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Introducing Combination of Nano-clay and Bio-char to Enhance Asphalt Binder's Rheological and Aging Characteristics

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Abstract: The life expectancy of Asphalt Binder is negatively impacted by the harsh bombardment of ultraviolet (UV) rays. UV rays cause asphalt to oxidize faster which results in deterioration of asphalt's rheological characteristics that can lead to pavement distresses. This paper investigates merits of application of combination of nano-clay and bio-char to increase effectiveness of nano-clay to reduce asphalt oxidative aging while enhancing nan-clay dispersion. The study was conducted using one control binder (PG 64-22), two nano-clay sources and one type of bio-char, as such several modified binder blends were prepared at varying concentrations of nano-clay;the specimens were then analyzed in terms of their rheological characteristics before and after laboratory oxidation aging. The modifiers used in this study wereorgano clays (Cloisite-11 and Cloisite-15) along with bio-char, which is derived from swine manure. Rolling Thin Film Oven (RTFO) was used to age all specimens; aged and un-aged samples were then tested using a Rotational Viscometer (RV) to evaluate the changes in their rheological behavior before and after aging. Four modified blends were formulated incorporating 3% and 6% of Cloisite-11 and Cloisite-15, in presence of 3% Bio-char. Bio-char was used to improve dispersion, flow and liquidity retention, while enhancing oxidation resistance.

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***Key words:** Asphalt; Oxidative aging; Nano-clay; Bio-char; Rheology.*

Introduction

Oxidative aging of asphalt binder has been recognized as one the main factors contributing to pavement distresses leading to reduced pavement service life. There have been many studies on developing additives to reduce asphalt aging; among those additives severalnano-particles including nano-clays have been shown to be promising additives. However, low dispersion capability of nano-clay in asphalt has been recognized as the main drawback reducing nano-clay's effectiveness. This paper investigates merits of application of bio-char as a dispersion agent for nano-clay to decrease the rate of asphalt oxidation. This in turn, can enhance long term rheological behavior of asphalt and extend pavement service life by reducing asphalt aging susceptibility.

Background

There have been various attempts to modify asphalt binder in order to improve its overall performance. This includes addition of various additives such as styrene butadiene styrene (SBS), styrene butadiene rubber (SBR), ethylene glycidyl acrylate (EGA) terpolymer, crumb rubber, organo-montmorillonite, waste tire rubber, fibers and waste fibers [1]. In addition, more recently warm mix asphalt (WMA) has been attracting a lot of attention due to various advantages such as reduction in energy consumption, reduced emissions, reduced binder aging and extended construction season. Al-Rawashdeh and Sargand looked at the effects of water on the adhesive and cohesive strength of WMA mixtures and hot mix asphalt (HMA) mixtures [2]. The adhesion and cohesion energy of WMA mixtures was as high as those of HMA mixtures [2].

Another study looked at the anti-aging properties of asphalt binders made from different crude oils. The study focused on the impacts that aging had on saturates, aromatics, resins and asphaltenes components as well as penetration, softening point and molecular distribution [3]. Results showed that as a result of oxidation, saturates content remained the same while the aromatics and resin decreased in quantity. Aromatics and resins reacted with oxygen to develop more asphaltenes leading to a decrease in penetration and ductility. The investigation also proved that asphalt with higher activation energy and lower reaction rate coefficient has superior resistance to age performance [3].

Among more recent additives used to reduce oxidative aging is nano-clay; nano-clay has been used commonly in the adhesive and polymer industry to enhance their mechanical and physical properties such as stiffness, toughness, strength and thermal stability [4]. The primary use of nano particles as modifiers in asphalt binders has been to enhance rutting and cracking resistance [5-7]. In the asphalt industry many organic and non-organic modifiers have been used to decrease bitumen viscosity, to reduce its carbon emissions, to reduce energy consumption and to improve bitumen workability [8].

Nazzal and his teamtook a look at the fundamental characteristics of asphalt clay nano composites, which indicated that when nano-clay is added to asphalt binder, its adhesive forces are enhanced significantly while having an adverse effect on the cohesive forces [9]. It was also shown that stiffness and hardness of the asphalt binder could be improved depending on the mixing temperature and nano-clay concentration [9].

