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# LABORATORY RESEARCH ON THERMAL BEHAVIOR AND CHARACTERIZATION OF THE ULTRAVIOLET AGED ASPHALT BINDER

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Thermal, chemical and rheological properties of ultraviolet aged asphalt binder were characterized by differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) and dynamic shear rheometer (DSR), respectively. Asphalt binder samples were made with different film thickness (50, 100, 200 and 500 μm) and suffered different ageing time (0, 48, 96 and 144 h), at a certain UV radiant intensity of 20 w $m^{-2}$ in a self-made accelerated ageing oven. The results indicate that the UV light ageing would lead to the improvement of thermal behavior and the growth of the glass transition temperature of asphalt binder. This type of ageing can be also reflected from the FTIR spectra in terms of the characteristic peaks of the carbonyl groups and sulphoxides. The UV light ageing can change some rheological parameters of asphalt binder, such as complex modulus and phase angle. The ageing degrees of asphalt binder by this type of ageing test are mainly related to the ageing time and film thickness of the sample.

***Keywords:*** *aged asphalt, chemical, rheological, thermal, ultraviolet*

## Introduction

When asphalt materials are exposed to the heat, air and ultraviolet (UV) radiation, a gradual degradation occurs [1]. Various accelerated ageing tests have been developed to stimulate the practical degradation of the asphalt binder. For example, the short-term ageing is addressed by the Rolling Thin Film Oven (RTFO) test, which simulates the ageing of asphalt binder during the mixture production, laying and compaction. The long-term ageing is evaluated by the Pressure Ageing Vessel (PAV) test under the condition of high pressure and temperature to stimulate the ageing of asphalt binder during service life [2]. The principle of these mentioned ageing tests is mainly related to thermal degradation. In the real environment, the ageing of the asphalt concrete during service life involves a series of complex physico-chemical changes. For example, that asphalt binder dramatically absorbs the solar radiation, especially UV radiation, will result in the photodegradation of itself, which has been normally ignored by traditional laboratory ageing tests. Therefore, some attention has been paid to the ageing test involving the UV radiation [3]. Traxler used actinic light to stimulate the photochemical ageing of asphalt binder. The test result revealed that the photochemical reaction had a significant effect on the asphalt film with a thickness of 3 μm, while a relatively slight effect on thicker films [4]. Montepara found that the volatilization, oxidation and polymerization of the asphalt binder occurred due to UV radiation [5]. Later, Airey reported that the standard ageing procedures using the RTFO followed by the PAV, had different ageing effects on the asphalt binder, when compared to the light ageing [6]. Burak presented the relationship between asphalt binder hardening, film thickness, voids and permeability of asphalt mixture, and suggested that increasing asphalt film thickness was considered to be an effective way to avoid longitudinal surface cracking [7]. So far there is no standardized test which allows quantitative evaluation of the photodegradation of asphalt binders.

This paper presented an experimental study on the thermal, chemical and rheological properties of the UV light aged asphalt binder. The pure asphalt binder was subjected to RTFO test at first, subsequently aged by the UV radiation through a self-made accelerated UV light ageing oven.

## Experimental

### *Materials*

Asphalt binder AH-70 used in this study was provided by Koch Asphalt Co., Ltd. China. Physical properties were listed in Table 1.

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**Table 1** Physical properties of pure asphalt AH-70

| Penetration at 25°C/dmm | Ductility at 15°C/cm | Softening point/°C | Viscosity at 60°C/Pa s | After RTFO ageing | | |
|---|---|---|---|---|---|---|
| | | | | Mass loss/% | Ductility at 15°C/cm | Retained penetration at 25°C/% |
| 65 | >150 | 48.0 | 410 | 0.01 | 65 | 62 |

*Ageing*

RTFO test for asphalt binder was performed according to test specification ASTM D2872. Four types of asphalt samples were made with film thicknesses of 50, 100, 200 and 500 μm respectively. To obtain the desired film thickness, asphalt binder after RTFO ageing was diluted by carbon disulfide to form a solution with a certain concentration. The solution was poured into a glass plate with a certain area. After the complete evaporation of the organic solvent at room temperature, asphalt samples with desired thickness will be obtained [8].

