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Apostolidis, Panos; Pipintakos, George; Liu, Xueyan; van de Ven, M.F.C.; Erkens, S.; Scarpas, Athanasios

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# Epoxy modified bitumen: Chemical hardening and its interpretation

P. Apostolidis[1], G. Pipintakos[1], X. Liu[1], M. van de Ven[1], S. Erkens[1] & A. Scarpas[1,2]
[1]*Section of Pavement Engineering, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, The Netherlands.*

[2]*Department of Civil Infrastructure and Environmental Engineering, Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates*

ABSTRACT: Epoxy modified bitumen (EMB) is a promising technology for long lasting paving materials ensuring higher resistance to rutting, oxygen- and moisture-induced damage. In this paper, an analysis of the chemical reactions that take place during the chemical hardening process (curing) of epoxy modified bitumen was conducted by means of Fourier Transform Infrared (FT-IR) spectrometer. For various amount of epoxy resin modification in bitumen, the hardening process was evaluated under various conditions. The fluctuation of the most crucial chemical groups occurring during the hardening process was identified and discussed. After the interpretation of chemical hardening, the critical hardening conditions were determined and fatigue tests were performed by Dynamic Shear Rheometer (DSR). Comparison with the unmodified bitumen shows that the fatigue resistance of epoxy modified binders improved significantly with increasing the amount of the epoxy resin in bitumen.

## 1. INTRODUCTION

Bitumen is the most widely used material in pavement engineering. Nowadays, the increased traffic loads in combination with extreme climatic conditions lead to the development and use of various bitumen modifiers to improve the sustainability and durability aspects. The main distress phenomena tackled with modified binders are related to rutting, low temperature cracking after oxidation, as well as moisture damage. Among other modifiers, the epoxy resins have been applied to address the aforementioned damages (Widyatmoko et al. 2006, Yidirim, 2007). Similar to the conventional polymer modified binders, EMBs have improved resistance to thermal susceptibility which will result to less rutting of mixes (Yu et al. 2009). Their excellent adhesive strength and their resistance against crack initiation at low temperatures make them excellent surfacing materials for pavements in tunnels, orthotropic steel decks and at intersections subjected to heavy traffic loads (Xiao et al. 2010; Bocci & Canestrari, 2012; Yin et al., 2015). Furthermore, a remarkable long-term improvement in durability has been demonstrated when bitumen was modified with epoxy resins (Herrington & Alabaster, 2008; Luo et al., 2015; International Transport Forum, 2017; Wu et al., 2017).

However, EMB mixes perform differently during their service life compared to the traditional modified binders. The epoxy resin is a thermoset material and becomes solid after certain chemical reactions. Moreover, the amount of epoxy resin in the EMB affects significantly the mechanical behavior and should be further investigated in the end product (Peilang et al. 2010, Wei & Zhang, 2012). Although an epoxy resin is an alternative solution for other modifiers it has also some limitations. The time window from production to transportation and construction is limited and the hardening process of the epoxy resin should be thoroughly investigated. In this research, these issues were taken into account at binder level. The presence of epoxy resin within the bituminous matrix changes the nature of the material from thermoplastic to quasi-thermoset and the material becomes solid after specific chemical reactions have taken place (Apostolidis et al. 2018). This process is called chemical hardening of EMB and was analyzed in this research by means of FT-IR spectrometer. Finally, the long-term durability of EMB was evaluated by means of fatigue tests.

## 2. OBJECTIVES

To develop a reliable EMB pavement, the chemical hardening of the material is of paramount importance. In this study, isothermal hardening conditions were selected and after a specific combination of hardening time and temperature, the structural performance in time of EMBs was explored by conducting fatigue tests. The results demonstrate the capability of improving the fatigue resistance of the bituminous materials and reducing maintenance needs in time by utilizing epoxy.

