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Rheological characterization of wax modified bituminous binders: Effect of specimen preparation and thermal history

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HIGHLIGHTS

- Effects of specimen preparation and thermal history on the rheology of wax modified binders were studied.
- The intactness of the microcrystalline structure largely affects rheological properties, especially at low strains.
- Manual handling of a specimen influences the microcrystalline network and thus rheological properties.
- The breakdown of the crystalline network structure is isothermally irreversible, but fully recoverable upon reheating.
- These findings help to develop improved guidelines for the rheological testing of wax modified binders.

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ABSTRACT

The use of synthetic waxes in bitumen modification has recently become increasingly popular due to its potential as warm mix additive and its ability to improve the performance of asphalt binders and mixtures. This paper explores the challenges encountered in the rheological characterization of wax modified bituminous binders. A dynamic shear rheometer (DSR) is used to measure viscoelastic properties of wax modified binders, and the influence of specimen preparation is evaluated. The viscoelastic properties of wax modified binders were found to be highly sensitive to the loading method and thermal history of the test specimens. Furthermore, deviations in the rheological behavior of different test specimens were attributed to the stress–sensitive crystalline network structure of the wax additive. Based on the findings of this research, it is clear that more specific guidelines for the rheological testing of wax modified binders need to be developed in order to improve test repeatability and reproducibility and in order to better predict the performance of wax modified asphalt pavements.

1. Introduction

Wax additives are used in bitumen to improve the rutting resistance at high service temperatures [1–5], as well as the flow and workability [5–7] at paving temperatures. Wax additives can significantly reduce the asphalt mixing and pavement construction temperatures [8,9], creating remarkable environmental benefits to the asphalt industry [10]. It is mainly due to these environmental aspects that the use of commercial waxes in bitumen modification has vastly increased during the past decade [11,12].

Rheological studies of pure waxes can be found mainly in the dental literature [13,14] and in the literature related to the modeling of geological deformation processes [15–17]. McMillan and Darvell [13] attributed the lack of further study to the difficulties associated with their handling as the measured viscosities of various waxes have been shown to be highly sensitive to the stress history of the specimen [18]. Moreover, McMillan [14] concluded that the properties of waxes are so stress–sensitive that conventional rheometry is essentially impossible. However, due to the greatly enhanced sensitivity of modern commercial rheometers, it has become possible, at least in some cases, to characterize rheological properties of even very stress–sensitive waxes, as shown by e.g. by Petersson et al. [19]. Still, investigations that have taken full account of the need for consistent handling of specimens and steady flow, like the one by Darvell and Wong [20], are very scarce. What is more, problems e.g. with phase separation and wall slip

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have been encountered when trying to characterize the rheological properties of waxy crude oils under certain testing conditions [21,22].

As compared to pure waxes, the rheology of wax modified bituminous binders has been characterized much more extensively [1–6,12,23–27]. However, despite the large amount of research dedicated to the rheological analysis of these materials, only a very limited number of investigations concern the dependence of these test results on specimen handling prior to the testing. Soenen et al. [28–30] pointed out that rheological properties of various modified binders, including wax modified binders, are highly dependent on their thermal history and storage prior to the testing. Furthermore, they concluded that deviations in the rheological data of wax modified binders are related to the crystallization (or melting) of wax. In addition, Soenen et al. [31] have indicated that there are serious concerns regarding the repeatability and reproducibility of the multiple stress creep recovery (MSCR) test results for modified binders, including wax modified binders.

As wax modified bituminous binders are becoming ever more important to the paving industry due to the booming popularity of the warm-mix asphalt (WMA) technology, this paper aims to underline the great importance of proper specimen preparation techniques with respect to their rheological testing. In this study, different methods are used to prepare specimens for rheological testing and deviations in the test results are interpreted by changes in their expected microstructure. Frequency sweep, strain sweep, time-resolved mechanical spectroscopy (TRMS) and MSCR measurements are used to characterize the influence of specimen preparation on the viscoelastic properties of the test specimens at a high in-service temperature of 50 °C. The significance of the observed differences in the test results is also discussed from a performance evaluation perspective. The authors want to emphasize that the primary aim of this paper is to raise critical discussion about the repeatability and reproducibility problems in the rheological testing of wax modified binders and, consequently, what this means in terms of pavement performance prediction. The development of final guidelines for the rheological testing of wax modified binders requires an extensive comparison between the laboratory test results and field performance of wax modified asphalt pavements, and thus it is not within the scope of this study. This study only focuses on the rheology of wax modified binders, but it can be expected that some of the observed effects may be more general and may also be observed when studying other types of modified bituminous binders. Results concerning the effect of processing and specimen preparation on the rheology of various polymer modified binders can be found elsewhere in the literature [28–30,32–34].

