Fourier transform infrared spectroscopy (FTIR)

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This reading pack provides an introduction to the use of Fourier Transform Infrared Spectroscopy (FTIR), a technique used to obtain infrared spectrum of absorption, emission, and photoconductivity of solid, liquid, and gas. The reading pack highlights the application of FTIR to the testing of bituminous mixes, its role in ascertaining optimal mix and performance as well as highlighting the need for harmonisation of data acquisition to allow comparability of findings across laboratories. The reading pack also highlights how the combination of FTIR with other techniques can support the reliable identification and quantification of additives in bituminous binders to ensure optimal performance.

Increased traffic loads, changing climatic conditions and the frequency of extreme weather events are impacting on roads globally. To improve the performance and longevity of road surfaces, various additives are being added to the bitumen. Polymer modifiers are one such additive and are increasingly being used in bituminous mixes in order to improve the performance and durability of pavement structures. Epoxy is a thermoset material which ensures enhanced fatigue performance and improved mechanical characteristics when used to modify bituminous materials. One of epoxy advantages is that its adaptability to climate as it improves resilience of pavements against both lower and higher temperatures. However, unlike conventional modification techniques, a series of experimental methods have to be conducted to evaluate the chemical-related phenomena occurring during the binder production and their effects on the performance of the epoxy modified bitumen. FTIR is probably the most recognisable of these methods.

Whilst FTIR is a commonly applied technique, studies have shown that the conclusions of analyses performed on the same set of raw spectra can differ considerably according to the FTIR oxidation index calculation method adopted. For FTIR spectra to be comparable between different laboratories, harmonisation of the data acquisition procedures is needed.

FTIR is a technique that is cost effective and has been shown to be applicable in the global south. By ensuring the consistency of findings, the application of FTIR testing can support the development of climate resilient sustainable road pavement surfacings. Further to this, the combination of FTIR with other techniques can ensure the robustness of quality assurance processes across the development and implementation of road infrastructure development.

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Key Readings

Reading 1: Pipintakos, G. (2018). *Experimental characterization of chemical and physical performance of epoxy modified bitumen*. Dissertation, Delft University of Technology.

https://repository.tudelft.nl/islandora/object/uuid%3A6f6740a0-1e69-4fed-bf39-a880dbea4e06

Increasing traffic load has led to the use of polymer modifiers in bituminous mixes in order to improve the performance and the durability of the pavement structures. Epoxy is a thermoset material which ensures enhanced fatigue performance and improved mechanical characteristics when used to modify bituminous materials. However, unlike conventional modification techniques, a series of experimental methods have to be conducted to evaluate the chemical- related phenomena occurring during the binder production and their effects on the performance of the epoxy modified bitumen.

In this thesis, the utilisation of epoxy modifiers was investigated at binder level. The chemical hardening (curing) process of epoxy modified bitumens (EMBs) was investigated by means of Fourier Transform Infrared (FT-IR) spectrometer and Dynamic Shear Rheometer (DSR). Different combinations of hardening conditions for three epoxy modification levels were studied. Properties, such as modulus and viscosity, were utilised to determine the workability of EMB. At the same time, by using the FT-IR spectrometer, the functional groups of EMBs during the chemical reactions were identified for the understanding of polymerisation in the epoxy components. Additionally, the DSR device was utilised to determine the fatigue and tensile strength of EMBs. It was found that, with increasing the content of epoxy modifier, the fatigue life and tensile strength were increased significantly compared to an unmodified binder.

Finally, the age hardening (aging) of EMBs was evaluated at different time intervals. For the simulation of short-term aging on EMBs, a short-term oven aging method (STOA) was used. For long-term aging, simulations were performed in a pressure aging vessel (PAV) under constant pressure and temperature. The results of chemical characterisation and rheological properties of the aged EMBs were obtained by using DSR and FT-IR and were compared to the unmodified bitumen.

