Article:
Ding, H, Nili, A, Rahman, A et al. (3 more authors) (2022) Role of asphalt binder compositions in the thermoreversible aging Process. International Journal of Pavement Engineering. pp. 1-9. ISSN 1029-8436

https://doi.org/10.1080/10298436.2022.2147524

Role of asphalt binder compositions in the thermoreversible aging phenomenon

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Acknowledgments

This study was supported by the Sichuan Applied Basic Research Project under grant number 2021YJ0533, Fundamental Research Funds for the Central Universities, SWJTU under grant numbers 2682021CX017 and 2682022CX002, National Natural Science Foundation of China under grant numbers 52008352 and 52178438. We would like to thank the Analytical and Testing Center of Southwest Jiaotong University for the thermal analysis and support of the 111 Project (B21011).

Role of asphalt binder compositions in the thermoreversible aging phenomenon

Abstract

In order to understand the contribution of asphalt components to thermoreversible aging, the extended bending beam rheometer (Ex-BBR) test, SARA fractions separation, and thermal analysis were performed on a series of asphalt binders from different sources. The results indicated that thermoreversible aging is not an inherent characteristic of asphalt, and some binders were not affected by thermoreversible aging. Grade loss caused by thermoreversible aging showed a high correlation with wax content in asphalt but had no apparent relationship with asphaltenes content and colloidal structure index used. Moreover, the thermal analysis results well explained the degree of thermoreversible aging in the asphalt binder. Finally, the endothermic peak and crystallites formed in asphalt binder could have resulted from the long side chains in naphthene aromatic molecules.

Keywords: asphalt binder, thermoreversible aging, physical hardening, four fractions, thermal analysis

Introduction

Asphalt-based materials are playing an increasingly important role in the construction of transportation infrastructures due to their waterproof resistance, vibration damping, and easy maintenance characteristics. Unlike cement-based materials, asphalt-based materials would continue to harden or become brittle with the extension of service life. The hardening effect will significantly reduce the crack resistance and water stability of asphalt materials utilized in the surface course, which makes the asphalt pavement prone to early damage (Ling *et al.* 2019). The tendency for asphalt to harden under the influence of the atmosphere has been known and studied for many years. Generally, the term "aging" is often used in engineering to describe the hardening of asphalt binder during storage, mixing, laying, and in-service conditions (Zhang *et al.* 2011a, Hofko *et al.* 2015). There are many factors that can cause asphalt to age, but the most important factors can be divided into four categories, namely, volatilization, oxidation, exudation, and reversible structuring (Ling *et al.* 2017, Angius *et al.* 2018).

Volatilization and oxidation are two aging modes that are most familiar to researchers. Volatilization happens when light components of asphalt evaporate during mixing the binder with aggregates in a hot drum. On the other hand, when the oxygen in the air reacts with the asphalt binder, oxidation occurs accordingly (Zhang *et al.* 2011b, Mirwald *et al.* 2020, Hofer *et al.* 2022, Mirwald *et al.* 2022). Current Superpave binder specification usually employs rolling thin-film oven (RTFO) and pressure aging vessel (PAV) aging tests to simulate these two types of aging in the laboratory, respectively. Exudative aging results from the movement of oily components that exude from the asphalt binder into the mineral aggregate. This phenomenon is energy driven in that the oils leaving the gelled binder would allow the latter to slowly shrink at low temperatures. Van Gooswilligen et al. (Gooswilligen *et al.* 1989) once developed the exudation droplet test in Shell laboratory to quantify the exudation aging tendency of asphalt binder. However, exudative aging did not get much attention due to a lack of direct evidence that illustrates the importance of this phenomenon to the durability of asphalt pavement.

Reversible structuring is another important aging mode that is ignored by most researchers (Babagoli *et al.* 2021, Xu *et al.* 2021, Zhang *et al.* 2021). This kind of aging usually refers to the isothermal hardening phenomenon in which the stiffness of asphalt binder will increase exponentially with storage time when asphalt binder is stored at room or cold temperatures (Claudy *et al.* 1991, Bahia and Anderson 1992, Claudy *et al.* 1992b, Bahia and Anderson 1993, Petersen *et al.* 1994, Claudy *et al.* 1998, Anderson and Marasteanu 1999, Huang *et al.* 1999, Romero *et al.* 1999, McKay *et al.* 2001, Robertson *et al.* 2001). In order to better reveal the mechanisms of thermoreversible aging, this study aims to determine the contribution of the composition and related structural parameters of asphalt binder to thermoreversible aging. In addition, modulated differential scanning calorimetry (MDSC) tests were performed to better understand the thermal behavior of representative asphalt binders undergoing different thermal histories.

