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# Rheological properties of lignosulfonate intercalated layered double hydroxides modified bitumen before and after ultraviolet aging

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## HIGHLIGHTS

- The introduction of LS-LDHs enhanced rigidity, high temperature performance and resistance to deformation of bitumen.
- The addition of LS-LDHs restrained instantaneous elastic, delayed elastic and viscous deformation.
- LS-LDHs could strengthen anti-aging ability of bitumen effectively and had excellent high temperature storage stability.

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## ABSTRACT

Rheological property of bitumen is closely related to the service life of bituminous pavement, which is mainly affected by temperature, vehicle load and ultraviolet (UV) ray. In this paper, lignosulfonate intercalated layered double hydroxides modified bitumen (LLMB) were researched by Fourier transform infrared (FTIR) spectrometer characterization, aging index and storage stability test. Meanwhile, rheological properties of LLMB before and after UV aging were investigated by temperature susceptibility, dynamic viscoelastic properties and rheological model analyses. The results showed that the introduction of lignosulfonate intercalated layered double hydroxide (LS-LDHs) could strengthen the anti-UV aging ability of bitumen more effectively and had better high temperature storage stability than layered double hydroxides (LDHs). From rheological performance measurement, LS-LDHs could weaken the temperature susceptibility of bitumen observably. Compared with pristine bitumen (PB), the values including loss tangent ($\tan\delta$), complex modulus ($G^*$) and rutting factor ($G^*/\sin\delta$) of LLMB got higher. According to rheological model analyses, the addition of LS-LDHs affected the models of bitumen hardly, but restrained instantaneous elastic, delayed elastic and viscous deformation. Therefore, LS-LDHs could enhance rigidity, high temperature performance and resistance to deformation of bitumen significantly. After UV aging, the rheological parameters variations and deformation arguments amplitudes of LLMB were lowest among PB, layered double hydroxides modified bitumen (LMB) and LLMB, which demonstrated that LS-LDHs improved the UV aging resistance of bitumen prominently.



## 1. Introduction

Bitumen is an adhesive materials, which is generally applied in the pavement [1,2]. As a typical viscoelastic material, the deformation of bitumen mainly depends on some external factors such as temperature, stress [3]. Bitumen is also a kind of organic materials, so it would be aged easily by ultraviolet (UV) light, oxygen and so forth [4]. With the effect of temperature, vehicle load and UV ray, some damages including low-temperature cracking, high-temperature rutting and deterioration of pavement structure would be generated easily [5,6]. In consequence, to lengthen the service life of the bituminous pavement, it is crucial to enhance anti-UV aging ability and investigate rheological property of bitumen.

Firstly, rheological characterizations of bitumen have been researched widely for many years. Overall, the rheological characterizations of bitumen could be investigated by performance measurement and model establishment. Rotational viscometer and dynamic shear rheometer (DSR) are usually applied to evaluate rheological behavior. The temperature susceptibility of bitumen would be acquired through calculating rotational viscosity at various temperatures, [7]. Cong et al. [8] measured viscosity and employed Arrhenius equation to research the temperature

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susceptibility of carbon black/styrene-butadienestyrene copolymer (SBS) modified bitumen.

DSR test, which is recommended by Strategic highway research program (SHRP), is a major method to estimate the viscoelastic performances of bitumen. Concretely, it is used to measure dynamic modulus and phase angle of bitumen [9]. Then the deformation resistance of bitumen could be evaluated. Soudani et al. [10] employed DSR test and revealed that waste nitrile rubber could improve dynamic rheological abilities of bitumen. Ahmedzade et al. [11] investigated the rheological property of recycled high-density polyethylene ($HDPE_{RE}$) modified bitumen. The results displayed that $HDPE_{RE}$-modified bitumen had lower temperature susceptibility and higher elastic response to shear stress compared to the base bitumen. Owing to these measurement instruments and evaluation methods, the study of bituminous material has been promoted memorably. However, the applicability of these researches based on given load and frequency is limited. For instance, it is difficult for DSR to establish the relationship between stress, strain and time, which is the major expression of rheological behavior [12].

The rheological model, which contains elastic elements, viscous elements and plastic elements [13], is used to research viscoelasticity of bitumen and law of bitumen deformation with time under external force [14]. Behzadfar and his co-workers [15] found the generalised Maxwell model was conformed to experimental results of bitumen at 30–90 °C. Gao et al. [16] employed a Burgers model and simplified its solution, then predicted the rutting of bitumen pavement. Nevertheless, there is still not an efficient method to establish of rheological model nowadays. Hence most of the rheological model reports are limited to theoretical research based on vast and complicated calculation. Lately, a rheological test and model analyser has been exploited by our research Group [17]. It could be used to build rheological model accurately and establish constitutive equation quickly for bitumen.

Secondly, to enhance the anti UV aging performance, some methods have been made. Rasool et al. [18] discovered highly reclaimed rubber/SBS modified bitumen had excellent aging resistance. Chen and his co-workers [19] revealed aging resistance of bitumen could be strengthened through adding organic expanded vermiculite and nano-zinc oxide. Nowadays, layered double hydroxides (LDHs) are used as anti aging agent in bitumen However, LDHs are a kind of rigid inorganic particles, which has poor compatibility with bitumen, so that the sufficient utilization of the UV resistance is limited [20]. Xu et al. [21] found that LDHs intercalated with sodium dodecylbenzenesulfonate could improve the compatibility with bitumen as well as its anti UV aging ability.

