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Effects of aging on rejuvenated vacuum tower bottom rheology through use of black diagrams, and master curves

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ABSTRACT

Bio-derived rejuvenating agents have the potential to enhance the rheological properties of the vacuum tower bottoms left over from the crude oil refining process. Enhancement of the rheological properties allows the stiff vacuum tower bottoms to be used as an asphalt binder in hot mix asphalt. This study investigates the use of several experimental bio-derived rejuvenating additives and compares them with a commercially available modifier. The experimental additives include a blend of, heat bodied linseed oil (HBO) and partially hydrogenated heat bodied linseed oil (PHBO). The effect of dosage level and aging influence on rheological properties was studied for the experimental materials and the commercially available additives. The findings show that all the rejuvenators used had similar effects in the reduction of vacuum tower bottom stiffness due to short-term and long-term aging. However, the commercial rejuvenator reduced stiffness the most. The results show that the material combination of HBO and PHBO better retain high temperature properties while lowering stiffness at intermediate and low temperatures, thus widening the continuous grade range better than the commercial rejuvenator. To better understand why these effects are taking place in vacuum tower bottoms from both the commercial rejuvenator and the combination of materials HBO and PHBO with aging it is felt that in the future analytical chemistry such as high definition mass spectrometry needs to take place. This will make it possible to understand why these effects are taking place with aging.

1. Introduction

There are many different terms used for materials that restore an aged binder rheological properties similar to its original unaged state. These terms are used interchangeably as rejuvenators, recycling agents, softening agents, fluxes, and extenders. These materials are then named interchangeably as either modifiers or additives. Restoration is achieved through the renewal of the volatiles and oils generally improving flexibility and adhesion properties. The additives aim to return an aged binder's ratio of asphaltenes/maltenes to its original state [1–7]. Asphalt binder is made up of asphaltenes and maltenes (resins and oils).

During the construction and service life of a pavement asphalt binder material properties change in such a way that asphalt binders become stiffer and less resistive to fatigue/low temperature cracking. This is because a binder's volatile components evaporate and oxidize from the time it is constructed to the end of its service life. Oxidation of the binder over its service life causes polymerization to occur. Polymerization is the process by which the binder becomes more viscous at high temperatures and less viscous at low temperatures, thus called aging [8]. The main determinant of an asphalt's viscosity is based on the amount of asphaltenes in the binder because they are more viscous than both resins and oils [9,10]. From oxidation the oil component in asphalt is converted to resins and the resin component is converted to asphaltenes. This is the reason hardening occurs in asphalt over time [10,11]. Rejuvenators are materials that contain saturates/oils and through a certain method of application are able to restore partially to fully the oxidized asphalt binder properties to its original viscoelastic state [12].

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There have been several past studies on the use of rejuvenators with aged asphalt binder/recycled asphalt pavement (RAP) extracted and recovered binder. Due to the increasing demand for recycling old asphalt pavement in new hot mix asphalt (HMA), the use of rejuvenators has increased [13]. Past literature on rejuvenator dosage levels in RAP extracted and recovered binder show that as the dosage increases the performance grade (PG) shifts down linearly at both high and low temperature [13–17]. Even waste products such as recycled motor oil (RO) have been examined for use as a rejuvenator in RAP extracted and recovered binder and have been shown to decrease permanent deformation over time and decrease mixing and compaction temperatures [6].

Vacuum tower distillation bottoms (VTB) are a very stiff form of asphalt produced from a refinery equipped with cokers using petroleum (process known as coking) running vacuum distillation. Coking is done to recover more of the light fractions from crude oil during the refining process. Lighter fractions are used to produce higher economic value products such as gasoline, and other fuels. When petroleum prices increase, gasoline, and jet fuel prices increase, thereby creating more incentive to increase production of refined petroleum lighter fractions. Due to loss of lighter fractions (saturates) in VTB binder, which makes it very stiff, VTB binders are not typically used for paving.

2. Objective

In past studies done at Iowa State University linseed oil bio-derived materials (BDM) have been shown to have the ability to restore very stiff VTB rheological properties akin to a performance grade (PG) PG 76-10 to a more typically used PG 70-22 and PG 64-22 in the Midwestern United States. The objective of this study is to examine the effect of aging on the rheological performance of VTB modified with BDM from linseed oil used as rejuvenators at two dosage rates and compare the performance against that of a VTB control group, and VTB modified with a commercially available rejuvenator at two dosage rates. To achieve this objective, frequency sweeps at several temperatures are performed using a dynamic shear rheometer on unaged, short-term aged, and long-term aged material, while analysis will be done through visual as well as statistical interpretation of master curve results and black diagrams to examine the effects of aging.

