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Full Length Article

Investigation of functional group distribution of asphalt using liquid chromatography transform and prediction of molecular model

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ABSTRACT

The present study investigated functional group distribution of virgin and aged asphalt binder through liquid chromatography (LC) transform, a device that combines the functions of Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC). The corresponding molecular models of virgin and PAV aged asphalt components were constructed. The temperature-dependent density of the model was calculated to verify the accuracy of the model. The chemical structure of the components was evaluated using a series of indicators, including the aromatic index, the aging index, the C=O index and the δ (CH_3)/δ (CH_3 + CH_2). The structural changes of components with molecular weight of the virgin and aged asphalt were also analyzed. The molecular simulation results indicated that the molecular model developed in this study was consistent with real asphalt.

1. Introduction

Asphalt binder is comprised of molecular species varying significantly in polarity and molecular weight [1,2]. To characterize the chemical structure of asphalt, researchers usually separate asphalt into different components according to properties including polarity, acidity or basicity and molecular size and so on. The most common method is the SARA, which divides asphalt into saturates, aromatics, resins, and asphaltenes based on polarity [3]. Many chemical analyses of asphalt such as molecular model construction are based on SARA method, which divides asphalt components by polarity first and then tests and analyzes the chemical structure separately [2,4].

Polarity and molecular weight are known as two factors that have relationship with the physical properties of asphalt [5]. In addition, the polarity is considered to be directly related to the performance of asphalt, which promotes the popularity of SARA method [6]. However, the studies also consistently show that molecular weight is a key factor that associates with asphalt performance [7], especially in the utilization of recycled asphalt material into pavement engineering [8]. For example, studies have shown that the molecular weight is the main factor that controlling the diffusion process between virgin and recycled asphalts [8]. Thus, the separation of asphalt into different components based on molecular weight to evaluate the chemical properties or formulate the molecular models can help to understand the relationship between the chemical structure and performance of asphalt.

Liquid chromatography (LC) transform is a combination of gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR) that commonly used to evaluate the chemical structure of molecules with a certain molecular weight. The LC conversion system consists of a collection module, an optical module and a controller which is used to create a link between GPC and FTIR. The GPC is attached to a collection module to remove the solvent phase and deposit the analyte on the disc. The disc is then loaded into an optical module suitable for the optical chamber of the FTIR spectrometer. The LC-transform has been used to determine the content and the properties of styrene-butadienestyrene (SBS) and styrene-butylene-styrene (SEBS) in the asphalt because the polymer exhibits much higher molecular weight than asphalt and is easily separated using GPC [9]. Based on the information above, the LC transformation can be an effective tool for the separation and the chemical structure evaluation of asphalt components with different molecular weight.

Oxidation is responsible for the conversion of irreversible asphalt hardening, resulting in the deterioration of the asphalt performance-related properties [10]. Although molecular size, carbonyl peak and sulfoxide and other indicators usually increase with age, these parameters are less relevant, suggesting that the aging of asphalt may be a continuous double process [11,12]. Therefore, the investigation of the aging process of the separated components may help to understand the asphalt oxidation mechanism.

Molecular dynamics simulation has been used to study the links

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between chemical compositions and mechanical properties of asphalt [4,13–17]. The precise molecular model is critical to the accurate simulation of asphalt properties. Currently, researchers select typical molecule with similar functional group content as molecular model [4,13]. The disadvantage of this method is that the selected typical molecules is not accurate enough to represent a component with complex structure. LC transform can correspond the functional group distribution of a molecule with molecular weight, which provides an effective way to formulate the molecular model.

2. Background

Many works have been conducted to investigate the chemical composition of asphalt using GPC, which is an analytical chemistry technique that yields the molecular weight distribution of a given medium in solution. The principle of GPC is the separation of molecules in solution over time through a column packed with different bead sizes. GPC has been used to determine the average molecular weight [18] and relate to viscosity of asphalt [19]. It is also applied to detect polymers within asphalt binders [20] and asphalt contaminant within fine aggregates [21] by examining the vast difference in the molecular weights. The changes in the GPC chromatogram of lab aged test of asphalt also have been investigated. The researches also indicate that evaluated the viscosity as well as the thin film oven test (TFOT) weight loss and can correlate to the changes in the GPC chromatogram [22].

FTIR is used to identify chemical functional groups within asphalt. The functional groups related to asphalt with respect to oxidation is the carbonyl (C═O) band found at 1695 cm^{-1} and the sulfoxide (S═O) group found at 1030 cm^{-1}. The growths in carbonyl and sulfoxide are due to the introduction of oxygen causing the maltenes to become asphaltenes [23] and can be related to the increase in the viscosity of the binder. The saturated C—C vibration band (1455 cm^{-1}) of asphalt remains relatively constant before and after aging, which allows for an aging index (AI) to be identified by using the area ratio of carbonyl band and saturated C—C vibration band [24].

