Long-term aging performance study of asphalt with different composition

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Abstract. Thin film oven tests (TFOT), pressure aging tests (PAV) for 5 h, 10 h, 15 h, 20 h were carried out on asphalts from 6 crude oil resources. Conventional and dynamic shear rheological tests (DSR) were carried out on samples at different aging degrees, respectively to evaluate the aging performance of asphalt with different composition. The main conclusions are as follows: asphalt composition had obvious influence on the long-term aging performance, in which the asphaltene content of asphalt is negatively correlated with the long-term aging performance of asphalt. According to experimental results of aging process influence on storage modulus G', A³, A⁵ and A⁶ asphalts had worse anti-aging performance than A¹, A² and A⁴. Meanwhile based on test results of aging process influence on loss modulus G'', A¹, A² and A⁴ asphalts had worse anti-aging performance than A³, A⁵ and A⁶ asphalt.

1. Introduction
Because of its excellent viscoelasticity, asphalt has been widely used in pavement construction [1,2]. Asphalt used in pavement performs as binder of aggregates which is rheological with elasticity, viscosity and plasticity. However in the application and service life (storage, transportation, construction and service, etc.), with effects of temperature, oxygen, ultraviolet radiation et al, a series of physical and chemical changes will occur in asphalt materials, resulting in changes in chemical composition and structure of asphalt, and finally make asphalt hardened and brittle cracking gradually, the irreversible change process was called aging, which is one of the key factors affecting the life of asphalt pavement [3]. At the same time, asphalt is a viscoelastic material, which shows different viscoelastic properties at different temperatures and loading modes. The rutting, fatigue, cracking and other diseases of asphalt pavement are directly related to the viscoelastic properties of asphalt [4-6]. Therefore, it is necessary to study the properties of different asphalt pre and post aging to improve the performance of asphalt pavement.

Rheology mainly focuses on the relationship between flow, deformation and stress of materials. Strategic Highway Research Program (SHRP) carried on systematic study of asphalt pavement performance and asphalt grading [7, 8]. The dynamic thermomechanical analysis method (abbreviated as DMA) is one of its main research fruits, which can detect change of dynamic mechanical properties...
of materials at various range of temperature and frequency fluctuations, and is an important method to investigate viscoelastic properties of materials [4;5;7-9].

Physical properties of asphalt would decrease after hot mixing and subsequent road use due to oxidation and volatilization [10]. Since composition of asphalt is very complex, asphalt from different oil resources with different composition may perform different. In this study, thin film oven aging test (TFOT, 163°C, 5 h) was used to simulate the aging of asphalt during hot mixing, and pressure aging tests (PAV 5 h, 10h, 15h, 20h) were used to simulate aging process of asphalt in 8-10 years of service life. Changes of performance pre and post aging of six different matrix asphalts were compared and studied.

2. Materials and experimental

2.1. Asphalt
6 kinds of commonly used and representative heavy traffic AH-70 asphalt in pavement construction were used in this study, marked as A1-A6, among which A1, A2, A3 were from CNOOC, CNPC and Sinopec respectively; and A4, A5 from Korea; A6 was from Venezuela oil source; the basic properties of 6 kinds of base asphalt were shown in Table 1

| Items                  | A1   | A2   | A3   | A4   | A5   | A6   |
|------------------------|------|------|------|------|------|------|
| Penetration, 25℃       | 64   | 69   | 68   | 62.1 | 68   | 67   |
| Softening point, ℃     | 50.1 | 48.3 | 40.9 | 47.7 | 48.9 | 48.3 |
| Ductility, 10℃         | >100 | >100 | >100 | >100 | >100 | >100 |
| Ductility, 15℃         | >100 | >100 | >100 | >100 | >100 | >100 |
| Viscosity, cp          |      |      |      |      |      |      |
| 80℃                    | 21650| 13550| 20800| 31333| 42167| 23500|
| 100℃                   | 3600 | 2470 | 3650 | 5325 | 6800 | 4275 |
| 120℃                   | 930  | 655  | 975  | 1410 | 1565 | 1180 |
| 135℃                   | 415  | 305  | 430  | 620  | 710  | 607.5|
| 160℃                   | 132.5| 125  | 142.5| 215  | 252.5| 307.5|
| Saturates              | 21.20| 17.1 | 10.23| 26.8 | 7.51 | 13.33|
| Aromatics              | 35.54| 41.4 | 50.56| 30.8 | 53.33| 17.36|
| Resin                  | 33.54| 29.6 | 29.74| 41.9 | 19.14| 39.71|
| SARA, %                |      |      |      |      |      |      |
| Asphaltene             | 9.72 | 11.9 | 9.47 | 0.5  | 20.02| 29.6 |