3. Experimental materials and methods

3.1. Material description

Vacuum tower bottoms is a very stiff form of asphalt binder that typically has a performance grade (PG) of 76-10, 82-10, or 82-16. Within this research two non-commercial bio-derived materials (BDMs) were used; Heat Bodied Linseed Oil (HBO), and Partially Hydrogenated Heat Bodied Linseed Oil (PHBO), while a commercially available bio-derived rejuvenator – commercial modifier (CM) derived from Tall oil was also used in this research work. The BDMs used are produced from locally grown materials in the Midwestern United States and are easy to come by, while the commercial modifier, CM is a popular rejuvenating agent for asphalt binders, and mixtures in the Midwestern United States. Past literature has shown that it is possible to convert heavier asphaltenes into maltenes through hydrogenation reactions [18]. It is thus felt that because one of the two linseed derived materials, part of the BDM combination is PHBO, this could be cause a reversal of asphaltenes to maltenes during the blend process. All vacuum tower distillation bottoms have much more asphaltenes than maltenes. Thus this process could be repeated with other sources of VTB. However, one source of vacuum tower bottoms from an Illinois refinery with a penetration grade of 20–30 and a performance grade (PG) of PG 76-10 was used for the work embodied in this paper due to local availability. The properties for the non-commercial BDMs, HBO and PHBO are shown in Table 1.

There is only 1 glass transition temperature (T_g) for HBO as it is an oily like liquid. However, there are 2 T_gs for PHBO as it is a wax type material and has two different phases at which the material changes in terms of the glass transition temperature. The melting temperature for PHBO is relevant because below the temperature of 42.92 °C there are big differences between viscosities of HBO and PHBO. Once PHBO is at 45 °C the viscosity results drop dramatically and by 65 °C are lower than viscosity results for HBO. The two materials are added at the same time to VTB during blending. HBO is poured in like a liquid while PHBO is scooped out of a can and put in the VTB before blending. Both HBO and PHBO have specific gravities similar to asphalt binder. For binder preparation, the BDMs HBO and PHBO, as well as a commercial rejuvenator CM were shear blended with VTB at 155 °C ± 5 °C at 3000 rpm for one hour using a Silverson shear mill. After all blending combinations were created, unaged materials were tested in the DSR. Subsequently the materials were then short term aged in a RTFO and material was reserved for DSR testing. Remaining RTFO aged material was aged in a pressure aging vessel (PAV) – long term aging for subsequent testing in a DSR. Five groups were tested and examined; VTB control group, 3% HBO + 3% PHBO, 5% HBO + 5% PHBO, 6% CM, and 10% CM. All the rejuvenator materials were added to VTB by percent weight of the binder.

In past testing at Iowa State University separation testing was done on VTB modified with the combination of HBO and PHBO as well as the commercial rejuvenator, CM at the same dosages as those used for this research work. This testing was done in accordance with ASTM D7173-14 and unaged binder testing was done in accordance with AASHTO T 315-10. The timing between the different procedures for this current research work was kept the same

Table 1
Properties of BDMs HBO and PHBO.

	HBO			PHBO		
Physical form	Amber liquid			Solid paste		
Specific gravity at 25 °C (77 °F)	1.02			1.05		
Molecular weight (Mn) [Da]	3400			3400		
T_g [°C]	−17.91			−24.89, 16.25		
Melting temp. [°C]	–			42.92		
Viscosity (Pa·s)	Shear rate (1/S)			Shear rate (1/S)		
	50	100	150	50	100	150
At 25 °C (77 °F)	3.57	3.56	3.54	52.6	42.24	36.35
At 35 °C (95 °F)	2.11	2.09	2.06	27.92	21	17.75
At 45 °C (113 °F)	1.2	1.19	1.18	9.26	7.09	6.23
At 55 °C (131 °F)	0.84	0.82	0.8	1.19	0.86	0.8
At 65 °C (149 °F)	0.48	0.48	0.47	0.06	0.14	0.16