Subsequently, the sample was put into a self-made UV light accelerated ageing oven for further ageing. This equipment was used to investigate the photodegradation behavior of asphalt binder. The radiation strength of the UV lamp was set at a constant value of 20 w $m^{-2}$ with the wavelength of 360 nm. For the sample with film thickness of 100 μm, it was irradiated for 0, 48, 96 and 144 h, which means the sample would absorb an accumulated irradiation energy of 0, 3.46, 6.92 and 10.37 MJ $m^{-2}$, respectively. Meanwhile, the samples with film thicknesses of 50, 100, 200 and 500 μm respectively were subjected to 120 h UV light radiation. The test temperature was controlled at 60°C through the air condition.

*Instrumental methods*

DSC and TG

A power compensation differential scanning calorimetry (DSC) Pyris 1 from PerkinElmer Instrument made in USA was adopted to characterize the thermal properties of asphalt binder. Samples of about 5 mg were held in sealed aluminum crucibles at an air flow rate of 50 mL $min^{-1}$ and heated at a rate of 10°C $min^{-1}$ from room temperature to 500°C. DSC curve and thermal gravimetric (TG) curve were obtained to evaluate thermal characteristics of asphalt binder. Sometimes these characteristics depend on some factors, such as the petroleum source and the refining process [9–14].

FTIR

Nicolet Nexus Fourier transform infrared spectroscopy (FTIR) from Thermo Nicolet Company was used to acquire FTIR spectra of aged asphalt binder sample. An asphalt binder and carbon disulfide solution was made with a certain concentration and poured onto a small KBr crystal sample plate. The test started after the complete volatilization of carbon disulfide. The width range of wavenumber was from 4000 to 400 $cm^{-1}$ [15].

**Table 2** Configurations and input parameters for the DSR measurements

| Temperature/ °C | Plate diameter/mm | Gap/ mm | Frequency/ rad $s^{-1}$ |
|---|---|---|---|
| –10, 0, 10, 20 | 8 | 2 | 0.1~400 |
| 30, 40, 50, 60 | 25 | 1 | |

DSR

A Dynamic Shear Rheometer DSR-MCR101 from Anton Paar Company, Germany, was used to characterize rheological properties of asphalt samples before and after ageing, through measuring some rheological parameters, such as complex modulus ($G$*) and phase angle (δ). The configurations and input parameters for the DSR measurements were listed in Table 2. The master curve was got on the basis of the time–temperature superposition principle (TTSP). This would provide fundamental information about ageing effects on rheological properties of asphalt binder. All of the tests were conducted under strain-controlled mode and the applied strain limited asphalt binder within the linear viscoelastic range. The aged asphalt binder samples in the form of thin film on the glass plate were carefully collected and sampled for the DSR test [16].

## Results and discussion

*Thermal behavior*

TG curves of different binder samples were shown in Figs 1 and 2. It can be seen from Fig. 1 that as the increase of ageing time, the starting point of the mass loss temperature for the sample with 100 μm thickness becomes higher. This means the ageing makes the asphalt binder more stable. As shown in Fig. 2, it can be found that as the increase of film thickness of the sample, the starting point of the mass loss temper-