*Ic=(asphaltene+saturates)/(aromatic+resin)*

2.2. Aging experiments
Chemical and physical changes occurred in aging of bitumen during the production of the pavement and throughout its service life. The process is usually accompanied by hardening of the binder, which generally influences the deterioration of the asphalt pavement. In order to determine the influence of aging on the rheological properties of bitumen from different oil and evaluate the composition of asphalt influence on aging process, the short and long term laboratory aging of bitumen were performed by using the Thin Film Oven Test(TFOT, ASTM D2872) and the Pressure Aging Vessel(PAV, AASHTO M320) respectively.

The standard aging procedures of 163 °C and 5 hours for the TFOT, 100 °C, 2.1 MPa for the PAV tests were used. The aged binders were evaluated by measuring their rheological properties and chemical composition

2.3. Conventional properties tests
The matrix and aged asphalt were conducted on the following conventional tests: Penetration (25℃, ASTM D5), Softening point test (ASTM D36), Viscosity test (ASTM D2170) Chemical compositions,
in terms of SARA fractions, were determined by Iatroscan MK-6 analyzer (Iatron Corporation Inc., Japan) coupling thin layer liquid chromatography on silica gel with a flame.

2.4. Dynamic mechanical analysis
Dynamic thermomechanical analysis (DMA) was performed on the matrix and post aged asphalt to determine their rheological properties using dynamic shear rheometer (DSR). Oscillatory shear tests (0.1-100 rad·s⁻¹) were conducted in a controlled-stress rheometer AR2000ex with parallel plate geometry (25 mm diameters, 1 mm gap). Stress and strain sweep tests were firstly carried out on each sample to determine linear viscoelasticity region. Temperatures for linear viscoelastic characterization ranged from 35 to 80°C. Temperature sweep tests, with the setting of temperature rate 1 °C·min⁻¹ and shear frequency 10 rad·s⁻¹, were also performed in rheometer AR in the linear viscoelastic region from 30 to 100°C. Frequency sweeps from 0.1 to 100 rad·s⁻¹ at 40 and 75°C were also carried out. Steady state flow behavior was determined in a controlled-stress rheometer AR2000ex from USA with parallel plate geometry (25 mm diameters, 1 mm gap). The flow curves were obtained by progressively increasing the shear rate imposed on the samples (10⁻³-10² s⁻¹, 60°C). Three replicates of specimen were done to obtain repeatable results.

3. Results and discussion

3.1. SARA analysis
It is generally believed that the aging of asphalt is composition of saturated, aromatic, resin and asphaltene changing. The effects on the performance of aging asphalt were different with various chemical composition of asphalt. The SARA composition of six asphalts is shown in figure 1.

![Figure 1. SARA composition of asphalts](image-url)

Figure 1 shows that A1-A6, The content of four fractions of asphalt from 6 different oil sources varies greatly. Among them, the aromatic content of A5 was highest which ranked 53.33%, the aromatic content of A6 had lowest aromatic content and higher resin content, and the resin content of A4 was highest which ranked 41.9%, with lowest content of asphaltene 0.5%. It was defined that component coefficient =(saturates + asphaltene)/ (aromatic + resin), the higher saturates and asphaltene content, the easier for the asphaltene in asphalt to form a flocculated network structure with elasticity, with unstable colloidal dispersion system, when aromatic and resin content is higher, asphaltene in asphalt preferred to form viscous system with stable colloid system.