Background

During the thermoreversible aging process, there is no chemical reaction, and the stiffness can be restored to its original state by heating. In the existing literature, many terms have been used to describe this process in asphalt binders such as aging hardening (Traxler and Shelby 1973), formation of equilibrium structures (Pechenyi and Kuznetsov 1990), setting (Hu *et al.* 2017), thixotropic hardening (Stefanczyk 1993), steric hardening (Masson *et al.* 2005), physical aging (Kriz *et al.* 2008b), physical hardening (Bahia 1991, Placnche *et al.* 1997), reversible aging (Hesp *et al.* 2007), and more recently thermoreversible aging (Berkowitz *et al.* 2019, Ding *et al.* 2021a, Ding *et al.* 2021b).

The term thermoreversible aging is used in this article because it can better reflect the thermal history dependence of this phenomenon. Laboratory and field test sections demonstrate that thermoreversible and oxidative agings are equally important to the durability of asphalt binders, especially in cold regions (Berkowitz *et al.* 2019, Ding *et al.* 2019). However, the magnitude of thermoreversible aging in asphalt binders produced by different asphalt refineries may be different. Grade loss caused by thermoreversible aging may range from negligible for binders derived from Alberta oil sand crudes to rather significant for some Chinese crude oil-derived asphalt binders (Lill *et al.* 2019, Lill *et al.* 2020). Therefore, it is imperative to understand the contribution of asphalt components to thermoreversible aging to provide a basis for the production of high-quality asphalt binders used in pavement engineering.

Many analytical theories of asphalt binders are based on universal ones, and thermoreversible aging in asphalt binders is no exception. Hence, it is necessary to review the relevant theoretical cornerstone, which will help to better understand the mechanism of thermoreversible aging. If we regard matter as a system in a broad sense, what we usually call a system is often in an equilibrium state, that is, a steady state or a metastable state (Rosa and Auriemma 2013). In this condition, its properties do not change with time, that is, the first derivative of free energy is zero, as shown in Figure 1.

Figure 1. Evolution of the mechanism of thermoreversible aging of asphalt as a system.

Free energy is a concept useful in the thermodynamics of chemical or thermal processes in engineering and science (Dosière 2012). The free energy function can describe the transition from state A to state B. State A is a metastable equilibrium state, which is the local minimum of free energy. Under small disturbances, the system is stable and will eventually evolve into a more stable state, however, it takes a long time. State B is a steady state, which is the global minimum value of free energy. During the transition from state A to state B, the free energy increases to a local maximum, that is, an unstable state and the unstable fluctuations of the system ultimately lead to a short life in this state. For metastable and steady states, the second derivative of free energy must be greater than zero. For unstable states, at least one derivative is less than zero. The phase transition process also changes between different equilibrium states. The system will go through a series of non-equilibrium or unstable states, and the properties of the system will change continuously.

Traxler is an earlier scholar who systematically studied various asphalt aging mechanisms and carried out a lot of pioneering works in the field of asphalt aging research. He has summarized as many as 15 different factors that influence asphalt aging, including thermoreversible aging, and stated that excessive hardening of asphalt from any cause is undesirable because it may reduce its adhesiveness and durability during its service life (Traxler 1963). The approximate order of importance in the hardening of asphalt binder is oxidation, volatilization, thermoreversible aging, polymerization induced by actinic light, and the last one is condensation polymerization induced by heat.

In the 1980s, Pechenyi conducted a relatively comprehensive study on the thermoreversible aging characteristics of asphalt binders (Pencheyi 1981, Pencheyi 1985, Pencheyi 1990). He attributed the internal state of asphalt binder changes with time to the chemical and physical (structural and phase) transformations, and for the first time applied a crystallization kinetics framework to describe volume changes during isothermal conditioning. Based on colloid chemical science, a model of the structure of asphalt binder was proposed by Pechenyi, which takes into account the degree of deviation of the dispersed system from the equilibrium state. In addition, he devised a probabilistic method for predicting the service life of asphalt concrete, incorporating structural and phase transformations in asphalt binder under operating conditions. Unfortunately, many studies of Pechenyi are less known to current scholars because most of his publications were recorded in old Russian papers. Moreover, many studies mainly focused on the effects of thermoreversible aging on the physical and mechanical properties of asphalt binders such as penetration, viscosity, and stiffness (Marasteanu and Anderson 1996, Basu *et al.* 2003, Marasteanu 2004, Marasteanu *et al.* 2004, Marasteanu and Falchetto 2018, Wang *et al.* 2019).

It is easier to observe the effects of thermoreversible aging on the mechanical properties and microscopic morphology in binder tests while similar trends are rarely observed in corresponding mixture tests. The main reason is that existing mixture characterization tests are not sensitive to microcracks in the binder phase (Huang *et al.* 1998, Dongre 2000, Shenoy 2002, Marasteanu *et al.* 2007, Falchetto *et al.* 2011, Togunde and Hesp 2012). Queen’s University in cooperation with the Ministry of Transportation of Ontario (MTO) built field pavement test sections, and their field test results clearly showed a correlation between thermoreversible aging of asphalt binder and the degree of field cracking (Li *et al.* 2021).

