Rheological analysis of the low-temperature dynamics of bitumens

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ABSTRACT

The low-temperature rheology of twenty-seven unmodified bitumens was studied using a 4-mm parallel plate geometry on a dynamic shear rheometer with torsional instrument compliance corrections. The collected data were analyzed by using advanced rheological analysis techniques, part of which were adopted from the field of glass rheology.

INTRODUCTION

The low-temperature thermal cracking performance of asphalt pavements is largely governed by the properties of the bituminous binder[1]. Therefore, it is important to characterize the rheology of bitumen at low temperatures. The low-temperature properties of bituminous binders have been traditionally measured by a bending beam method or by various forms of fracture testing. In 2010, Sui et al.[2] proposed a novel technique for measuring these low-temperature rheological properties with small amounts of material. This measurement method, often referred to as “4-mm DSR”, uses a 4-mm diameter parallel plates on a dynamic shear rheometer (DSR) with instrument compliance corrections, following the ideas originally put forward by Schröter et al.[3]. This technique has earlier been successfully applied for the low-temperature rheological characterization of various types of bituminous materials.

However, because of the newness of the 4-mm DSR technique, only little data is available in the contemporary literature that has been produced by this method. Consequently, analysis techniques used to process this type of data are still not fully developed. This contribution reports perhaps the most extensive set of 4-mm DSR data in the current literature and introduces and discusses associated analysis techniques. The aim is to extract fundamental information about the low-temperature glassy dynamics of bitumen and to provide a framework for future studies that will investigate the low-temperature rheological properties of bituminous materials. In particular, bitumen is here considered to be a chemically and structurally complex glass-forming liquid and, subsequently, some concepts adopted from the field of glass rheology are introduced and applied in this contribution.

MATERIALS AND METHODS

Materials

Twenty-seven bitumen samples originating from various crude oil sources and produced with various refining methods were investigated. None of these bitumens was modified by polymers or by special chemicals. However, it is worth noting that some of them contained a significant amount of natural wax, while others were non-waxy. A detailed description of the physical and thermal properties of the bitumens is given elsewhere[4,5].

Rheological measurements

The rheological properties of the investigated bitumens were measured with a stress-controlled Malvern Kinexus Pro rheometer using a 4-mm diameter parallel plate geometry and a 1.75-mm gap. The rheometer was equipped with a Peltier plate and active hood and a Julabo CF 41 refrigerated circulator to facilitate accurate temperature control of the test specimen down to -40 °C. Linear viscoelastic frequency sweep measurements were performed from 10 to 0.01 Hz in the temperature range of 10 to -40 °C with 10 K increments. The measured data were corrected for torsional instrument compliance ($J_{instrument}$ = 0.00964 rad N^{-1} m^{-1}) following the procedure of Schröter et al.[2]. The details of the specimen preparation, test procedure and instrument compliance correction are described elsewhere[5].

In addition, 8-mm and 25-mm diameter parallel plate geometries were used to perform linear viscoelastic frequency sweep measurements (0.01 to 10 Hz) at higher temperatures (up to 110 °C in the case of the stiffest bitumens). These experiments were performed on a stress-controlled Paar Physica MCR 500 rheometer, equipped with a double Peltier temperature control system. The main purpose of these experiments was to extend the experimental temperature range in order to facilitate the construction of master curves over a wide range of frequencies. The details of the specimen preparation and testing procedure are given elsewhere[4].

Rheological data analysis and plotting was performed with the Interactive Rheology Information Systems (IRIS) software[6].

SUMMARY OF THE RESULTS

Van Gurp-Palmen (vGP) plots[7] $\delta(\log|G^*|)$ are used to investigate the thermorheological simplicity/complexity of the investigated bitumens. It is found that the low-temperature frequency sweep data of each bitumen form a continuous, temperature-independent curve in this plot, irrespective whether or not the sample contained wax. Further, this indicates that bitumen is a thermorheologically simple material at least at and below 10 °C and, consequently, the time-temperature superposition (TTS) principle is valid. However, it is observed that at higher temperatures the TTS principle fails in waxy bitumens, notably because of the melting/crystallization of bitumen wax[4,8,9].

It is also learned from the vGP plots that the glassy modulus G_g values vary only slightly among the investigated bitumens, being in the range of 1-1.35 GPa. Similar G_g values have been reported for bitumen by various other researchers (see e.g. Lesueur[10] and the citations therein).

