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Characterization of petroleum pitch using steady shear experiments

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ABSTRACT

Asphalt for highway and runway construction is processed by either air blowing or blending with different petroleum streams. In the blending process, petroleum pitch, a byproduct of solvent deasphalting of the vacuum residue is mixed with heavy extract to produce asphalt of the desired specifications. The rheological response of blended asphalt hence depends to a large extent on the constitutive property of petroleum pitch. In an aim to develop robust models for blended asphalt, modeling the mechanical behavior of petroleum pitch hence becomes necessary.

In this work reported here, petroleum pitch from crude sources such as Basrah Light, Arab Mix and Arab Light are subjected to steady shear for 99 min at temperatures ranging from 70 to 120 °C for different shear rates. Each of these material exhibited different stress overshoot and decay during steady shear depending on the temperature and shear rate. A viscoelastic fluid model of the rate type is selected to model the response of the material. Using the recent thermodynamic framework based on Gibbs potential proposed by Rajagopal and Srinivasa [27], restrictions on the proposed model are obtained. The rotational flow problem is solved and the material parameters are estimated. The model predictions are corroborated with the experimental observations and they are found to be reasonably good.

1. Introduction

It is well known that most of the highways and runways throughout the world use asphalt as the key material in construction. Asphalt, the binder is a refinery processed material and is quite complex in its rheological response [17,18]. The influence of crude source and processing methods play a significant role in the mechanical and thermodynamic response of asphalt. Mainly, asphalt is produced from the petroleum crude residue from the bottom of vacuum tower either by air blowing or by blending with different petroleum streams. Each process is completely different and results in asphalt with widely varying rheological properties [15,28]. Since asphalt is produced based on the technical specification required (penetration at 25 °C or viscosity at 60 °C or performance-grade properties based on linear viscoelastic properties over a range of temperature), there has been little interest in the systematic characterization and quantification of the mechanical response of the material. The complexity of the physical and chemical characteristics of asphalt together with the widely varying field conditions (random traffic loading coupled with varying temperature regimes) are some of the reasons why these studies have not been attempted.

An interesting process related to asphalt production is the blending process. The residue from the vacuum fractionating tower in a refinery is subjected to different processes such that a variety of lower boiling point streams result. These

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processes can be normally classified under six heads. They are visbreaking, solvent deasphalting, delayed coking, fluid coking/flexicoking, fixed bed hydrocracking, and fluidized bed hydrocracking [29]. Our main interest here lies in the by-product of solvent deasphalting. In this process, the vacuum residue is contacted with a paraffin solvent. The portion of the residue which dissolves in the solvent is called as deasphalted oil and the rejected raffinate is called as petroleum pitch [29].

Petroleum pitch, over and above its use as a blending component finds application in various industrial products such as high-performance carbon–fibers, carbon–carbon composites, etc. In the literature, the phrase petroleum pitch is used generically (see for instance [31,25], for details). Typically, the nonvolatile product resulting from thermal or catalytic cracking of heavy petroleum or the high boiling point fraction obtained through vacuum distillation of catalytic cracking bottoms or the solvent deasphalted bottoms are classified together as petroleum pitch. Sometimes even the coal tar pitch which is a result of destructive distillation of tar is also classified as a petroleum pitch and some of the standard ASTM test procedures for measuring viscosity [10] do not distinguish the wide difference between these materials.

Petroleum pitch is a complex mixture of condensed aromatic compounds and is eutectic in nature. At ambient temperature, pitch behaves as a glassy solid and when heated in an inert atmosphere, it passes through a glassy region with no defined melting point to become a liquid. During the transition from solid to liquid, the viscosity of the pitch changes drastically and due to the difficulties associated with capturing the transition, petroleum pitch is normally characterized based on a *softening point*. This softening point is the temperature at which the petroleum pitch has a viscosity of about 10^3 Pa s. Due to the complexity of the material as well as due to the availability of wide variety of petroleum pitch, at least five different ASTM standard test methods are in vogue to measure this softening point [10]. The main characterization is only related to measurement of Newtonian viscosity in the range of softening point temperature using ASTM D5018 [2].

Petroleum pitches are thermally treated to convert them to a discotic nematic crystal state known as the carbonaceous mesophase [30]. Much of the literature available related to modeling the mechanical response of pitch focus only on these carbonaceous mesophase pitch (see for instance references such as [23,24,9,12,21,16,8,20,19]) due to the important industrial applications. However, one cannot say the same about the rheology of petroleum pitch with specific reference to its use as a blending component for production of asphalt. Few limited investigations, however, exists purely related to characterizing petroleum pitch. Turpin et al. [34] carried out controlled stress oscillatory tests and appealed to time–temperature superposition principle to explain the experimental data over a wide range of temperature. Fitzer and Kompalik [11] and later Khandare et al. [16] among many others have related the rheological properties of petroleum pitch with the mesophase pitch as the rheology of mesophase pitch depends on the degree of polymerization and the nature of the precursor material.

Our main interest in this investigation is to model petroleum pitch more due to its use as a blending component for asphalt. Table 1 shows the typical blending proportion used in Indian refineries equipped with solvent deasphalting unit to produce blended asphalt. Two different grades of asphalt, VG10 and VG30 are normally used for paving applications in India as per Indian standards BIS [4]. The ‘consistency’ of VG30 is slightly harder than VG10. This increased consistency is arrived at by increasing the dosage of petroleum pitch. Production of commercial asphalt is carried out by blending vigorously for few hours under inert atmosphere to make sure that the blends have ‘homogenized’.

Scant literature exist related to the rheology of blended asphalt. Also, most of the blending proportions arrived at are based on the specification limits to be achieved for the end product. For instance, Tabolina et al. [32] discuss an analytical expression for finding the softening point of the final blend based on the individual blend softening points. Rajan et al. [28] discuss in detail the various approaches for arriving at blend proportions and it is seen that all of them use the classical Arrhenius approach in some form or other [14].

From the perspective of developing constitutive relation for asphalt, the influence of production process cannot be neglected. In the air blowing operation discussed in the earlier paragraphs, the petroleum crude residue having lower viscosity is transformed into a material having higher viscosity. In the blending operation, the petroleum pitch having higher viscosity is transformed into a material having lower viscosity. The blowing and the blending operations aim to produce asphalt with some specified technical parameter at a given temperature. However, the manufacturing process in each case takes the material through a completely different thermal history resulting in diverse response at different testing conditions and temperature.

The requirement to have a robust constitutive model for asphalt which considers explicitly the production process need not be overemphasized. For instance, to develop a systematic understanding of blended asphalt, one needs to understand the rheology of petroleum pitch, heavy extract and the possible interactions between these two materials as a mixture. The issues related to whether these two constituents can co-exist as a mixture without any separation also needs to be looked into. To start with one can first develop a systematic model for petroleum pitch since the mechanical behavior of blended asphalt depends to a large extent on petroleum pitch. The focus of this work is just that.

Table 1
Asphalt blending proportion.

Asphalt grade (as per [4])	Petroleum pitch (% by weight)	Heavy extracts (% by weight)
VG10	87–88	12–13
VG30	91–92	8–9