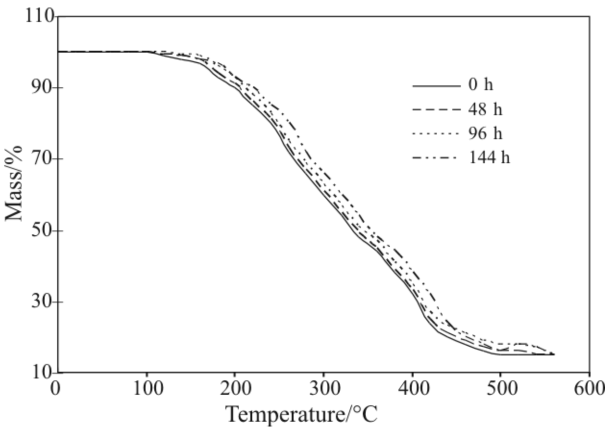

**Fig. 1** TG curves for the samples suffering UV light with different ageing time

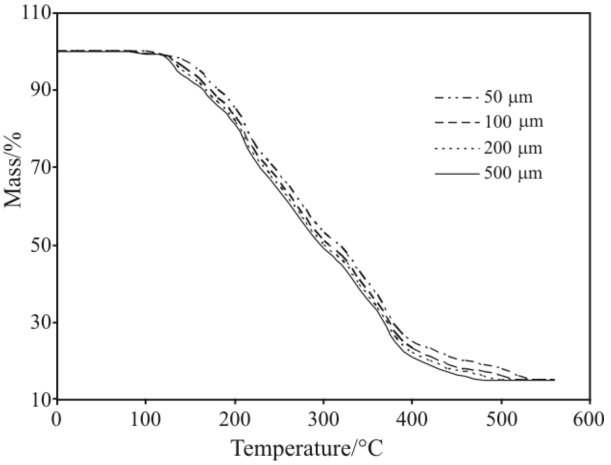

**Fig. 2** TG curves for the samples with different film thickness

ature becomes lower, and at the same temperature, the mass loss of the thicker sample is higher. This may be that the increase of the thickness will weaken the ageing effect. The mass loss for the sample with film thickness of 50 μm was obviously smaller than that of the sample with film thickness of 500 μm. Comparing the curves in both figures, it seems that ageing time has more remarkable influence on the thermal properties than film thickness.

The glass transition temperature for different asphalt binder samples was listed in Table 3. The $T_g$ for the sample with long ageing time is high. There is an increase of 5.8°C for the $T_g$ of the sample suffering ageing time from 0 to 144 h. For the samples suffering the same ageing time, the $T_g$ increases as the decrease

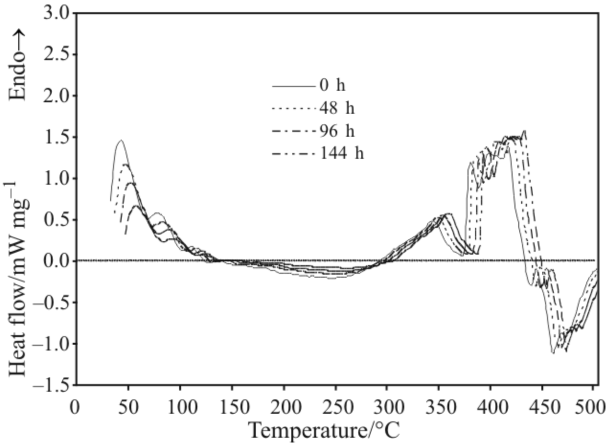

**Fig. 3** DSC curves for the samples suffering UV light with different ageing time

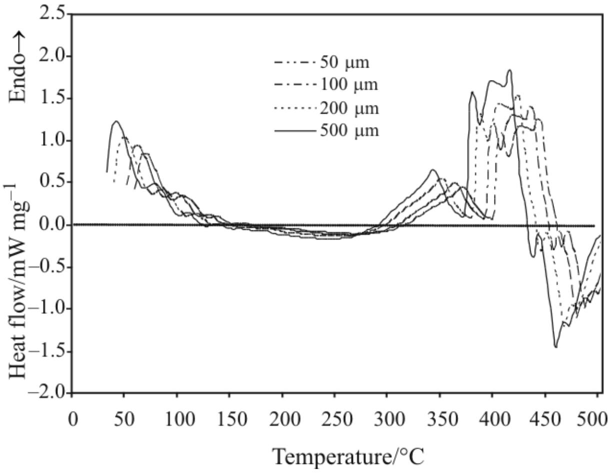

**Fig. 4** DSC curves for the samples with different film thickness

of the thickness of the sample. The $T_g$ decreases from –46.4 to –50.7°C when the thickness of the sample increases from 50 to 500 μm. In general, the $T_g$ is related to the molecule mass of the asphalt binder. Both the increase of the ageing time and the decrease of film thickness of the asphalt binder would strengthen the ageing degree of the asphalt binder and increase its molecule mass.