3.2. Effect of asphalt composition on penetration ratio of asphalt residue in long-term aging
Among the three properties of asphalt (penetration, softening point, ductility), penetration is the most suitable to characterize the anti-aging performance of asphalt, so the residual penetration ratio is selected
to analyze the influence of asphalt composition on asphalt aging performance. The residual penetration ratio of asphalt reflects the change of consistency pre and post asphalt aging. The value of residual penetration ratio of asphalt was greater, the better the anti-aging performance of asphalt; conversely, the worse the anti-aging performance. It can be seen from fig1 that the content of saturates and aromatic content of A3, A5 was close and higher than 60%, but the content distribution of resin and asphaltene was different, the asphaltene content of A3 is lower than resin content, the resin and asphaltene of A5 content was close; A6 had lower contents of saturate and aromatic, the content of resin and asphaltene was more than 60%. Meanwhile, asphaltene content of A3 was obviously lower than others, the asphaltene content of A5 and A6 was close, with A5 slightly lower. Figure 2 shows the variation of residual penetration ratio of A3, A5, A6 at different aging stages.

From figure 2, it can be seen that with the prolongation of aging time, the residual penetration ratio of three kinds of asphalt showed a significant decreasing trend, indicating that the aging degree of asphalt is deepening continuously. The residual penetration ratio of A3 asphalt was obviously larger than that of the other two asphalts at different aging stage, indicating better anti-aging performance of A3. The residual penetration ratio of A3 asphalt was still higher than 60% at PAV 20 h aging stage, meanwhile, the residual penetration ratio of other two asphalts were around 30%, it can be seen that the A5 has close changing curve with A6 with slightly higher residual penetration ratio at any aging stage.

3.3. Effect of Asphalt Composition on the Sensitivity of Asphalt Aging Temperature

A viscous temperature index VTS was selected to investigate the influence of asphalt composition and aging time on the temperature sensitivity of asphalt after aging. The viscosity of 80°C, 100°C, 120°C, 135°C and 160°C of asphalt with different aging degree were tested. In a wide temperature range, the viscosity and temperature of asphalt obey the Saal formula:

\[
\eta = \eta_0 \exp \left( \frac{m}{t + 273.15} \right)
\]

Where: \( \eta \): the viscosity at the corresponding temperature with unit mPa.s, \( t \) is the temperature, with unit °C; \( n \): ordinate at the origin, \( m \): the slope of the straight line, representing the temperature sensitivity of asphalt. The absolute value of \( m \) is expressed in VTS, which is called viscous temperature index. Higher VTS value shows higher temperature sensitivity of asphalt. The characteristics properties of asphalt due to temperature change are called temperature sensitivity. The viscosity at different temperature is substituted into E.q (1) to get the m value, that is, VTS. Selected and the variation curves of the VTS values of A3, A5, A6 asphalt after different long-term aging stages is shown in figure 3.
It can be seen from figure 3 that the temperature sensitivity of all three kinds of asphalt is enhanced with the deepening of aging degree, that is because the light component of asphalt gradually decreased with the deepening of aging degree, while heavy fraction that provided viscosity increased gradually. the VTS of A3 increased gradually from the initial to PAV 5 h aging stage, and when the long-term aging time was more than 10 h, the temperature sensitive performance of asphalt tended to be stable, mainly because at this time the light components in the asphalt were almost converted into the heavy fraction, and the content of the heavy fraction has little effect on the temperature sensitivity of asphalt. VTS of A5 increased gradually with the aging degree. VTS of A6 increased significantly from initial to the TFOT aging process, indicating that the TFOT aging process had a greater impact on the viscosity of asphalt, while VTS growth of A6 during PAV aging process was relatively flat.

