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Full Length Article

Evolution of molecular packing and rheology in asphalt binder during rejuvenation

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ABSTRACT

Effective rejuvenators that restore the thermo-mechanical properties of aged asphalt would extend pavement service life and increase utilization of recycled material, cutting material and environmental costs. However, the efficacy and mechanism of action need to be characterized in order to optimize rejuvenator formulation and dosage. This study introduces the RIPS method (**R**ejuvenation **I**ndex based on **P**olydispersity and **S**tiffness) which applies rheological characterization to build a simple model for examining and predicting the effect of rejuvenation on the rheology, polydispersity, and microstructure of aged asphalt binder. RIPS showed that addition of a specific bio-rejuvenator significantly improved the low-temperature properties of highly aged binder. The method accurately predicted the binder relaxation modulus and could calculate the exact rejuvenator dosage needed to restore the performance grade to specification. The rejuvenation mechanism was further examined using DSC, FTIR, and quantum level computational modeling, which found that polar chemical groups in the bio-rejuvenator could be responsible for solubilizing similar polar groups in aged binder leading to reduced molecular aggregate size and restoration of the thermo-mechanical properties of aged binder. These results provide insight into the molecular mechanisms of rejuvenation and offer a path towards more rational design and deployment of rejuvenator formulations.

1. Introduction

As a result of global environmental awareness and a national movement toward more sustainable infrastructure materials, the reuse of oxidized asphalt from reclaimed asphalt pavement (RAP) and recycled asphalt shingles (RAS) has been promoted by the US Department of Transportation to reduce the carbon footprint of highway pavements. In addition, fluctuations in price and availability of quality asphalt binder and aggregates have encouraged asphalt contractors to increase their level of recycling to reduce consumption of virgin asphalt while increasing profit margins. However, the asphalt binders in RAP and RAS are highly oxidized, leading to greatly reduced toughness and compliance. Therefore, effective rejuvenators capable of restoring properties of aged asphalt are of significant interest. However, there might be variation between batches of RAP/RAS depending on the original material source, duration of service, and environmental conditions of aging [1–4]. Adding an inappropriate amount of rejuvenator could result in material that is too stiff or too compliant. Thus, there is a need for a simple method to determine the optimal rejuvenator dosage required to achieve specific material performance targets and avoid waste. In addition, the development and deployment of more effective rejuvenating agents requires a better understanding of the rejuvenation mechanism in terms of its impact on microstructure and molecular conformation and how those characteristics are reflected in thermo-mechanical properties.

The method of time-temperature superposition (TTS) is well established in rheological theory [5–7] and overcomes the difficulty of extrapolating limited laboratory tests at shorter times to longer term, more real-world conditions. The basic assumption underlying TTS is that in a series of relaxation or retardation mechanisms, a change of temperature multiplies all relaxation or retardation times by the same factor. TTS or time physical hardening time superposition (TPHTS) applies to thermorheologically simple asphalt binders, but even for non-simple binders such as those with moderate to large amounts of polymer, TTS and TPHTS tend to still hold at temperatures roughly below 20 °C. Both temperature and physical hardening are reversible processes and the shift factors are based on temperature or physical hardening time, respectively.

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Similar to TTS, time-concentration superposition (TCS) assumes that a change in concentration from C_o to C changes the characteristic relaxation time from τ_{Co} to τ_C, leading to a concentration shift factor, $a_C = \tau_{Co}/\tau_C$ [8]. TCS was initially considered for this study, but both oxidative aging and the addition of a rejuvenator are non-reversible and substantially change the composition and microstructure of the binder. The rejuvenation effect is thus not a case of simple dilution; not only the temperature shift factor but also the shape of the master curve is affected, and a more rigorous analysis is necessary.

This paper introduces a new method rooted in rheometry to examine the rejuvenation mechanism, while also exploring the microstructure of aged asphalt before and after rejuvenation. The RIPS method proposed herein applies the Christensen Andersen (CA) model [9] to describe the complex shear modulus (G^*) in terms of two parameters, the crossover frequency (ω_c) and crossover modulus (G_c^*) that describe the shift factor and shape parameter, respectively, of the master curve. The dependence of these parameters on rejuvenator concentration describes the rejuvenation effect. In polymer rheology, G_c^* is occasionally used as a measure of molecular weight polydispersity [10,11], although this relationship is not necessarily valid for other polymers [12]. A relationship between G_c^* and polydispersity has also not been clearly demonstrated for asphalts; however, polydispersity has been used to demonstrate a shift in the sol/gel transition of some asphaltene-rich asphalts [13] and of a polyphosphoric-acid-treated asphalt [14]. In conjunction with physiochemical characterization and computational molecular modeling, the RIPS method offers a new way to understand not only the effect of rejuvenators on asphalt rheology but also binder micro-structuring and polydispersity.