Figures 3 and 4 are the DSC curves of asphalt binder samples in the air environment. It can be seen that an obvious endothermic peak occurs at the temperatures ranging from 50 to 100°C for each sample. During this temperature range, the viscosity of the asphalt binder decrease and itself gradually transforms

**Table 3** Glass transition temperature ($T_g$) of different asphalt binder samples

| Ageing condition | Binder samples | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Ageing time/h | 0 | 48 | 96 | 144 | 120 | | | |
| Film thickness of the sample/μm | 100 | | | | 50 | 100 | 200 | 500 |
| $T_g$/°C | –53 | –51.6 | –49.8 | –47.2 | –46.4 | –48.5 | –49.1 | –50.7 |

from solid-state to liquid state as the growth of the temperature. However just physical change occurs. A wide exothermic peak can be found during the temperature range from 150 to 300°C. This implies that some chemical combination reactions occurred during this temperature range when binder samples were exposed to the air. Subsequently two strong exothermic peaks appear during the temperature range from 300 to 450°C, which may be due to some chemical decomposition reaction occurring in terms of carbonization. All peaks in each curve shift towards high temperature when the sample suffers more severe ageing effect. As the increase of the ageing degree of asphalt binder, the saturated and aromatic hydrocarbon and resin fractions will reduce, at the same time the asphaltene fraction will increase. These changes will lead to the improvement of the thermal properties of asphalt binder.

### *Chemical structure analysis*

The FTIR spectrums of the UV light aged asphalt binder sample were shown in Figs 5 and 6. The strong peaks within 1458–1377 cm$^{-1}$ region are typical C–H bending vibrations in aliphatic chains. The characteristic absorption peak around 1690–1720 cm$^{-1}$ means the existence of carbonyl (C=O) compounds, and detailed check of the wavenumbers indicates that C=O comes from the ester structure (normally in the 1710–1695 cm$^{-1}$ region). Besides this C=O absorption peak, there is a distinctive peak at 1700 cm$^{-1}$, which is due to the absorption of asymmetrical C=O stretching in carboxylic dimer. The weak peak at 1600 cm$^{-1}$ is assigned as C=C stretching in aliphatic chains. In the 1000–1050 cm$^{-1}$ region, this absorption peak (1030 cm$^{-1}$) is induced by the stretch absorption of sulphoxide (S=O) and commonly applied to characterize the evolutions of the chemical structures of aged asphalt binder.

