for different times; (a) EB0, (b) EB20, and (c) EB50

FIGURE 5 Relationship between sulfoxide compounds and viscoelastic properties over OH hardening: (a) complex modulus and (b) phase angle

FIGURE 6 Relationship of (a) reactants, and (b) products during oven-hardening in time at 130 °C

FIGURE 7 Relationship of G_{∞} and T_g versus time of the binders during CH at 130 °C

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493 **FIGURE 8** Monotonic tensile test results : (a) representative tensile force versus
 494 displacement curves and (b) tensile strength of fully chemically hardened binders at
 495 temperature of 0°C and 0.05 mm/s of displacement rate

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FIGURE 9 Cyclic shear test results of fully chemically hardened binders at temperature of 0°C and frequency of 10 Hz