2. Experimental

2.1. Materials

For this research, various wax modified bituminous binders were produced by adding commercially available synthetic Fischer–Tropsch wax to various penetration grade bitumens while stirring them at 160 °C. The stirring temperature and time were fixed in order to keep the thermal histories of all samples as equivalent as possible, and they were selected so that homogeneous blends of bitumen and wax were obtained. Two unmodified penetration grade bitumens were added to this study for reference purposes. The conventional properties of the investigated wax modified and neat binders are presented in Table 1. The sample selection is based on two concentrations of wax, 3 and 5 wt%. Concentrations as high as 5 wt% were used to amplify the effect of wax on the sensitivity of asphalt binder rheology. For both wax contents, the grade of the base bitumen was gradually changed. This way of selecting samples allows establishing the characteristics determined by the base bitumen from those determined by the wax crystallinity. For example, it is already clear from Table 1 that the softening point ($T_{R\&B}$) of the binders containing 5% wax is almost fully determined by the wax and is rather independent of the base bitumen grade. In order to have an idea about the crystallization and melting temperatures of the wax, a Mettler Toledo differential scanning calorimeter (DSC1) was used. For the pure wax, the melting point of approximately 100 °C can be detected as a sharp peak in the DSC thermogram, see Fig. 1. When adding wax to bitumen, the crystallization temperature decreases slightly as can be observed in the thermogram of Fig. 2. Note the different scales on the *Y*-axes.

Table 1
Conventional properties of the investigated binders.

Binder code	Base bitumen[a]	Wax content (wt%)	Pen @ 25 °C (dmm)[b]	$T_{R\&B}$ (°C)[c]	Penetration index PI (-)[d]
B10/20	B10/20	0	20	62.4	−0.46
B50/70	B50/70	0	64	47.4	−1.31
B50-3W	B50	3	35	78.9	3.27
B70-3W	B70	3	40	75.4	3.10
B80-3W	B80	3	54	64.6	2.10
B120a-5W	B120[e]	5	60	96.7	6.82
B120b-5W	B120[e]	5	60	93.6	6.49
B140-5W	B140	5	63	94.8	6.76
B160-5W	B160	5	67	93.5	6.80
B180-5W	B180	5	74	96.9	7.46

[a] Penetration grade according to EN 12591 [35].
[b] Penetration according to EN 1426 [36].
[c] Ring-and-Ball softening point according to EN 1427 [37].
[d] $PI = (1952 - 500 * \log(Pen) - 20 * T_{R\&B})/(50 * \log(Pen) - T_{R\&B} - 120)$.
[e] These base bitumens are of the same penetration grade but from different material batches.

2.2. Rheological characterization

Rheological properties were measured with a stress-controlled Paar Physica MCR 500 rheometer equipped with a double Peltier temperature control system. Experiments include frequency sweep, strain sweep and MSCR tests, all at a constant temperature of 50 °C using a 25-mm parallel plate geometry and a 1-mm gap. Frequency sweep measurements were conducted at a strain amplitude of 0.1%. In addition, time-resolved mechanical spectroscopy (TRMS) experiments were conducted with a stress-controlled Malvern Kinexus Pro rheometer equipped with an active hood Peltier plate cartridge. In these measurements the temperature was also set at 50 °C and a parallel plate geometry with a diameter of 20 mm and a gap of 1 mm. The test temperature of 50 °C was chosen since it represents a typical high in-service temperature of asphalt pavements in the Nordic countries and Continental Europe. The correctness of the rheological data was verified by a careful analysis of the rheometer raw data and by visual inspection, and there were no indications of the occurrence of wall slip or edge fracture. Detailed descriptions of the testing conditions in each measurement are given in connection with the test results in the following sections.

2.3. Specimen preparation

Different techniques were used to prepare test specimens for the rheological measurements. In the first one, hot binder is poured into a silicone mold where it is allowed to cool down at room temperature, and afterwards the binder specimen

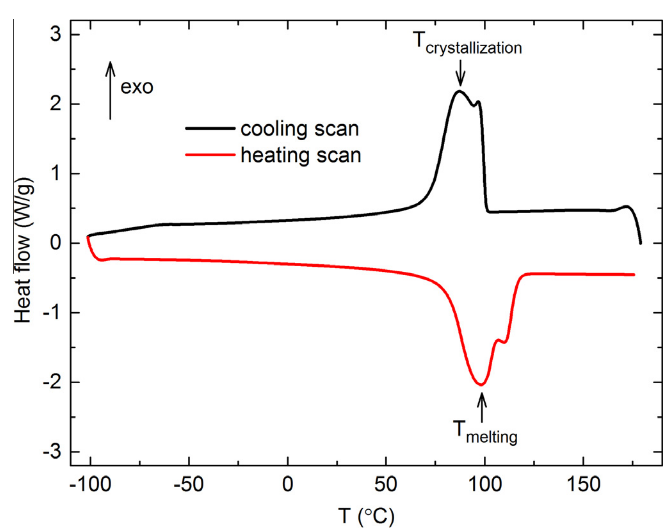

Fig. 1. DSC thermogram of the pure wax. The cooling and heating rate was 10 °C/min.