2. Experiment and computational details

2.1. RIPS method

The Christensen Anderson (CA) model of the complex shear modulus (G^*) relates the frequency dependence of G^* to the glassy modulus (G_g), ω_c, and the rheological index (R):

$$G^*(\omega) = G_g\left[1 + \left(\frac{\omega_c}{\omega}\right)^{\frac{\log 2}{R}}\right]^{\frac{-R}{\log 2}} \quad (1)$$

The crossover frequency (ω_c) and the crossover modulus (G_c^*) are defined as the point where the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ intersect (where the phase angle is 45°). ω_c can be considered as a scaling or shift factor that moves the master curve left or right on the frequency axis. G_g represents the limiting complex modulus for a given asphalt cement at low temperatures or high frequencies. Accurate determination of G_g is difficult, but it is generally estimated to be 1 GPa for most asphalts [15]. R is defined as the difference between $\log(G_g)$ and $\log(G_c^*)$. In the CA model, R is considered the shape parameter of the G^* master curve. If G_g is assumed to be constant, then the CA model simplifies to a function of two parameters, ω_c and G_c^*, that describe the shift factor and shape parameter, respectively, of the master curve. Based on the model defined above, a larger value of R (and by extension G_c^*) correlates to a broader relaxation spectrum.

The first step in the RIPS method is evaluation of G_c^*. For a thermorheologically simple binders, a black space plot is typically used to determine G_c^*, that is temperature independent in these systems. Black space plots of the aged and rejuvenated binder are reasonably simple, and superposition appeared to be applicable. G_c^* and ω_c at 0, −15, and −30 °C were determined by applying the Baumgärtel and Winter [16] relaxation spectrum, which is available through the RHEA™ software package.

The next step is to plot G_c^* and ω_c in logarithmic space. It was initially hypothesized that such plot would be linear based on a linear logarithmic relationship reported by Farrar et al. [17] for several oxidatively aged binders. The empirical power law relationship is of the form

$$\omega_c = A(G_c^*)^B \quad (2)$$

A common slope (B) and temperature-dependent power law coefficient (A) were determined using EXCEL™ solver. For this material, a common slope $B = 5.43$ was calculated. The temperature dependence of ω_c is determined by plotting the $\log(A)$ versus temperature, which in this case can be fit well with a simple linear fit. The relationship between G_c^* and rejuvenator concentration can also be described by a simple linear fit.

The final step is to apply these relationships to the CA model assuming G_g is essentially unchanged by rejuvenator concentration. For a desired rejuvenator concentration and temperature, G_c^* and A are calculated from the empirical linear functions determined above, and ω_c is then calculated from equation (2). Once values for G_c^* and ω_c are determined, then the CA model is used to determine $G^*(\omega)$. The phase angle $\delta(\omega)$ can be approximated as the first derivative of the log $G^*(\omega)$ with respect to $\log(\omega)$. This is based on the Booij and Thoone [18] approximation from Kramers-Kronig relations [19] connecting the real and imaginary parts of certain complex functions. In terms of the CA model [9], the Booij and Thoone approximation can be written as:

$$\delta(\omega) = \frac{\pi}{2}\left(\frac{d\log|G^*(\omega)|}{d\log(\omega)}\right) = \frac{90}{\left[1 + \left(\frac{\omega}{\omega_c}\right)^{\frac{\log 2}{R}}\right]} \quad (3)$$

The storage modulus $G'(\omega)$ is determined by direct conversion of $G^*(\omega)$ and $\delta(\omega)$. $G'(\omega)$ is then interconverted to the relaxation modulus $G(t)$ using the approximate expression developed by Christensen [20].

$$G'(\omega) = G^*(\omega)cos(\delta) \quad (4)$$

$$G(t) \approx G'(\omega)|_{\omega=2/\pi t} \quad (5)$$

2.2. Experimental characterization

2.2.1. Materials

The neat asphalt binder selected for this study is a Superpave PG 64-22 (Sharpe Brothers, Greensboro, NC), a binder grade commonly used across the U.S. The rejuvenator studied was derived from a bio-oil produced by hydrothermal liquefaction of swine manure as described elsewhere [21]. This rejuvenator has previously been shown effective at restoring the rheological properties and surface microstructure of both laboratory-aged and field-aged asphalt binders [22]. This rejuvenator is composed of a mixture of different compounds, many of which are surfactant-like compounds such as alkyl amides and alkyl carboxylic acids. FTIR of the rejuvenator and molecular models of selected compounds are provided in Section 3.

The neat binder was aged in the laboratory following the method documented by Bowers et al. to produce a binder resembling field-produced RAP in terms of an FTIR-measured aging index [23]. This method combines rolling thin film oven (RTFO) aging and Pressure Aging Vessel (PAV) aging. RTFO aging was performed following ASTM D2872, in which samples were subjected to an RTFO aging oven at 163 °C and 4 L/min airflow for 85 min to simulate conditions at an asphalt-mixing plant. The sample was then exposed to two cycles of PAV aging according to ASTM D6521. In the standard procedure, binder samples in portions of approximately 50 g each are subjected to a pressure of 2.10 MPa at 100 °C for 20 h. To create the artificial RAP, the samples were aged for 40 h, which is referred to as "2 × PAV". Samples were then degassed in a vacuum oven at 170 °C for 30 min at 15 kPa. To prepare rejuvenated samples, 2 × PAV was hand-blended with 5–30% bio-rejuvenator (by weight of binder) for 5 min at 135 °C.