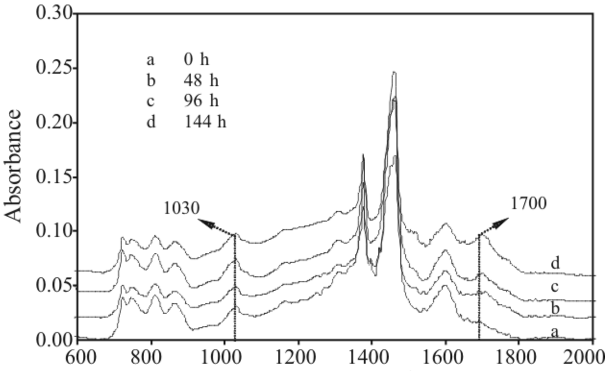

**Fig. 5** FTIR spectra for the samples suffering UV light with different ageing time

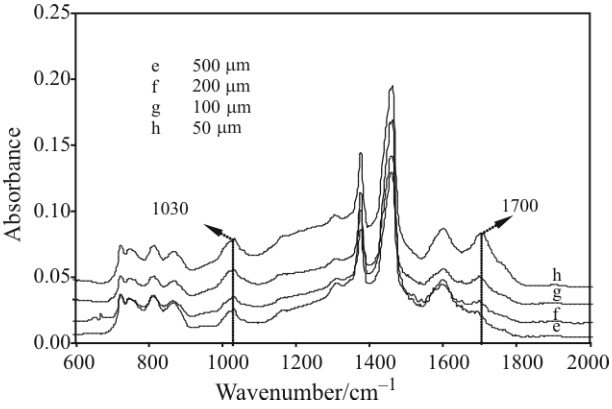

**Fig. 6** FTIR spectra the samples with different film thickness

As an indicator of UV light ageing degree, the intensity of absorbance peaks at 1700 and 1030 cm$^{-1}$ changes as the variation of ageing time and the thickness of the sample. As shown in Fig. 5, it can be found that the absorption peaks at 1030 and at 1700 cm$^{-1}$ are highlighted for the sample suffering 144 h. The intensity of absorption peaks at 1700 and at 1030 cm$^{-1}$ decreases as the sample's thickness increases from 50 to 500 μm, which means the existence of less carbonyl groups and sulphoxides. Comparing the spectrum in Figs 5 and 6, it can be found that the trends of these curves are very close, especially for the curves d and h.

### *Rheological properties*

Figures 7 and 8 presented the master curves of complex modulus and phase angle of different asphalt binder samples. The reference temperature for all master curves is 25°C. It can be observed that ageing induced hardening has a significant effect on asphalt binder rheological properties. As shown in Fig. 7, for each curve, the complex modulus $G^*$ values and the phase angle $\delta$ gradually increase and decrease respectively, as the increase of the frequency; at the same frequency, the UV light ageing results in the

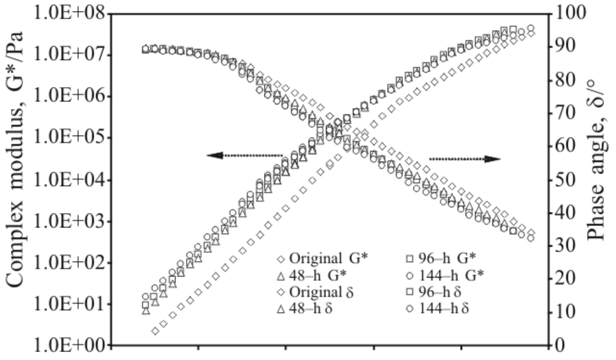

**Fig. 7** Influence of ageing time on rheological parameters

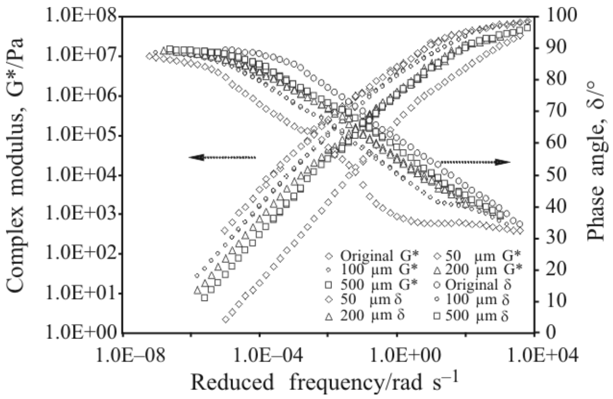

**Fig. 8** Influence of film thickness on rheological parameters

increase of *G** and the decrease of δ respectively. Figure 8 indicates that the increase of film thickness will weaken the photodegradation ageing of the asphalt binder and improve its durability. It seems that the film thickness of 100 μm could be a critical value. When the film thickness is smaller than this value, the ageing effect caused by UV light radiation is much more pronounced. The reason for this may be that the ageing penetration depth is limited to some extent below the film surface when the sample is exposed to a certain radiation environment.

## Conclusions

The asphalt binder samples with different film thickness were aged by UV light for different time at a self-made accelerated ageing oven. Thermal, chemical and rheological properties of aged samples were characterized by DSC, FTIR and DSR respectively. UV light ageing would lead to the improvement of thermal behavior and the growth of the glass transition temperature of asphalt binder. This type of ageing can be also reflected from the FTIR spectra in terms of the characteristic peaks of the carbonyl groups and sulphoxides. The UV light ageing can change some rheological parameters of asphalt binder, such as complex modulus and phase angle. The ageing degrees of asphalt binder by this type of ageing test are mainly related to the ageing time and film thickness of the sample.

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