



Chemical analysis of surface and bulk of asphalt binders aged with accelerated weathering tester and standard aging methods



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HIGHLIGHTS

- Asphalt binders were aged with an accelerated weathering tester using UV radiation.
- FTIR and XPS detected more chemical changes with this method than standard methods.
- As aging proceeded, oxygen, nitrogen and sulfur concentrations on the surface increased.
- Binder oxidation is much higher on the surface than in deeper layers.
- In homogenous samples surface composition differed from bulk due to microstructures.

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ABSTRACT

This paper presents analysis of chemical changes in asphalt binder samples that were aged using an accelerated weathering tester, which involves UV radiation and direct aging of the binder surface. It also provides a comparison with chemical changes in the same binders but aged with standard methods. Fourier Transform Infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) results show that the accelerated weathering tester caused more extensive chemical changes, such as higher oxidation and inclusion of nitrogen from the air, compared to standard aging methods. The amount of oxygen, nitrogen and sulfur on the surface was observed to increase as aging time increased. In addition, the XPS etching analysis highlighted that the depth profile of binders changed from the surface to deeper layers and showed that the directly aged samples using the weathering tester were heavily oxidized on the surface and less on the underlying layers. Unaged binders and binders aged with standard methods displayed a fairly uniform depth profile. However, slight differences in the chemical composition were detected on the surface of these samples, which were associated with the surface microstructure developed during sample preparation. The results of the chemical characterization are compared in this paper with previous findings in terms of microstructural configuration that were obtained using Atomic Force Microscopy (AFM).

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1. Introduction

A previous paper by the authors discussed the evolution of the surface microstructure of asphalt binders aged using an accelerated weathering tester for different durations [1]. The aging protocol with the weathering tester exhibited two clear advantages compared to the standard aging methods using Rolling Thin Film Oven (RTFO) followed by Pressure Aging Vessel (PAV). RTFO simulates production and placement aging (short-term aging). In this method, asphalt binders are placed in cylindrical glass bottles in a rotating carriage and exposed to elevated temperatures [2,3].

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PAV simulates in-service long-term aging (7–10 years). This method involves placing asphalt binders in stainless steel pans in a heated and pressurized vessel [4]. The first advantage of the accelerated weathering tester is the application of UV radiation, which is not considered in standard asphalt aging protocols. However, in countries such as Qatar, where this research is conducted, the UV radiation is very intense and present for most part of the year during daytime, and its impact on aging of pavements should be considered. The second advantage is that with the new aging protocol, the binder' surface is directly aged and the same exposed surface is investigated with Atomic Force Microscopy (AFM). With standard aging and analysis protocols, the binder samples are heated after aging and subsequently investigated with AFM [5]. However, molecular rearrangements occur in the binder during heat treatment and create a new surface configuration. Therefore,

the microstructure is believed to be influenced by sample preparation parameters along with chemistry of the samples [6]. This causes discrepancies in the microstructural observations of aged binders in the literature [7–11].

An earlier study showed that the microstructure observed after varying durations of direct aging was completely different from the original microstructure of the unaged binder and any binder microstructures previously observed [1]. New structures with different shapes were detected at different stages of aging. Squares, rods and spheres were observed after varying aging extents. The microstructure detected in the most aged samples was defined as “flower or leaf” microstructure, due to the shape of the configurations observed. Based on chemical analyses present in the literature, it was hypothesized that these microstructures were composed of oxidized and polymerized binder. The UV radiation was hypothesized to cause free radicals on the surface of the asphalt binder, which combined and formed longer polymer chains [12].

In addition, the macroscopic appearance of the aged asphalt surface was different from that of a sample freshly prepared with the heat cast method. The rippling and degradation of the surface due to direct aging was observed in optical photos. Menapace and Masad [1] stated that the macroscopic surface ripples were generated by the presence of a sheet of aged binder which is stiffer than deeper layers. These observations were correlated with the hypothesis of the formation of a thin film on the aged surface, which was proposed by Das, Kringos and Birgisson [10], in which the viscosity and elastic stiffness result increased [10,13]. Therefore, it was hypothesized that the top sheet is richer in oxygen (in the form of carbonyl (C=O) and sulfoxide (S=O) groups) and is expected to have larger molecules compared to the underlying layers, due to polymerization reactions.