## 3. MATERIALS AND METHODS

### 3.1 *Materials*

The epoxy provided by ChemCo Systems Co. used for EMB consists of two parts; part A is the epoxy resin without containing any kind of agent in its composition and part B is a homogeneous blend of bitumen and hardener. The exact composition of part B is a tightly guarded proprietary secret from the material supplier. Due to the fact that this study aims to implement the epoxy modification technology in the Netherlands and taking into account the economic aspects, a 70/100 penetration grade virgin bitumen, used mostly for porous bituminous mixes in Dutch roads, was selected to dilute the commercial product.

### 3.2 *Sample preparation*

According to the supplier, the parts A and B are mixed together at weight ratio 20:80 and the epoxy modifier is produced. Before mixing, part A and B were placed in ovens for 1 hour at 85 $^oC$ and 110 $^oC$, respectively. After that, the epoxy modifier was diluted with the already preheated bitumen 70/100 at 120 $^oC$. The content of epoxy modifier was varied to evaluate its impact. Two different modification levels were investigated; 20:80 and 50:50, where the ratio stands for modifier:fresh bitumen. A temperature of 130 $^oC$ was used to study the different stages of chemical reactions of hardening. After the aforementioned preparation process, the chemical hardening of EMBs was performed at three different time intervals of 2, 5 and 8 hours. After the material preparation, all the samples were placed in a refrigerator at -10 $^oC$ to prevent any further reaction.

### 3.3 *Chemical characterization with FT-IR*

The chemical hardening of EMB blends was analyzed for different time intervals with a FT-IR spectrometer equipped with an Attenuated Total Reflectance (ATR) fixture. The FT-IR spectra collected for all the samples ranged from 600 $cm^{-1}$ to 4000 $cm^{-1}$. An amount of material was placed directly in the ATR crystal pedestal, pressed with a constant force to ensure proper contact to the surface, and the spectra were analyzed based on the absorbance intensity method of peak difference (Van de Bergh, 2011). Three replicas were used for each sample and 20 scans per sample were performed.

### 3.4 *Fatigue characterization with DSR*

A DSR device was used to evaluate the fatigue behavior of EMB of two different modification levels and compare them with the unmodified bitumen. Time sweep tests under constant temperature of 0 $^oC$, a frequency of 10 Hz at three different stress levels of 0.4, 0.5 and 0.6 MPa were performed for three replicas. The DSR testing geometry of 8 mm diameter was used with 2 mm gap according to the Superpave specifications (Superpave Series No. 1, 1996). For the hardening of modified binders, the most critical conditions (i.e., temperature and time) were distinguished in the previous step. To prevent damage occurred in the bitumen with lower initial stiffness the test conditions (Motamed & Bahia, 2011) and hardening of the samples was selected accordingly.

## 4 RESULTS

The groups of oxirane (absorbance band at 917 $cm^{-1}$) and methylene (at 3050 $cm^{-1}$) are the responsible functional groups for the formation of epoxy resin. During the chemical hardening, oxirane and methylene groups react with the carbonyl acid group (at 1709 $cm^{-1}$) resulting into a carbonyl ester (at 1735 $cm^{-1}$) and hydroxyl group (at 3500 $cm^{-1}$). Successively, a second chemical reaction takes place between the oxirane and methylene groups resulting into carbonyl ether (at 1040 $cm^{-1}$). **Fig 1** shows the FT-IR spectra of EMB (20 % of epoxy modified) recorded at different hardening times.