Reading 2: Marsac, P. et al. (2014). Potential and limits of FTIR methods for reclaimed asphalt characterization. *Materials and Structures* volume 47. **https://link.springer.com/content/pdf/10.1617/s11527-014-0248-0.pdf**

This paper gives a brief overview of asphalt oxidation and the FTIR principle. It then presents the results from four different calculation methods for the oxidation parameters applied to a set of more than 100 spectra obtained during the RILEM TC-ATB-TG5 round robin test. During the life of a pavement, as well as the structural damage induced by traffic, the intrinsic properties of asphaltic materials are affected through the oxidative ageing of the bituminous binder. The molecular changes associated with this oxidation can be monitored via variations in Fourier transform infrared (FT-IR) spectra. Therefore, if the relationships between binder properties, such as penetration, softening point and complex shear modulus and the spectra parameters can be established, the characterisation of RA produced by the milling of old pavements can be greatly improved.

However, the interpretation of oxidation parameters from these spectra is not straightforward, and many different techniques are used to calculate them in the asphalt community. From this study, it is clear that the conclusions of the analysis performed on the same set of raw spectra can differ considerably according to the FTIR oxidation index calculation method adopted. Using the RILEM database, the potential links between a given ageing index and the physical properties are then evaluated. As a result of this study it can be concluded that ageing comparison through FTIR should be considered as relative and restricted for use in measurements at different ageing steps on the same type of initial mixture. For FTIR spectra to be comparable between different laboratories, harmonisation of the data acquisition procedures is needed. Also the different calculation methods of the oxidation indicators seem to reflect different physical properties.

Reading 3: Weigel, S. and D. Stephan (2017). The prediction of bitumen properties based on FTIR and multivariate analysis methods. *Fuel* 208. **https://link.springer.com/article/10.1617/s11527-021-01763-1**.

This article aimed to demonstrate that the combination of Fourier transform infrared (FTIR) spectroscopy with attenuated total reflexion (ATR) technique and multivariate evaluation is a well-suited method to reliably identify and quantify additives in bituminous binders. Bitumen is a crucial building material in road construction, which is exposed to continuously higher stresses due to higher traffic loads and changing climatic conditions. Therefore, various additives are increasingly being added to the bitumen complicating the characterisation of the bituminous binder, especially concerning the reuse of reclaimed asphalt. For this research, various unmodified and modified binders, directly and extracted from laboratory and reclaimed asphalts, were investigated with FTIR-ATR spectroscopy. The determined spectra, pre-processed by standard normal variate (SNV) transformation and the determination of the 1st derivation, were evaluated using factor analysis (FA), linear discriminant analysis (LDA) and partial least square regression (PLSR). With this multivariate evaluation, first, a significant model with a very high hit rate of over 90% was developed allowing for the identification of styrene-butadiene copolymers (SBC), ethylene-copolymer bitumen (ECB) and different waxes (e.g., amide and Fischer-Tropsch wax) even if the additives do not show any additional peaks or the samples are multi-modified. Second, a quantification of the content is possible for SBC, ECB, and amide wax with a mean error of RMSE ≤ 0.4 wt% and a coefficient of determination of $R^2 > 90\%$. Based on these results, FTIR identification and quantification of additives in bituminous binders is a very promising method with a great potential.

Reading 4: Hofko B., et al. (2018). FTIR spectral analysis of bituminous binders: reproducibility and impact of ageing temperature. *Materials and Structures*, 51 (45). **https://doi.org/10.1617/s11527-018-1170-7**. **https://link.springer.com/content/pdf/10.1617/s11527-018-1170-7.pdf**