The goal of this paper is to shed light on the chemistry of binder samples aged either with an accelerated weathering tester or with the standard aging methods (RTFO and PAV). These binders were previously analyzed with AFM [1,5]. The microstructures observed with AFM are the surface meta-stable configuration of the binder molecules with a determined chemistry. The changes of the chemical composition during aging with the weathering tester causes the development of the meta-stable molecular configuration, leading to the evolution of the microstructure. For this reason, it is important to investigate the chemical build-up of the asphalt samples subjected to varying aging times. The chemical analysis was performed using the Fourier Transform Infrared (FTIR) and the X-ray photoelectron spectroscopy (XPS). The XPS is a powerful tool to investigate the chemical composition of the surface of asphalt binders exposed to direct aging in the weathering tester. XPS etching analysis was also performed in order to evaluate the chemical profile of the sample throughout different layers under the surface.

2. Materials and methods

2.1. Asphalt binders

Unmodified binder Pen60/70 (PG64-22) and polymer modified binder PG76-22 supplied by Qatar Fuel (Woqod) company in the State of Qatar were used. The unmodified binder was imported from BAPCO, Bahrain.

2.2. Aging processes

2.2.1. Accelerated weathering tester

The unaged asphalt binder samples were prepared with the heat cast method according to the procedure described in Menapace, Masad, Bhasin and Little [5]. A small amount of asphalt binder

was removed from its container and placed on a glass slide, which was positioned horizontally in an oven at 160 °C for 15 min. After 5 min in the oven, the binder was spread with a spatula.

The samples were subsequently exposed to aging agents using a new protocol in a QUV Accelerated Weathering Tester supplied by Q-Lab Corporation (Westlake, Ohio, United States) [1,14]. The parameters of the accelerated weathering tester were chosen in order to simulate climatic conditions in Qatar. In order to simulate day and night, a UV cycle (lasting 8 h) was followed by a dark cycle (lasting 4 h). The irradiance set at 0.89 W/m² as per ASTM G154 standard [15]. The temperature was set at 50 °C during the UV cycle and 42 °C during the dark cycle in order to simulate typical temperatures encountered in the asphalt pavements of Qatar during day and night in the summer months. The weathering was conducted for different time spans: 2, 7, 13, 26, 40, 67 and 104 days, which simulated 7, 26, 49, 97, 149, 250 and 388 days outdoor in Qatar, respectively [1,14]. The time spans were chosen in order to have a complete overview of the chemical and microstructural changes due to aging up to one year.

2.2.2. Standard aging methods

The RTFO/PAV aged samples were prepared first by short-term aging in the RTFO, supplied by James Cox & Sons, Inc., for 85 min at 163 °C, and then long-term aged with the PAV system, provided by Prentex Alloy Fabricators Inc., which was set at 2.10 MPa of pressure for 20 h at 110 °C. After aging, the air trapped in the binder was extracted with a vacuum oven supplied by the same company as the PAV, operating at 15 ± 2.5 kPa and 170 °C. RTFO/PAV samples for XPS analysis were prepared with the heat cast method.

2.3. Chemical characterization methods

The unaged and aged binders were characterized using the ATR of a Spectrum One FTIR Spectrometer by Perkin Elmer precisely, with wavelength range 1000–650 nm.

In addition, the surfaces of the unaged and aged binders were investigated with an AXIS Ultra DLD XPS by Kratos Analytical Ltd, a Shimadzu Group Company, Manchester, United Kingdom. A Mg K (alpha) radiation (1253.6 eV) was operated at 15 kV and 10 mA emission current. First, a survey was carried out in low resolution (pass energy 80 eV) with 0.1 eV step size to detect all elements present. Then, the peaks relative to C 1s, N 1s, O 1s and S 2p were separately investigated in higher resolution (pass energy 5 eV, 0.1 eV step size). The depth profile of C 1s, N 1s, O 1s and S 2p of binder samples was obtained with the alternation of a sequence of ion gun etch cycles and XPS measurements. First, a survey and high resolution spectra of the sample surface were obtained. Then the sample was subjected to bombardment with Ar ions with beam energy of 4 keV and beam rate of 125.24 Å/min for 30 s followed by another cycle of survey and high resolution spectra collected on the new surface. The estimated depth of an etched layer is in the order of hundreds of nanometers. The procedure was repeated for 30 times. The high resolution XPS spectra were deconvoluted with OriginLab[®] to identify different peaks. The quantification of the areas, in terms of mass concentration of the detected elements, was performed on the survey spectra with Kratos Vision data processing software. As the asphalt binders are non-conductive, a charge neutralizer was used during the XPS measurements. However, charge neutralization was not fully achieved on some samples, which caused a shift in the peaks, and a manual charge correction was required on the measured spectra. The charge correction was performed in order to set the deconvoluted C–C (adventitious carbon) peak at 285.0 eV in the C 1s spectrum and the same correction value was applied to the N 1s, O 1s and S 2p spectra.

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