When the master curves of dynamic material functions (storage modulus G', loss modulus G'' and loss tangent $\tan\,\delta$) are constructed from the low-temperature frequency sweep data, it is observed that also small modulus (vertical) shifts b_T are needed to obtain smooth master curves below the glass transition temperature (T_g). However, the nature of modulus shifting is not yet clearly understood. Moreover, it is demonstrated that the Cole-Cole plot[11] $G''(G')$ is a more sensitive tool for detecting the need of modulus shifts in the glassy regime – and also for performing the actual shifting – than the vGP plot.

It was observed that, as expected[12], the Williams-Landel-Ferry (WLF) equation[13] is not suitable for describing the temperature dependence of frequency shift factors a_T below T_g. However, as suggested by Rowe and Sharrock[14], the Kaelble[15] modification of the WLF equation (Eq. 1) can be used to model the temperature dependence both above and below T_g.

$$\log a_T = -c_1 \left(\frac{T - T_d}{c_2 + |T - T_d|} - \frac{T_r - T_d}{c_2 + |T_r - T_d|} \right) \qquad (1)$$

where c_1 and c_2 are fitting parameters, T_d is the defining temperature at which the curvature of the shift factor curve changes, and T_r is the reference temperature. It is found that this equation fits accurately with the experimental shift factor data over the entire experimental temperature range (in this case T_g-30 K to T_g+115 K). However, it is acknowledged that in this study the test specimens were not aged into equilibrium near to and below T_g, and it is expected that frequency shift factors would be a bit different if the aging times were prolonged.

Further, by using the equations developed by Laukkanen[5], the values of the parameters in Eq. 1 are used to determine the dynamic fragility m and apparent activation energy E_g at T_g of the investigated bitumens. These parameters are used to describe the temperature dependence of the dynamics at T_g. It is shown that m and E_g are strongly positively correlated with T_g (R^2 = 0.94 and R^2 = 0.95, respectively). Moreover, it is observed that the T_g dependence of m is significantly higher in bitumen than in any previously studied glass-forming liquid[16], the slope of m with respect to T_g being approximately 0.74.

Finally, the relaxation time spectra $H(\tau)$ of the studied bitumens are calculated using the method of Baumgaertel and Winter[17,18]. It is found that at short relaxation times τ (in the glassy regime) bitumen is, similarly to the previously studied glass-formers[19], described by a powerlaw spectrum with positive exponent. However, the spectrum of chemically and structurally complex bitumen is not abruptly cut off at long relaxation times, as is the case with monodisperse glass-formers[19], but is rather characterized by a broad cutoff. Consequently, a new model is proposed to describe the relaxation time spectrum of bitumen. A tentative fit of the proposed model is shown in Fig. 1 with experimental data. Moreover, this type of spectrum is speculated to be universal for polydisperse glasses; however, more research is needed to validate this hypothesis.

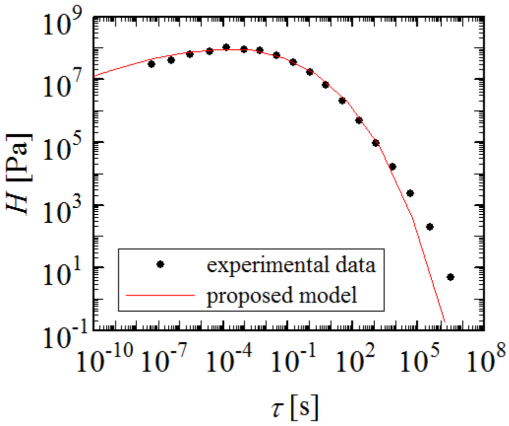

Figure 1. Tentative fit of the proposed model for describing the relaxation time spectrum of bitumen.

CONCLUSIONS

This contribution investigated the low-temperature rheology of unmodified bitumens by means of the 4-mm DSR technique. It was found that bitumen is a thermorheologically simple material at low temperatures (≤ 10 °C). However, small modulus shifts are needed to apply the TTS principle, as evidenced by the Cole-Cole plot. The frequency shift factors were observed to accurately follow the Kaelble-WLF equation at least in the temperature range of T_g-30 K to T_g+115 K. Further, positive linear correlations of m and E_g with T_g were established. Finally, a new model was proposed to describe the relaxation time spectrum of bitumen.

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