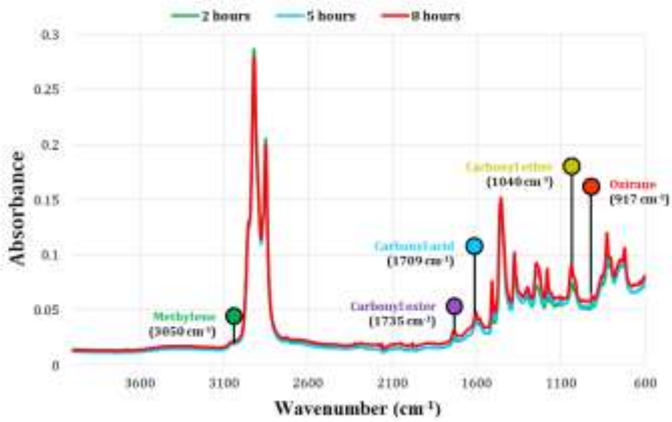


Figure 1. FT-IR spectra at different chemical hardening times

The processing of the results was conducted using a specific baseline with discretized bonds near the examined peak and the distance of the governing peak of the spectrum to this baseline is calculated as the absorption intensity. **Fig. 2** demonstrates all the chemical groups observed in the studied FT-IR spectra, which shows that the intensity of the oxirane group decreases over time. Since oxiranes take place in the esterification and etherification reactions during the hardening process, increase of the relative groups through the hardening was expected initially while remaining constant after a specific period. Further, the methylene group fluctuates the first 5 hours of hardening and remains constant afterwards in both EMBs indicating that it has completely reacted after 5 hours.

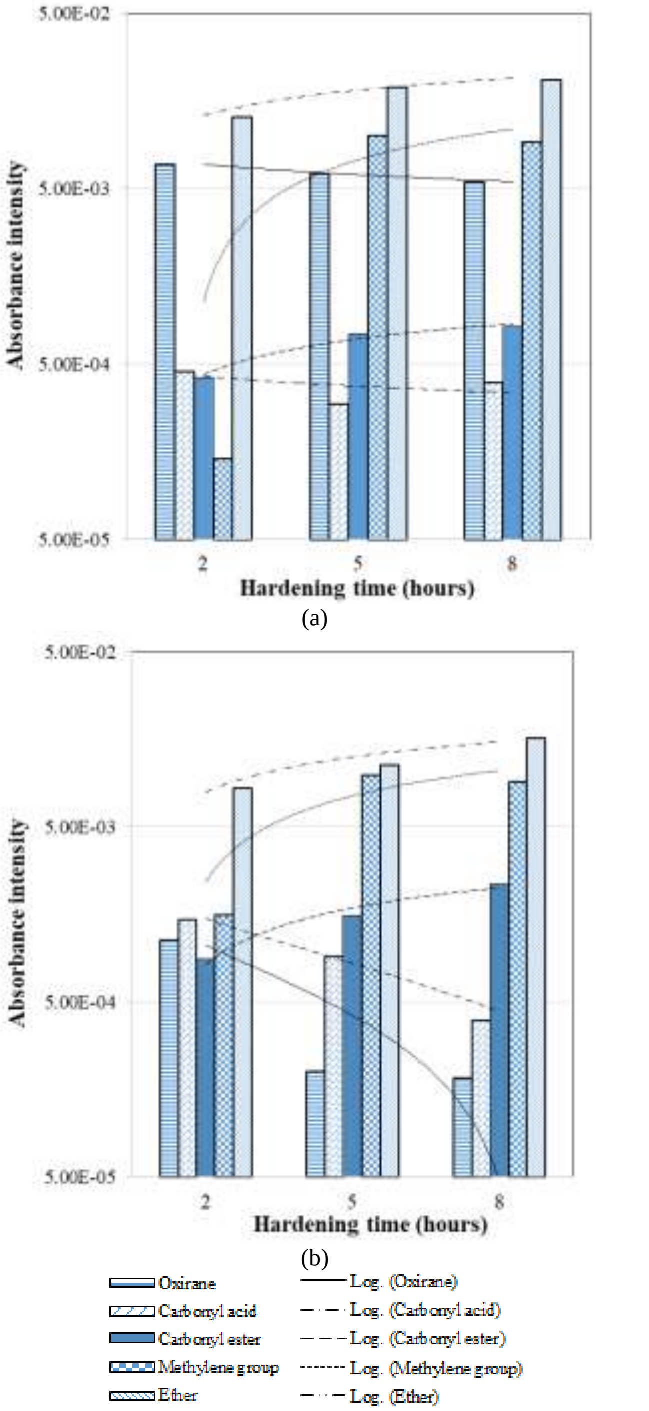


Figure 2. Chemical groups during chemical hardening for (a) 20 % and (b) 50 % EMB

After the critical hardening conditions had been chosen based on the chemical analyses discussed above, DSR fatigue tests were performed in materials hardened for 5 hours at 130 $^{o}$C and the results are given in **Fig. 3**. For three different stress levels the repeatability of the results as well as the regression lines were in an acceptable range as it is demonstrated from the coefficient of determination. The results were chosen to be demonstrated when the maximum load repetitions reached 50% of the initial stiffness.

