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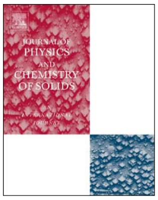

Tuning the glass transition of asphalt binder based on viscosity criteria under zero shear rates

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ABSTRACT

With the theory of absolute reaction rate or transition-state approach together with the boundary perturbation method we calculate the possible temperature-dependent viscosity of bitumen or asphalt binder via tuning of activation volume as well as activation energy for the first time under zero shear rates. Before we present our novel approach and numerical results we firstly verify our calculations with both ambient temperature and high temperature viscosity measurements for bitumen conducted previously. Our tuning activation volume of bitumen will be useful to the current needs of intelligent compaction and application of nanotechnology to easily handling or processing asphalt binder.

1. Introduction

Bitumen is the binder material of asphalt and the only material phase in asphalt exhibiting thermorheological properties. Sometimes bitumens as well as asphalts are seen as a colloidal suspension of asphaltenes. But the composition of asphalt varies with the source of the crude oil and the method of processing [1–11]. Asphalt is normally divided into four groups according to the chemical nature: saturates, naphthene aromatics, polar aromatics, and asphaltenes. The first three groups are usually lumped together under the name maltenes [1,2]. Bitumen also called asphalt binder (these two words will be used interchangeably throughout below), which comes from the process of fractional distillation of petroleum, is a complicated mixture of mainly hydrocarbons whose structure could be suitably described by the colloidal model: solid particles (the asphaltenes) with a radius of a few nanometres dispersed in an oily liquid matrix (the maltenes).

The chemical composition of bitumen is very complex in that it is composed of up to 106 different types of molecules, typically with molar masses above 200 g/mol. Bitumen is not chemically unique in the sense that its composition depends on the crude oil source, the age of the bitumen, and possible chemical modifiers. The functional chemistry includes heteroatoms such as sulfur and nitrogen, cyclic structures, aromatics compounds, and saturated hydrocarbons, and these enter larger and complicated molecular structures [1,2]. Bitumen plays important roles in some scientific applications. It can be used as the basic binding agent in asphalt concrete, as a key component in damping systems such as rubber, and as an indispensable additive in paint and ink. In pavement applications, asphalt is subjected to wide ranges of temperatures. To be specific the pavement temperature varies depending on the geographical location. During such temperature changes, the asphalt layers exhibit diverse responses and these can be viscoelastic solid-like material, viscoelastic fluid-like material, and brittle elastic material [12–16].

Nowadays, asphalt is frequently modified by blending it with various polymers. Nanomaterials were also used for the improvement in the performance of asphalt. Such modified asphalt has shear rheological properties that differ from the properties of the base asphalt. To be precise the activation energy will be varied after chemical modification [17–19] and then influence the viscosity of the modified material. Factors that contribute to the performance of asphalt include volatilization, oxidation, polymerisation and rearrangement of the physical structure [17–20]. The viscosity of asphalt relates to the mixing and compaction temperatures of asphalt mixtures and also determines the workability of asphalt binders. In fact asphalt binders are thermoplastic materials and their rheology is highly sensitive to temperature. Some of the binders are of PG 64-22 grade [13] for the comparison in this study. They exhibit semisolid behavior at ambient temperatures but can be made fluid-like by heating. High temperatures make them fluid enough to coat aggregates and they need to remain hot enough to minimize resistance as the asphalt-aggregate mixture is compacted in the laboratory or on the road.

Note that recent advances in intelligent compaction offer significant advantages for achieving targeted hot-mix asphalt density. Compaction is a densification process during which air voids are reduced by packing

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aggregates closer to each other. It is affected by asphalt viscosity because moving of aggregates requires flow of the asphalt binder films connecting the aggregates. Higher viscosity which implies resistance to flow results in more resistance to packing [21]. Meanwhile zero shear viscosity (ZSV) is being paid to more attention by researchers as a possible measure for the rutting resistance of modified asphalt binders [12]. Here ZSV, as it is a theoretical concept, is the viscosity measured in shear deformation, when the shear rate is almost zero. With such low shear rates, the binders undergo deformation so slowly, that it can adapt continuously to maintain equilibrium, despite the total amount of shearing being large because the corresponding viscosity is the highest.

While it is clear that asphalts need to be heated to reduce viscosity and thus enable mixing and compaction, the fluidity required for each process is not a simple matter [22]. For instance, asphalt rheology is sensitive to heat-catalyzed oxidation and to volatilization of lighter fractions. If heated too much, asphalts oxidize at such a high rate that hardening can cause significant damage. This means that to achieve a desired level of fluidity behind the paver unaged asphalts with similar initial rheology may have to be heated to different temperatures. Furthermore volatile emissions emanating from overheated mixtures may not be friendly to the environment. Most importantly, asphalt construction temperatures should not exceed what is necessary to achieve sufficient density and satisfy maximum moisture requirements. While there is agreement in the research community about the need for an *optimum fluidity temperature*, there is no consensus regarding answers to below two main questions: (i) What physical property controls the role of the binder for mixing and compaction of hot-mix asphalt (HMA)? (ii) What is the optimum fluidity (viscosity?) [23–26] for best-practice pavement construction?

Salomon et al. [20] introduced activation energy as the binder physical property best related to effective HMA mixing and compaction. When mixture compaction was investigated, the results indicated that the higher the activation energy for flow, the higher the compactive effort needed to achieve the same density. Production is challenging owing to the immobile nature of heavy oil and bitumen and reducing the in-situ viscosity of the oil is considered as the main objective of any recovery process [23–26]. However at temperatures just above the glass transition temperature, materials behave differently: Once the temperature increases just above the transition temperature, some have a much more drastic decrease in the viscosity than others. These materials become more fluid-like more rapidly than the others, as if the physical bonds that were causing the solid-like state below the transition temperature were breaking apart quickly.

