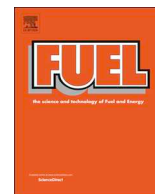




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Full Length Article

Molecular weight distribution of asphalt binders from Laser Desorption Mass Spectroscopy (LDMS) technique and its relationship to linear viscoelastic relaxation spectra

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ABSTRACT

Asphalt binder is a complex viscoelastic hydrocarbon, whose performance depends upon interaction between its physical and chemical properties, both of which are equally important to the successful understanding of the material. In this research effort, a physico-chemical relationship is developed by utilizing the technique of Laser Desorption Mass Spectroscopy (LDMS) to relate the molecular structure of asphalt binders to its viscoelastic properties. The molecular weight distribution (MWD) data obtained from the LDMS technique is used to develop a relationship between number average molecular weight and width of relaxation spectrum of asphalt binders obtained from linear viscoelastic characterization using dynamic shear rheometer. The relationship shows that as the molecular weight of asphalt binders increase, they require more time to relax the developed stresses. Also, the shape descriptors of the molecular weight distribution suggest that asphalt binders possessing greater asymmetry and kurtosis require more time to relax the developed stresses.

1. Introduction

Complex organic composites such as asphalt and polymers are made of up combinations of molecules of varying weight and complexity. The relative contribution of each of these molecules to the overall composite composition is captured by measuring and quantifying the individual or cumulative distribution of weights in these composites. These molecular weight distributions (MWD) represent a fundamental compositional characteristic of these materials and ultimately govern many of their mechanical and chemical properties. While the molecular weight distribution of polymers is well established, there has been relatively less interest in examining the molecular weight distribution of asphalt and much less its association to linear viscoelastic (LVE) behaviors. In this study, effort is made to relate the LVE properties, specifically the relaxation properties, of asphalt binders to their molecular weight distribution. While studies specifically relating molecular weight of asphalt or its subfractions to LVE properties are limited (Branthaver et al. (1992) [1], Petersen et al. (1994) [2] and Branthaver et al. (1996) [3]), those that attempt to relate molecular structure of asphalt to its LVE parameters are well established (Christensen and Anderson (1992a) [4] and Leseur et al. (1996) [5]). Though the structure of asphalt is not universally agreed upon, there exist two primary models,

the dispersed polar fluid (DPF) model and the colloidal model.

The DPF model theorized by Christensen and Anderson (1992a) assumes asphalt as a single-phase system and that the mechanical properties of asphalt are dependent not upon the relative abundance of dispersed and continuous phases, but upon the magnitude and dispersion in molecular weights as well as intermolecular forces. Based on the assumption of the DPF model, the authors present a mathematical model for describing the linear viscoelastic behavior of asphalt binders and subsequently develop a series of empirical chemical-physical property relationships. These relationships relate the chemical compositions of these binders to the viscoelastic model parameters. The authors argue that while the relationships are semi-empirical in nature and cannot be used for engineering design purposes, they are useful for a semi-quantitative evaluation of the effect of chemical compositional parameters on the mechanical behavior of asphalts and thereby predict the performance of a given asphalt. One of the behaviors that this model helps to explain is the temperature and rate of loading dependence of the modulus. The model postulates that the viscoelastic properties of asphalts are the result of the polar-polar interactions of the asphalt molecules. These weak interactions might be broken through action of heat or shear forces, explains why asphalt behaves as a Newtonian fluid at elevated temperatures.

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Another structural model is described by Leseur et al. (1996) and is based on assuming a colloidal structure for bitumen. Based on this assumption, the authors developed their own set of physico-chemical relationships. They stated that the existing models used time-temperature superposition principle (TTSP) to develop mastercurves for storage and loss modulus and subsequently derive relationships based on parameters used to derive these mastercurves, an example of which is the model presented by Christensen and Anderson discussed above. Leseur et al. use phase angle mastercurves to show that TTSP holds good only at low temperatures but fails at higher temperatures especially in asphalt which have high asphaltene contents and which contain high crystallized fractions. While both molecular structures and the subsequent physico-chemical models developed have gained acceptance, in the current study, credence is given to the DPF model which assumes that mechanical properties of asphalt are based on dispersion in molecular weights, in other words, molecular weight distribution.

An important aspect to understanding the mechanisms and therefore the rheology from the perspective of the DPF model is quantification of the molecular weight distribution of asphalt. Traditionally, the molecular weight distribution of asphalt binders has been characterized using chromatographic and mass spectroscopic techniques such as size exclusion chromatography (SEC), gas permeation chromatography (GPC), plasma desorption mass spectroscopy (PDMS) (Domin et al. 1999 [6], Branthaver et al. 1993 [7]). Strategic Highway Research Program (SHRP) projects of the early 1990's used Vapor pressure osmometry (VPO) to obtain the number average molecular weight (Branthaver et al. 1993 [7]). In SHRP study, it was reported that, the solvent pyridine formed molecular associations with polar asphalts thereby resulted in a higher number for molecular weights. While there are some limitations with techniques such as VPO, all techniques are still very much in use.