There are some perceived limitations of using GPC and FTIR separately to test the chemical structure of asphalt. Namely, when FTIR is used to test the function distribution of a component, the results cannot be related to certain molecular weight and used to sketch the molecular structure. Thus, as previously shown, the LC transform which can connect GPC to FTIR can be used to explore more information on the chemical information of asphalt.

3. Objectives

The objectives of the present study were to investigate the properties of asphalt components corresponding to certain molecular weight and study the possibility of using some parameters such as aging index, aromaticity index to evaluate the chemical structures of components. Then the molecular model of asphalt components with a certain molecular weight was formulated to study the relationship between chemical structure and performance of asphalt.

4. Material and methodology

4.1. Material

One typical performance grade (PG) 64-22 asphalt used in Tennessee was used in this study. The asphalt was subjected to short term aging using the rolling thin film oven (RTFO) test following AASHTO T 240-03 standard first [25]. The asphalt was then placed in a pressure aging vessel (PAV) for a long-term aging at 100 °C according to ASTM D 6521-13 standard [26].

4.2. Experimental procedure

The asphalt was first dissolved in tetrahydrofuran (THF) at a concentration of 1.5 mg/ml and shaken at high speed for 1 min in a solution shaker to completely dissolve. Then the solution was injected through a 0.2 μm filter to filter the undissolved impurities. The prepared samples were collected using an auto sampler and placed in a PL-GPC 220 which equipped with an autoinjector and a Hitachi differential refractive index detector. The separation of the asphalt components was performed with two TSK gel Super MultiporeHZ-M column which was packed with 4 μm cross-linked poly (styrene/divinylbenzene) particles.

The asphalt solution from GPC was placed on a rotating dish in a vacuum oven at 60 °C. Solvent THF was evaporated immediately so that the asphalt could be attached to the disc (as shown in Fig. 2). This process was performed concurrently with the GPC test. Thus, the asphalt at a point on the disc could be associated with the value of the GPC spectrum. The disc was divided into 360° to calibrate the location and rotate at a speed of 10°/s. The rotation time of LC transform was 36 min and the elution time of GPC test was 45 min. The rotation of LC disc began 9 min late than GPC test, which means that all the asphalt components eluted out after 9 min was written on the disc. This procedure can guarantee all the asphalt components were deposited on disc because the elution of asphalt components began at 30 min of retention time. In this study, the asphalt was attached at region between 60 and 150° (as shown in Fig. 1 left). The asphalt on the disc was then tested using a Nicolet IS 50 FTIR (Shown in Fig. 1 right). Each FTIR curve corresponded to one point on the GPC spectrum. Data were processed using the OMNIC software that is standard with the equipment.

The height of the FTIR spectrum is controlled by the thickness of the sample. To quantify the content of functional group, the FTIR spectrum was divided by the sample thickness which was determined by the height of the GPC spectrum. Thus, the height of the FTIR spectrum was divided by the corresponding value on the GPC spectrum.

4.3. Asphalt model formulation and simulation

To further describe the chemical structure of asphalt, a series of molecular models of asphalt components were predicted according to some empirical equations from the research of Castro et al. [27]. The research of Castro et al. suggests that there are linear relationships among the hydrogen aromaticity indexes from NMR (Ar_H), carbon aromaticity indexes from NMR (Ar_C) aromaticity indexes from FTIR (Ar_{FTIR}), and (C/H) ratio as shown in Eqs. (1), (2) and (3). Therefore, the parameters such as (C/H) ratio, carbon aromaticity index and molecular weight can be calculated based on the results of LC transformation experiments, and a series of asphalt molecular models can be constructed.

$$Ar_C = 29.14 + 1.25 \times Ar_H \quad (1)$$

$$Ar_H = 9.89 + Ar_{FTIR} \quad (2)$$

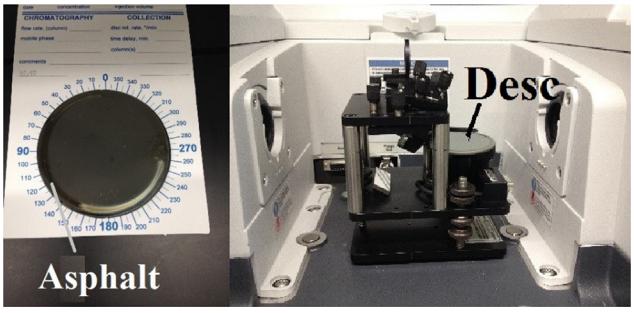

Fig. 1. LC Transform plate and FTIR test.