Understanding the formation mechanism of thermoreversible aging is essential for predicting the degree of thermoreversible aging in asphalt binders and developing related additives to eliminate the detrimental effects of thermoreversible aging. The aggregation of asphaltene components in asphalt during isothermal conditioning is considered to be one of the causes of thermoreversible aging (Masson *et al.* 2005). This gradual association of asphaltenes is motivated by the Brownian motion and diffusion process. During the Strategic Highway Research Program (SHRP), researchers used the conception of free volume collapse to explain the thermoreversible aging of asphalt binder at low temperatures (Bahia and Velasquez 2010). However, it is still unclear which components cause volume shrinkage in the asphalt binder. In addition, not all volume changes associated with free volume contribute to molecular mobility. Therefore, the accuracy of the term "free volume collapse" is debatable.

Results of thermal analysis conducted by Claudy et al. (Claudy *et al.* 1992a), Qiu et al. (Qiu *et al.* 2020), and Frolov et al. (Frolov *et al.* 2016) indicated that crystallization of waxes in asphalt may contribute to thermoreversible aging. More recently, variable-temperature Fourier-transform infrared spectroscopy (VT-FTIR) was developed to quantify solid waxes in asphalt binder and it was observed that thermoreversible aging can significantly increase the wax melting temperature of asphalt binder (Ding and Hesp 2020b, Ding and Hesp 2020a). Kriz et al. Kriz *et al.* (2008a) hold the opinion that not all crystalline waxes will lead to thermoreversible aging and proposed a theoretical model based on a rigid amorphous phase. Essentially, the rigid amorphous phase also depends on the crystalline wax in the asphalt binder. In addition to the crystalline wax content, thermoreversible aging may also result from wax restructuring (Nivitha *et al.* 2019). In other words, solid-solid transitions were identified in asphalt binder which can be attributed to the change in conformation of crystalline wax from orthorhombic to hexagonal. Having demonstrated that a considerable variation in susceptibility to thermoreversible aging exists among commercial asphalt binders, the question now arises as to the causes of these differences. It is proposed that the answer may be found in the chemical compositions of the various asphalt binders.

Experimental program

Materials

The asphalt binders used in this study are several representative samples collected from the routine quality inspection of the Key Laboratory for Highway Engineering of Sichuan Province. Because these asphalt binders are applicable to different pavement grades, there are big differences in the properties of asphalt binders. Moreover, these asphalts are all unmodified asphalts, but their crude oil source and production process are unknown. The sample codes and general properties of asphalt binders used in this study are listed in Table 1. The wax content of each asphalt sample was determined by the solvent precipitation method (JTG E20-T0615) (Transport 2011). It can be seen that the wax content of asphalt binders used in this study is distributed in a wide range, so the contribution of wax to thermoreversible aging can be verified.

Table 1. General properties of asphalt binders used in this study

Extended bending beam rheometer (Ex-BBR) test

The asphalt binder is still in a thermodynamically non-equilibrium state when short-time isothermal conditioning (1 hour) is used, so it is necessary to use the properties after long-term (3 days) conditioning to determine the low-temperature performance of the binder in the equilibrium state. Generally, the grades of binders that are classified by conventional BBR are distributed in a narrow range while the Ex-BBR test has a higher degree of discrimination for asphalt binders and is more sensitive to the formula and chemical composition of the binder.

Separation of asphalt into four fractions

As asphalt binder is a mixture of various hydrocarbons and their non-metallic (oxygen, sulfur, nitrogen) derivatives, it is difficult to divide it into several single compounds. For the convenience of analysis, it is usually divided into several components according to the polarity of asphalt to the solvent (Helm 1969). Column chromatography is a common method for the purification and separation of organic or inorganic substances. Usually, the substance to be separated is uniformly added to the glass column containing the stationary phase, and then an appropriate eluent is added for washing. Owing to the different speeds of each component moving with the mobile phase in the column, the components are separated by quantitatively collecting the eluent in sections. Finally, the elution solvent is removed by a rotary evaporator to obtain the asphalt components. To be specific, the asphalt binder is separated into four fractions according to the ASTM D4124 method. The four fractions are defined as iso-octane insoluble asphaltenes, naphthene aromatics, polar aromatics, and saturates. In this study, each separation experiment was performed in duplicate in order to allow repeatability. To characterize the dispersion in the polarity of the constituent molecules of a selected asphalt binder, the Gaestel index was used:

$$GI = (A+SAT)/(PA+NA) \tag{1}$$

where Gaestel index (GI) is an empirical parameter characteristic of the degree of dispersion in polarity of an asphalt binder; A is asphaltenes content; SAT is saturates content; PA is polar aromatics content; and NA is naphthene aromatics content.