In this study, an alternative approach for mass spectroscopy, Laser Desorption Mass Spectroscopy (LDMS) has been used to obtain MWD and subsequently molecular weights of asphalt. The molecular weight distribution obtained from the LDMS technique is based on the relative abundance/intensity of the molecular mass of each molecule that makes up the analyte (Hillenkamp 1986 [8]). The analyte in the current study refers to asphalt. The method popularly known as Matrix Assisted Laser Desorption and Ionization (MALDI) gained popularity in the field of bio-chemistry and soon found its way into asphalt science, wherein the researchers used it both with as well as without the use of ionizing matrix. The latter process was termed as Laser Desorption Mass Spectroscopy (LDMS) (Lazaro et al. 1997 [9], Fannesbeck 1997 [10], Domin et al. 1999 [6]).

As mentioned earlier, the main objective of the study is to relate the relaxation properties, of asphalt binders to their molecular weight distribution. In the case of the viscoelastic materials when stress is applied, some energy is stored in the material during deformation and is used for returning to equilibrium state whereas as some energy is dissipated as heat. The time taken for the material to relax (reach equilibrium) is called the relaxation time. The distribution of these relaxation times is the relaxation spectra. A broader relaxation spectrum implies a material will require more time to relax the stress, and a narrower spectrum suggests that a material will relax the induced stresses faster. The theoretical interest in calculating relaxation spectra is based on the supposition that it provides insights to dynamics of molecular structure, which includes the molecular weight distribution, branching, and network formation. (Malkin, 2006 [11]).

The approach undertaken in this study to meet the study objectives is to first establish the linear viscoelastic properties of the study asphalts, deduce the relaxation parameters and subsequently develop the relationship between these parameters to the molecular weight distribution and the subsequent molecular weights calculated from LDMS.

The remainder of the paper is segmented as follows: First, the materials used in the study are discussed. Followed by the description of experimental methods used to obtain molecular weight distribution and

Table 1
Asphalt Binder Grades Used in the Current Study and their Notations.

Group	Supplier	Grade	Group	Supplier	Grade
1	X	PG 76-16	2	X	PG 64H-22
		PG 70-16			PG 64V-22
		PG 76-16			PG 76-22
	Z	PG 64-22		PG 70H-16	
		PG 70-22		PG 70V-16	
		PG 70-10			
		PG 76-16			

the relaxation spectra. Next, the results from these tests and the subsequent relationship between MWD and relaxation spectrum and the overall conclusions from the study are presented.

2. Study materials

For this study 12 asphalt binders have been sourced from the three asphalt suppliers in Arizona. Seven of the 12 binders are non-polymer modified (referred to as the Group 1 Asphalts) and five are polymer modified (referred to as the Group 2 Asphalts). All asphalt binders from supplier X are based out of crude from Canadian Bow River. The non-polymer modified binders of supplier Y are based on Western Canadian Select (WCS) crude, where as its polymer modified binders are a blend of WCS and West Texas Intermediate (WTI). The origins of supplier Z's asphalts are unknown. All 12 binders with their designations are presented in Table 1.

While the polymer used in PG 64(H,V)-22 and PG 70(H,V)-16 is SBS, the type of SBS and its dosage is proprietary to the supplier. However, since PG 76-22 is a specification binder in state of Arizona, details regarding its composition are available. The binder has 8–10% of digested crumb rubber, along with 3% of SBS.

All asphalt binders were subjected to short term aging using Rolling Thin Film Oven (RTFO) and subsequently long-term aging using Pressurized Aging Vessel (PAV) at 110 °C. The short-term aging in RTFO was conducted in accordance with AASHTO T 240, where in the samples are aged for a period of 85 minutes at a temperature of 163 °C and air flow rate of 4l/min. After short term aging, the asphalt binder samples were aged in a pressurized aging vessel (PAV) to simulate long term aging. The samples were aged for 20 h at 110 °C, and 2.1 MPa pressure.

3. Experimental methods

3.1. Laser Desorption Mass Spectroscopy (LDMS)

An Applied BioSystems LDMS instrument, MDS SCIEX, shown in Fig. 1 was used in the current study. The laser employed was a Nd:YAG laser, 355 nm wavelength and the data was collected MS Linear mode with an ion path length of 150 cm. In the following paragraphs, sample preparation techniques along with techniques to obtain distribution spectra with good signal to noise (S/N) ratio are discussed.

3.1.1. Sample preparation

Before carrying out the experiments on the binders, a pilot study was carried out by performing trials to identify the most suitable method for preparing LDMS specimens. These trials included testing binders at different dilution ratios, both with and without use of matrix. The matrices and their preparation methods are presented in Table 2 below. The dilution ratios and the binders used for evaluation are presented in Table 3. Please note the binders used for the evaluation do not belong to this study. The attributes that were evaluated among the different methods included the general shape of the spectra, the signal quality, and noise. After evaluating the different matrices and dilution ratios, it was decided that a dilution level of 125 mg/ml will be used for

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