This RILEM round robin study investigated bitumen ageing, its effect on chemical properties and its reproducibility. The impact of temperature used for short term (RTFOT) binder ageing on the combined short and long-term (PAV) aged samples was investigated; thereby the effect of reduced mixing temperature such as those relevant for warm mix asphalt technologies on long term ageing was examined. Four 70/100 penetration graded bituminous binders from different sources were selected. In addition to the standard RTFOT temperature of 163 ◦C, two additional temperatures, 143 ◦C and 123 ◦C were used. The Fourier transform infrared spectroscopy (FTIR) analysis was carried out using an integration method which considers the area below the absorbance spectrum around a band maximum using baseline and tangential approaches. A statistical investigation into the reproducibility of FTIR spectra analysis based on the accumulated data was done. To assess the reproducibility, the coefficient of variation (CV) was taken as a benchmark parameter. Carbonyl and sulfoxide indices were calculated using different baseline correction methods and tangential and baseline integration, respectively. It was shown that the tangential method was not influenced by the applied baseline correction. However, in all considered cases, the tangential method led to significantly worse reproducibility (CVs ranging from 20 to 120%) compared to the baseline method. The sulfoxide indices calculated by both methods were not affected by the baseline correction method used. Impacts of changes in the short-term ageing temperature on short- or long-term aged samples could not be found whereas differences between different binder sources could be detected. RTFOT temperature and therefore mix production temperature had a stronger impact on the formation of sulfoxide structures than for carbonyl structures. The findings from this study show the most reproducible of all considered methods when more than one laboratory is providing FTIR data.

Reading 5: Rathore M., et al. (2021). Rheological and chemical evaluation of aging in 100% reclaimed asphalt mixtures containing rejuvenators. *Construction and Building Materials*. 318.

https://doi.org/10.1016/j.conbuildmat.2021.126026

This study evaluated the effect of four different rejuvenators on aging characteristics of 100% reclaimed asphalt mixtures. Rheological tests on extracted bitumen revealed that tall oil-based rejuvenator showed highest reduction and petroleum-based rejuvenator showed lowest reduction in stiffness of binder in the long term. At lower strain levels, the fatigue life calculated from linear amplitude sweep test was significantly higher for long-term aged binder compared to unaged binder due to increase in stiffness of bitumen. All the rejuvenated binders showed rutting performance comparable to that to virgin binder. Fourier transform infrared spectroscopy showed increased carbonyl peak intensity after long-term aging, but no clear implications were made for effect of aging on sulfonyl index.

Reading 6: Xiao, Y. (2013). *Towards a Performance Evaluation Method for Durable and Sustainable Thin Surfacings*. PhD thesis, Delf University of Technology.

https://scholar.archive.org/work/3ymwhkjuofdshgiws4btkfq4fa/access/wayback/http://repository.tudelft.nl/assets/uuid:eccb2deb-b329-4c7c-abf0-9250af716422/Yue%20thesis%20TUD%20Final.pdf

This research focuses on the definition of requirements for alternative thin surfacing on airfield runways as well as specifying design approach. Specimens with tar-containing antiskid layers on the surface were collected from six airfields' runways. Fourier Transform Infrared, surface characteristics, tensile adhesion and shear adhesion at the interface were investigated. The conclusions from these test results were used as benchmarks for alternative antiskid surfacings. The research then explored newly designed binders, which are considered as potential binders for antiskid surfacings. These included Copolymer modified bitumen emulsion (MBE), 2-component Modified Epoxy Resin (MER) and 2-component Epoxy Modified Bitumen (EMB). Test results indicated that 2-component epoxy modified bitumen can be designed as a suitable binder for antiskid surfacing, with good high temperature resistance, qualified relaxation behaviour, sufficient tensile strength and enough failure strain. One of the researched 2-component epoxy modified bitumen was then used to design antiskid surfacing in the lab. The results showed that EMB based antiskid layers can provide better adhesion at the interface than tar-containing antiskid layer and polymer modified bitumen based antiskid layers.

Questions to guide reading

1. What is Fourier transform infrared spectroscopy (FTIR)?
2. How is FTIR applied to the analysis of bituminous road surfacings and how does this support the development of road infrastructure?
3. How can FTIR support the development of climate resilient sustainable road pavement surfacings?
4. What are some of the challenges associated with FTIR tests for epoxy modified bitumen mixes?

References

Hofko B., et al. (2018). FTIR spectral analysis of bituminous binders: reproducibility and impact of ageing temperature. *Materials and Structures*, 51 (45).

Marsac, P. et al. (2014). Potential and limits of FTIR methods for reclaimed asphalt characterization. *Materials and Structures* volume 47.

Pipintakos, G. (2018). Experimental characterization of chemical and physical performance of epoxy modified bitumen. Dissertation, Delft University of Technology.

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