In addition, introduction of nano-clay n asphalt binder reduces binder's temperature susceptibility and oxidative aging while

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increasing the complex modulus and decreasing the phase angle [10]. If adequate dispersion is achieved the spacing between silicate layer in nano-clay will be increased when blended with asphalt binder indicating interaction between asphalt and clay particles. Yao and his group used polymer and nano-clay in an effort to reduce the oxidative aging of specific asphalt (PG 58-34) at concentrations of 2% and 4% [11]. An increase in viscosity and complex shear modulus was observed when non-modified nano-clay was added to the base asphalt. However, a decrease in viscosity and complex shear modulus was observed when polymer modified nano-clay was added to the base asphalt. Furthermore, polymer modified nano-clay showed to improve rutting and fatigue cracking resistance of asphalt binder [11].

While nano-clay found to be effective in enhancing bitumen properties, one of its main drawbacks is related to agglomeration and difficulty of uniform blending due to electrostatic forces between particles. These forces are known to cause the nano-particles to agglomerate and reduce their surface area. As such, those modifiers are commonly accompanied by surfactant and flow modifiers. Among those modifiers nano-clay has been shown to be a promising candidate to reduce oxidative aging provided uniform distribution and dispersion can be achieved. Due to their polar nature and excessive attractive forces among silicate layers, nano-clay particles tend to agglomerate when exposed to asphalt matrix containing nonpolar hydrocarbon chains; this in turn led to low level of dispersion especially when high dosage of nano-clay is introduced in asphalt binder. This paper introduces bio-char as a dispersion agent and flow modifier to reduce nano-clay agglomeration.

Bio-char (biologically derived charcoal) is a finely grinded by-product from a hydrothermal process used to produce bio-binder from swine manure [12, 13].

Materials and Methods

In this paper two nano-clays: Cloisite-11 and Cloisite-15 are blended separately with asphalt binder to reduce oxidative aging. Furthermore, the above mentioned nano-clays are mixed with bio-char individually while blending with asphalt binder to study effectiveness of bio-char to facilitate nano-clay dispersion. The selected asphalt binder for this study is PG 64-22, which is commonly used in North Carolina. This bitumen is a petroleum-based refined product. Typical heating temperature of the bitumen is 177˚C with its flash point being 325˚C. Preferred storage temperatures range between 140 to 168˚C [14].

Rotational Viscosity (RV) Test

The rotational viscometer (RV) test was conducted using the Brookfield rotational viscometer and according to the ASTM D4402 standard specification [15]. Test results were used to compare the viscosity of all un-aged samples to the viscosity of all aged samples. In order to determine the viscosity of each modified sample, 10.5 grams of each sample was poured into different aluminum chambers to gain better sampling of the entire blend. The tubes were then placed into a 30 minute pre-heated thermosel where thermal equilibrium was attained before proceeding with the RV test. Tests were conducted at 150℃ and 175℃ at speeds of 50, 100 and 200 rpm. The spindle SC27 was used for testing, where the first viscosity reading was recorded after 15 minutes of shearing. Two more readings were recorded at three minute intervals (three readings for each rpm at a given temperature) to ensure consistency of viscosity measurements. This procedure was used for un-aged and aged samples.

Table 1. Properties of Base Binder (PG 64-22).

Specific Gravity @15.6℃	Flash Point, Cleveland Open Cup, ℃	Change in Mass RTFO	Absolute Viscosity at 60℃, Pa.s
1.039	335	-0.0129	202

Rolling Thin Film Oven (RTFO) Test

Short-term aging of asphalt binder mixtures was performed using Rolling Thin Film Oven (RTFO) procedure in accordance to the ASTM D2872 standard specification [16].

Asphalt Binder

The base asphalt in this study was a PG 64-22 asphalt binder from Sharpe Bros Inc., Division of Vecellio & Grogan in Greensboro, NC, USA. It should be noted that PG 64-22 (Table 1) is one of the most commonly used asphalt binders in North Carolina.

Nano-clay

Cloisite-11 and Cloisite-15A consists of organically modified layered silicate platelets. The surfaces of these platelets are chemically modified to allow dispersion into thermoplastic systems such as asphalt binder. Nano-clays are found naturally; hence they are environmentally safe, economical, and sustainable. Nano-clay was acquired from BYK Additives& Instruments.