As one of the most important bioresources, lignin is a by-product of the pulping process. Over the past decades, the profitable utilization of lignin in abundance has been a crucial and urgent problem in the world [22]. On the one hand, owing to the benzene ring structure, lignin was selected to synthesize UV-absorbent film, which could chemical absorb the UV light reaching up to 96.2% [23]. On the other hand, lignin was dispersion agent for rubbers due to the hydrophobic structure (benzene ring and carbon chain) [24]. Lignosulfonate (LS), which is a kind of lignin materials, has been inherited plentiful features and properties from lignin [25,26]. Once LS is intercalated into LDHs, the UV blocking property of LDHs would further enhance through endowing the ability of chemical absorption and compatibility of LDHs with bitumen could be improved.

In this paper, lignosulfonate intercalated layered double hydroxides modified bitumen (LLMB) were researched by Fourier transform infrared (FTIR) spectrometer characterization, aging index and storage stability test. Meanwhile, rheological properties of LLMB before and after UV aging were investigated by viscosity-temperature curves, DSR test and rheological model establishment.

## 2. Experimental

### 2.1. Materials

LDHs ($Mg_2Al\text{-}CO_3^{2-}$) were obtained by Tech-layer Co., Ltd., Beijing, China. LS were provided from Chenyi Biotechnology Co., Ltd, Shanghai, China. Bitumen was produced by SK Corp., Korea and physical properties are revealed in Table 1.

### 2.2. Preparation of lignosulfonate intercalated layered double hydroxides

6 g LDHs and 100 mL ethanol was taken into a flask, and they were stirred at 70 °C for 60 min. Then, 400 mL deionized water and 20 g LS were added. HCl solution was used to maintain the pH value about 3. In addition, the mixed solution should be stirred at 70 °C for extra 3 h under $N_2$ atmosphere. Next, filtering and washing the precipitate to wipe off excess LS after cooling down, and dried at 100 °C till constant weight. Finally, the lignosulfonate intercalated layered double hydroxides (LS-LDHs) were obtained after grounding.

### 2.3. Preparation of LS-LDHs modified bitumen

3 wt% LS-LDHs or LDHs (determined by previous study [21,27]) and the pristine bitumen were taken into a pot heated the mixture to 140 °C with oil-bath temperature control system. Then the mixture was stirred with the speed of 2000 rpm for 1 h to ensure homogeneous blending, to obtain LS-LDHs modified bitumen or LDHs modified bitumen. Finally, they were applied to do relevant experiments and test. The bitumen modified by LS-LDHs and LDHs were denoted by LLMB and LMB, respectively. Meanwhile, pristine bitumen was denoted by PB.

### 2.4. Aging procedures

Specimens were carried out at 163 °C for 5 h according to ASTM D1754, then they were put into an UV aging oven with the UV light intensity of 1200 $\mu W/cm^2$ for 9 days at 60 °C.

### 2.5. Characterization and test

#### 2.5.1. FTIR

The spectra of specimens were recorded by a FTIR spectrometer (Nexus, Thermo Nicolet Corp., USA). The samples were dealed with KBr. Meanwhile, the range of wavenumber is 4000–400 $cm^{-1}$.

#### 2.5.2. Storage stability

The specimen was poured into an tube and vertical placed for 48 h at 163 °C. Then it was cooled at −5 °C for 4 h and cut into three sections. Finally, the softening point of the bottom and the top were measured according to ASTM D36. The storage stability was reflected by $\Delta S$ (difference of softening point).

#### 2.5.3. Physical properties

Penetration (25 °C), ductility (10 °C) and softening point of specimens were tested according to ASTM D36, ASTM D113 and ASTM D5, respectively.

#### 2.5.4. Rotational viscometer test

According to ASTM D4402, the rotational viscosities of specimens were measured by Brookfield rotational viscometer. Meanwhile, the viscosity-temperature curves were confirmed from 60 to 150 °C on the basis of ASTM D2493.

#### 2.5.5. DSR test

DSR was applied to test the dynamic rheological properties of specimens. According to the requirements for pavement performance indicators in SHRP, temperature sweep test (frequency: 10 rad/s; increment: 2 °C/min) was implemented ranging from 30 to 80 °C (high temperature region) and −10 to 30 °C (low temperature region), respectively.

#### 2.5.6. Rheological model establishment

The deformation of the viscoelastic material is relevant to time and temperature, and it partially recovers when loads are removed. In order to comprehend better, viscoelastic creeping and recovery curves is displayed in Fig. 1. When a stress is given, the total strain is $\sigma_0$. Once the loads are removed, the instantaneous elastic deformation and delayed elastic deformation could be recoverable, while viscous deformation remains. This is the typical process of viscoelastic deformation.

**Table 1**
Physical properties.

| Peneration (25 °C, dmm) | Ductility (10 °C, cm) | Softening point (°C) | Viscosity (135 °C, Pa·s) |
|---|---|---|---|
| 74 | 26.7 | 49.5 | 0.52 |