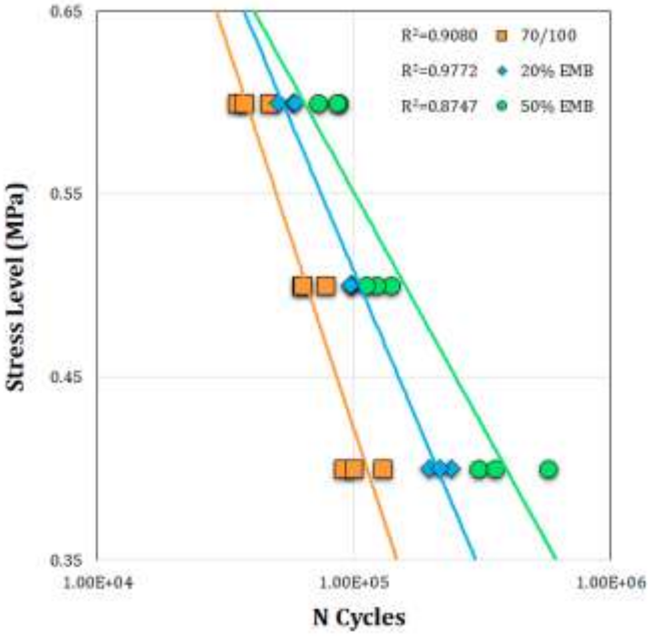


Figure 3. Fatigue life curves of various EMBs

## 5 DISCUSSION AND FUTURE WORK

The level of epoxy modification affects the chemical hardening process accelerating the reactions when higher epoxy percentages are used. The cross-linking three-dimensional network of epoxy modifier, resulted from the polymerization of part A with the assistance of part B, is formed slightly faster when higher modification levels are applied, mainly because less bituminous molecules prevent the network evolution. The hardener included in the part B of modifier was considered as acid-type agent because the group of carbonyl acid was reduced during the hardening process. Additionally, based on the fact that methylene group remains constant after 5 hours of chemical hardening, time of 5 hours at 130 $^{o}$C is considered as the condition in which EMBs are fully cured, named critical hardening conditions in this research. The phenomenon of limited alteration in methylene group after 5 hours was observed for both crosslinking materials. Furthermore, the production of ether and ester groups indicates that the chemical hardening of EMB involves the mechanisms of esterification and etherification. However, it should be mentioned that ether and ester groups participate in material aging as well and it is difficult to conclude about the contribution of these groups on chemical hardening process.

The critical hardening time for a specific temperature was chosen for fatigue analyses. It is known that the incorporation of thermosets into bituminous binders results blends of high toughness and ductility but limited evidence exists about their long-term performance in binder level. From the fatigue tests presented in Figure 3, the higher the epoxy modification level in bitumen is the higher the resulting fatigue life is. The current results validated the expectations of durability improvement with the epoxy resin into the bituminous matrix. The prediction at high stress levels gives better performance compared to unmodified material, whereas for lower levels the differences in fatigue life were more obvious. Also, the long-term material performance is satisfied in order to relate the results to material crack initiation. The improved durability of epoxy modified bituminous mixes at low temperatures prevents the cracking-type distresses in pavement structures offering lower maintenance demands.

Future research should include a discrimination of the chemical groups that participate both in chemical and physical hardening (i.e., oxidative degradation). It is important to identify the favorable time of conditioning the modified blends when the chemical reactions due to the polymerization of epoxy modifier into the bituminous matrix stops and the aging initiates. In addition, the evolution of viscosity is considered essential for the determination of pot life of EMBs. Finally, a more intensive study of isothermal chemical hardening process in shorter time intervals during the first two hours, which are crucial for the pavement construction, is needed.

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