Bio-char Production

Bio-char is the waste product of a thermochemical process used to convert swine manure into bio-oil [12]. Bio-char is obtained mainly after the filtration and fractional distillation process. A vacuum pump is placed in a confined environment to prevent the spilling of the bio-oil. One end of a transparent hose is then connected to the vacuum end of the pump and the other end of the transparent hose is connected to a glass beaker. A rubber stopper is placed in the top of the glass beaker. A sieve is connected to a funnel and placed inside the rubber stopper. A sheet of filter paper is placed inside the sieve. Bio-oil is poured over the filter paper and vacuum pump is switched on. When all the liquid has been pulled through the filter paper and sieve into the glass beaker, a solid black residue remains on top of the filter paper. The residue, so called “bio-char” is then graded for application as modifier in this paper.

Mixture Design

Due to the weight and size of the nano materials used in this study,

Table 2. Experimental Mixture Design.

	PG 64-22	bio-char	Cloisite-11	Cloisite-15A
Control	100%			
CL-11-6% BC-0%	94%		6%	
CL-15-6% BC-0%	94%			6%
CL-11-3% BC-3%	94%	3%	3%	
CL-15-3% BC-3%	94%	3%		3%

the mixing of each sample had to be done in controlled clean environment to prevent contamination and loss of nano material. Nano materials (Cloisite-11 [CL-11], Cloisite-15A [CL-15], Bio-char [BC]) were placed by weight of dry mass into individual aluminum container (Table 2).

Virgin asphalt binder is then carefully poured into each aluminum container. Blending took place for ten minutes where a shear mixer was used at a rotational speed of approximately 800 rpm for 40 minutes.

Data Analysis

Analyzing the experimental data, the extent of age hardening was quantified in terms of change in viscosity before and after oxidation. Aging Index (AI), which is defined as the ratio of a rheological parameter of the aged bitumen to that of the original bitumen, was determined for each mixture; high values of the aging index indicate a high level of asphalt hardening (Zhang et al. 2012). In this paper the viscosity aging index (VAI) was used to evaluate the aging extent, and is calculated by measuring the viscosity of the samples before and after short-term (RTFO) aging. It is computed according to the formula shown in Eq. (1):

$$VAI = \frac{RTFO\ aged\ \text{viscosity value - Unaged viscosity value}}{Unaged\ \text{Viscosity value}} \quad (1)$$

Values of VAI are recorded and analyzed for nano-clay modified asphalt binder and bio-char modified asphalt binder (Fig. 1). It was found that the VAI value for the mixture including 6% Cloisite-11 is significantly lower than all other mixtures. However, with a lower percentage of Cloisite-11 combined with bio-char similar viscosity aging index could be achieved. With the inclusion of 6% Cloisite-15A, the susceptibility to aging improved but the impact was not as great as that of 6% Cloisite-11. When the percent of Cloisite-15A was reduced to 3% combined with 3% of bio-char, the improvement of VAI was not as significant as that of 3% Cloisite-11 combined with bio-char. This could be attributed to level of agglomeration and the dispersion properties of each of the nano-clay used in this study.

As can be seen in Fig. 2, the viscosity increase due to the addition of Cloisite-11 is much more than that of Cloisite-15A; this in turn could indicate occurrence of more agglomeration in the case of Cloisite-11. Accordingly, when bio-char was blended with each nano-clay to reduce the agglomeration, the viscosity of the blend containing Cloisite-11 dropped 77% compared to Cloisite-15A blend which only dropped 24% in presence of bio-char at 150℃. Whereas, the viscosity of the blend containing Cloisite-11 dropped 85% compared to Cloisite-15A blend which only dropped 20% in presence of bio-char at 175℃. This further can be attributed to the significance of bio-char in reducing level of agglomeration leading to enhancement in mixture flow and workability.

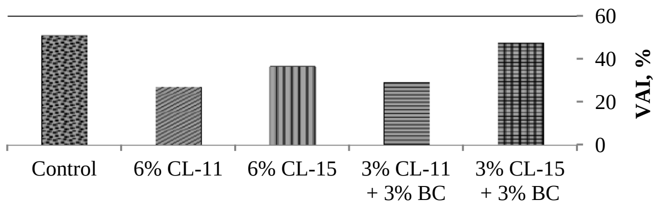


Fig. 1. Viscosity Aging Index for all Proposed Samples.