3.4. Effect of Composition on Long-term Aging Resistance to Rutting of Asphalt
The change trend of anti-rutting factor $G^\prime\sin\delta$ and phase angle $\delta$ at 60°C is shown in figure 4. The size of rutting factor directly reflects the strength of asphalt resistance to rutting, the greater value indicates that asphalt resistance to rutting is stronger; otherwise, the weaker. The phase angle reflects the proportion of viscous composition and elastic composition in asphalt. The larger the phase angle indicates that the more viscous composition in asphalt, the less elastic composition and the worse resistance to deformation. The aging process of asphalt will lead to the change of molecular structure and chemical composition in asphalt, which will lead to the increase of stiffness, the decrease of asphalt viscosity and the increase of elasticity during aging. Although the conventional properties of the six kinds of asphalt are close, the rheological properties of the asphalt are quite different. It can be seen from figure 4 that during the aging process A2 the rutting factor of asphalt is the smallest, which is obviously smaller than that of the other five kinds of asphalt, and the phase angle is the largest, which indicates that the elastic composition in the asphalt A2 is lowest.
3.5. Effect of asphalt composition on long-term aging viscoelastic properties of asphalt

Asphalt will show the properties of both viscous and elastic materials under certain conditions. Elastic modulus $G'$ was known as storage modulus, represents the ability of the material to recover to its original state after the force deformation, and the asphalt resistance ability to deformation mainly depends on the elastic modulus $G'$. Viscous modulus $G''$ was also called loss modulus, represents the energy lost in the form of heat during the material's mechanical deformation, and those lost energy could not be recovered.

DSR was used to carry out 60°C frequency sweeping tests on asphalt samples from 6 various oil sources at different aging stages to analyze the dependence of viscous modulus $G''$, elastic modulus $G'$ on frequency, to explore the variation of viscoelastic parameters of asphalt different types after long-term aging, and to reveal the influence of asphalt composition on viscoelastic properties pre and after asphalt aging. The results of the comparison of the viscoelastic properties of the six original and PAV aged 20 h samples are shown in Figure 5.

![Figure 4: The effects of asphalt composition on $G*/\sin\delta$ and $\delta$ at different aging stage](Image)

![Figure 5: $G'$ and $G''$ changing with frequencies of original and PAV 20h asphalt](Image)
It can be seen from fig5 that G’ of A1, A2, A4 increased with the frequency. G’ of A3, A5, A6 increased with the frequency, however decreased with the frequency when the frequency was above 100 rad/s, indicating that the viscoelastic range of the asphalt was exceeded, G" of the A2 increased with the frequency, however when the frequency was above 100 rad/s, it also appeared to decrease with the frequency increasing, and the G" of other 5 asphalts always increased with the frequency. The G" and G’ of six asphalts increased with the increase of frequency after of PAV 20h aged. After 20 h of PAV aging, the G’ of aged asphalt was larger than that of original asphalt. Under the same aging condition, the G" of A1, A2, A4 is less than G’, that is, the asphalt viscosity component was lower than the elastic component, and the G" of A3, A5, A6 was larger than G’, that is, the asphalt viscosity is larger than the elastic component. The effect of aging process on storage modulus G’ of A3, A5 and A6 was higher than that of A1, A2 and A4. The influence of aging process on the G" of A1, A2 and A4 was more obvious than A3, A5 and A6.

4. Conclusion
(1) The asphalt composition has obvious influence on the long-term aging performance, in which the asphaltene content in asphalt is strongly and negatively related to the change of asphalt performance during the long-term aging process, the less the asphaltene content, the greater the residual penetration ratio.

(2) The temperature sensitivity of asphalt increases with the increase of aging degree, because the light component of asphalt decreases gradually with the increase of aging degree, and the recombination component that provides viscosity increases gradually.

(3) Under the same aging condition, G" of A1, A2 and A4 was less than G’ which shows asphalt viscosity is less than elastic property. G" of A3, A5 and A6 is greater than G’ which shows asphalt viscosity is greater than elastic property. The effect of aging process on storage modulus G’ of A3, A5 and A6 was higher than that of A1, A2 and A4. The effect of aging process on the G" of loss modulus of A1, A2 and A4 was more obvious than that of A3, A5 and A6.

Acknowledgments
This work was financially supported by National Natural Science Foundation of China (NSFC) fund. No.51608511

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