In this short paper we shall demonstrate the tuning of glass transition [13,27] for bitumens or asphalt binders by either activation energy [17–20] and activation volume which is related to compaction considering bitumen's viscoelastic nature via its thermal properties. Our focus will be the temperature-dependent bitumen viscosity under zero shear strain rates in nanodomains which are presumed to be cylindrical or via nanotechnologies [25] by using the verified absolute reaction theory or transition state theory [22] which originates from the quantum chemistry approach [34,35]. We noticed that, in linear Styrene-butadiene-styrene polyblock copolymers (SBS), two polystyrene blocks are positioned at the ends of an elastomeric block (polybutadiene) [36]. Polystyrene has a glass transition temperature of about 368.15 °K while the elastomeric block (of rubber) has a glass transition temperature of about 193.15 °K. This difference in the glass transition temperatures of the building blocks of SBS makes this polymer very interesting for asphalt modification [36].

2. Theoretical formulations

We shall adopt the quantum chemistry approach [34,35] to handle asphaltic bitumens. The majority of asphaltic bitumens contain substances which are insoluble in low-molecular aliphatic hydrocarbons, and which when heated do not soften, but decompose, swell, and finally sinter together. This fraction is generally called the asphaltene fraction, as distinguished from the soluble or maltene fraction consisting of heavy, purely viscous oil. The asphaltenes in all probability consist of high-molecular hydrocarbons of a predominantly aromatic character, with a comparatively low hydrogen content, formed by condensation and dehydrogenation from aromatic-naphthenic hydrocarbons of lower molecular weight. As a result some oxygen, some sulfur, and a still smaller quantity of nitrogen are present. Thus the mechanical response of asphalt is highly susceptible to temperature change [36,37]. Asphalt exhibits a Newtonian response at high temperatures, say, approximately above 393.15 °K, a viscoelastic response at intermediate temperatures, say, approximately between 293.15 and 343.15 °K, and glassy behavior below glass transition temperature [1,2,5,13,38]. Here we adopt one common definition for the glass transition temperature [13,27,38]: Glass transition temperature (T_g) is defined as the temperature at which the viscosity of the material reaches 10^{12} Pa s.

Before we introduce the Eyring's approach we like to emphasize that Eyring's approach has been successfully applied to high-temperature regimes like solid metals [31], molten metals [34], etc. The Eyring's theory states that in order for a liquid molecule to move, the other surrounding molecules must move into the adjacent vacant sites or holes to create a free space for the molecule to enter [22]. Meanwhile an activation energy is required to break the energy barrier and it is the minimum energy needed to flow. The viscous flow of any liquid can be generally regarded as a thermally activated process. At a higher temperature, the liquid molecules have higher thermal energy so that they can more easily overcome an energy barrier and move into the adjacent vacant sites. Roughly a molecule moves approximately one molecular distance, κ, into a neighbouring hole in the liquid. Nevertheless once no external force is applied, the number of times per second that molecules passes over the energy barrier and hence moves in either direction, i.e, their diffusion rate, is given by $\nu_d = B_0 \exp[-\Delta E/(k_B T)]$. Here ΔE is the activation energy for flow, k_B being the Boltzmann constant, T being the absolute temperature, and B_0 contains the ratio of the partition functions of the activated and initial state [32,33].

With the Eyring's absolute reaction model or transition-state approach [31–35] together with considering the stress-biased thermal activation, structural rearrangement is associated with a single energy barrier (height) ΔE that is lowered or raised linearly by a shear (yield) stress τ. If the transition rate is proportional to the shear strain rate ($\dot{\zeta} \equiv (\tau_e/\eta_n)\sinh(\tau/\tau_e)$ with a constant ratio: $K_0 \approx 2V_v/V_m$ where τ_e is the Eyring stress, η_n is the low shear rate Newtonian dynamic viscosity of the material), we can calculate the shear stress [39–41]

$$\tau = 2\left[\frac{\Delta E}{V_v} + \left(\frac{k_B T}{V_v}\right)\ln\left(\frac{2\,\dot{\zeta}}{K_0 \nu_0}\right)\right], \tag{1}$$

where $V_v \equiv \kappa\kappa_2\kappa_3$ is the activation volume, $V_m \equiv \kappa_2\kappa_3\kappa_1$ is the flow volume, $\kappa_2\kappa_3$ is the area of the flow unit in the shear plane [31–34]. $\dot{\zeta} = 2\nu_d(\kappa/\kappa_1)\sinh[\tau V_v/(2k_B T)]$ is also the rate of shear corresponding to the velocity with which one molecular layer slips over the other divided by κ_1, the distance between layers, ν_0 is an attempt frequency [31–35], e.g., for temperatures (T) being within the range of the order of the magnitude: $T \sim O(1)$ K (kelvin): $\nu_0 \approx k_B/h \sim O(10^{11})$ (1/s) with h the Planck constant. Normally, the value of V_v is associated with a typical volume required for a molecular shear rearrangement.

We consider a steady, fully developed transport of the locally amorphous asphalt under high pressure loading in a wavy-rough nanotube of a_0 which is the mean-averaged outer radius with the outer wall being a fixed wavy-rough surface: $r = a_0 + \epsilon \sin(k\theta)$ where ϵ is the amplitude of the small wavy roughness and k is the wave number: $k = 2\pi/\lambda_w$ with λ_w being the wave length. We can obtain

$$\dot{\zeta} = \dot{\zeta}_0 \sinh(\psi) + \text{HOT} \tag{2}$$