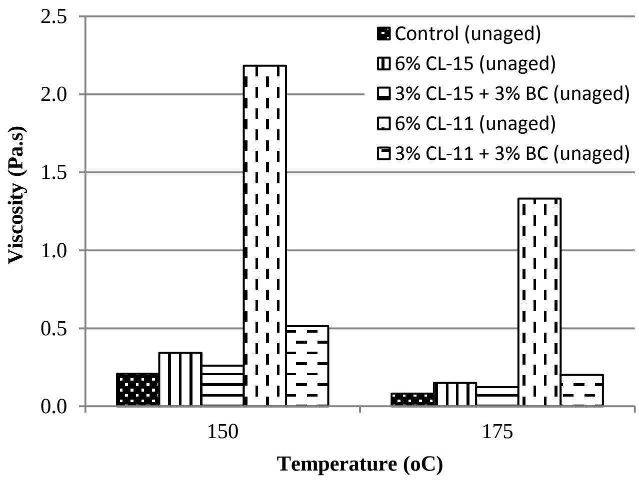
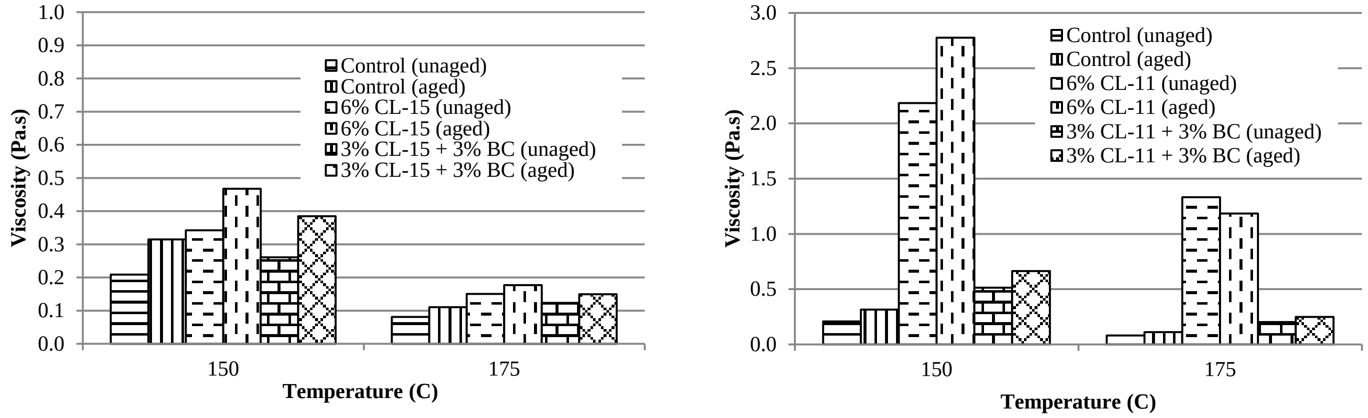


Fig. 2. Viscosity of un-aged Samples.

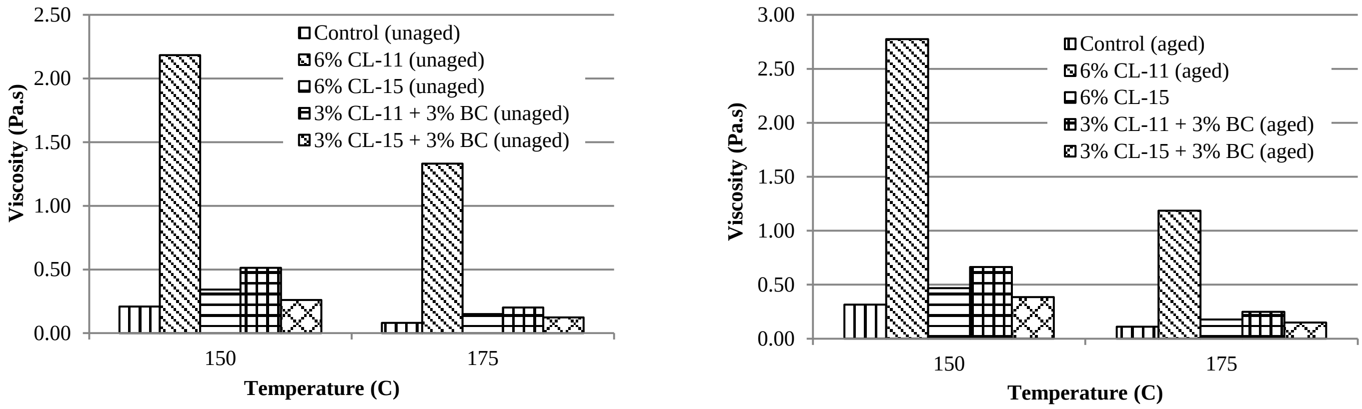
Fig. 3(a) and (b) shows the viscosity increases in all cases after the sample has been aged. It can be seen that the rate at which each individual sample has aged is dependent on the type of additive used. An increase in viscosity after aging implies that oxidation has occurred, which increases the viscosity and stiffness (of the modified asphalt) leading to higher susceptibility to cracking and rutting. It can also be shown that the modified blends show less increase in viscosity as due to aging. In addition, presence of bio-char showed significant reduction in viscosity of modified blends before and after aging.

Fig. 4(a) and (b) compares the viscosities of all un-aged samples, as well as the viscosities of all aged samples. In comparison to control binder PG 64-22, as indicated in these figures, the mixtures including Cloisite-11 are the most viscous. The mixture that includes 6% Cloisite-11 has an average viscosity that is significantly



(a) Cloisite-15 (b) Cloisite-11

Fig. 3. Rotational Viscosity of Un-aged Sample Compared to Aged Sample for (a) Cloisite-15 (b) Cloisite-11.



(a) Unaged Samples (b) Aged Samples

Fig. 4. Rotational Viscosity Comparison (a) between All Un-aged Samples (b) between all Aged Samples.

higher than all other samples. When 3% of Cloisite-11 was replaced by bio-char, the viscosity of the blend reduced 75% while the aging index did not change significantly. It is therefore evident that the addition of bio-char positively affected the blend by facilitating better dispersion. In other word 3% nano-clay could be as effective as 6% nano-clay on aging resistance provided it is adequately dispersed; this is when higher percentage of nano-clay could increase the ultimate modified asphalt cost without significant improvement in aging resistance while negatively affecting workability of the blend.

With 6% Cloisite-11 having significantly the highest viscosity, it is safe to say that the workability and energy consumption needed to evaluate this mixture is greater than any other mixture in this study. However, when comparing the VAI of the mixture that includes 6% Cloisite-11 to the VAI of the mixture that includes 3% Cloisite-11 and 3% bio-char, there is no significant difference. This indicates that inclusion of bio-char could facilitate the workability and lead to decreases of the energy consumption while enhancing aging resistance.

Conclusion

The purpose of this study was to evaluate the combined effects of nano clay (Cloisite-11 and Cloisite-15A) and bio-char on the rheological characteristics and aging susceptibility of asphalt binder. Nano-clays (Cloisite-11 and Cloisite-15A) along with bio-char (derived from swine manure) were blended at different percentages with asphalt binder (PG 64-22). Study of the rheological characteristics and aging susceptibility of the nano-clay and bio-char modified blends showed that viscosity values of all specimens increased after addition of nano-clay; however, the increase in viscosity varied depending on nano-clay type and its propensity for agglomeration. In addition, it was found that addition of nano-clay to asphalt binder could be a promising venue to enhance asphalt aging resistance provided adequate dispersion is achieved. This finding was in line with the results of previous studies.

Furthermore, it was found that introduction of Cloisite-11leads to a higher increase in viscosity compared to Cloisite-15A when used at the same volume concentration; this in turn indicates that Cloisite-11 is more prone to agglomeration. This was further evidenced when bio-char was introduced to each of the nano-clay modifiers to facilitate silicate platelets dispersion by reducing electrostatic forces between the nano-particles. It was noticed that introduction of bio-char led to a more significant reduction in the viscosity of Cloisite-11 blend (the blend with more propensity to agglomeration) compared to that of Cloisite-15A. In addition, it was shown that viscosity of all blends increased after short-term aging

(RTFO), however, those which had modifiers showed less increase in their viscosity values. The aging resistance improvement found to be significantly higher in Cloisite-11 blends compared to those of Cloisite-15A. In addition, 6% Cloisite-11 found to be as effective as 3% Cloisite-11 combined with 3% bio-char to improve aging resistance of base asphalt. This could be attributed to the improved nano-clay dispersion in presence of bio-char.

This can further increase effectiveness of nano-clay allowing for reduction of its dosage. This is when application of higher percentage of nano-clay for instance 6% Cloisite-11 results in significant increase in viscosity and loss of workability, which will increases energy consumption during mixing. In this study replacing 6% nano-clay with a blend of 3% Cloisite-11 and 3% bio-char showed similar aging resistance improvement while much lower viscosity when compared to the blend of 6%Cloisite-11. As such bio-char could be a promising candidate for enhancing nano-clay dispersion and flow modification.

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