Modulated differential scanning calorimetry (MDSC) test

Thermal analysis by MDSC is an automated method for studying the thermal history dependence of asphalt binders. Compared to VT-FTIR and nuclear magnetic resonance spectroscopy (NMR) methods, it is less affected by the proficiency of the operator and can accurately control the rates of heating and cooling. For research on the thermoreversible aging of asphalt, different thermal histories are usually applied through the cooling stage, and the influence of thermal history on the thermal behavior of asphalt is reflected through the heating stage. Therefore, it is only necessary to record the data of the heating process. Different transformation processes may occur in the same temperature range, and it is difficult for traditional DSC curves to give an accurate explanation. In many cases, MDSC can distinguish these overlapping processes and reflect them on the reversible and irreversible heat flow curves. Since the reversible process corresponds to the change of sample enthalpy, which is a thermodynamic process, it can be expected that the glass transition will appear on the reversible heat flow curve. The processes of enthalpy relaxation, crystallization, volatilization, decomposition, and vulcanization will be reflected in the irreversible heat flow curve because they are kinetic processes. The explanation of the melting transition is not so straightforward. The melting process may be reflected in both reversible and irreversible heat flow curves.

Results and Discussion

Extended bending beam rheometer (Ex-BBR) test results

Grade loss, which is the grade difference between 1 and 72hr of conditioning, is used to measure the magnitude of thermoreversible aging. The grade loss of different asphalt binders after going through isothermal conditioning is given in Figure 2. It can be seen that the low-temperature grades of some asphalt binders are hardly affected by thermoreversible aging, such as samples A, B, F, and K. However, low-temperature grade loss of some binders was significant after suffering from long-term cold storage, such as samples C, G, and I. It can be inferred that thermoreversible aging is not an inherent characteristic of asphalt, and some binders are not affected by thermoreversible aging. By considering thermoreversible aging as a criterion, one can better distinguish the asphalt binder with good performance from the one with poor performance. This basic point of view is important. However, some scholars based on their limited tested data got concluded that all kinds of asphalt binders would be affected by thermoreversible aging, so this characteristic does not need to be reflected in the specification. According to a statistical analysis of a large number of asphalt binders performed by the Ministry of Transportation of Ontario (MTO) and Queen's University, it is considered that the grade loss between two asphalt binders has a significant difference when the value is higher than 3℃ (Ma *et al.* 2022). In order to keep in the frame of the Superpave binder performance grading system, the threshold of 6℃ is established as the acceptance criterion for thermoreversible aging in most pavement contracts.

Figure 2. Grade loss of different asphalt binders after going through isothermal conditioning.

SARA analysis of asphalt binders

Although it is difficult to establish a direct relationship between the components of asphalt and its performance, a reasonable distribution of SARA fractions is the key to ensuring the formation of a stable colloidal structure in asphalt binder. Test results of four fractions of eleven asphalt binders are shown in Figure 3. It can be seen that there is a big difference in the proportion of the components of different asphalt binders. It is interesting to observe that sample A has the highest saturation content while the lowest wax content. In contrast, sample G has the lowest saturation content while relatively high wax content. Generally speaking, wax in asphalt binder is mainly composed of saturated linear long-chain molecules. The higher the saturation content is, the higher the wax content would be. The extremely low saturates fraction in sample G may be due to the inability of the solvent to extract all the saturates fraction. In order to quantify the colloidal dispersion structure of asphalt binder, the four fractions result was used to calculate the *GI* index according to Equation (1) and establish a relationship between asphalt dispersion structure and thermoreversible aging. *GI* is interpreted as being approximately proportional to the dispersion of the polarity of a given asphalt binder's constituent molecules. Increasing values of *GI* indicate a broader distribution of polar functional groups.

Figure 3. The proportion of each component in the asphalt binder.

Grade loss correlation with physical and chemical properties

The relationship between thermoreversible aging and asphalt components-related indices is displayed in Figure 4. Data in this study indicate that the grade loss shows a high correlation with the wax content in asphalt, but has no obvious relationship with asphaltenes content. These results are inconsistent with the earlier conclusion by Bahia et al. who stated that low-temperature reversible aging has no linkage with wax content (Bahia and Anderson 1991). They hold the opinion that thermoreversible aging continues for a very long time. It is highly improbable that the crystallization of wax extends for such long times and continues to affect the creep compliance in a such significant way. Our experiments, however, show a different trend from Bahia et al.'s observation due to using different parameters. Obviously, the correlation between wax content and thermoreversible aging is also affected by the molecular weight distribution of crystallizable fractions. Generally, a lower *GI* value indicates that asphalt colloidal structure is close to that of a sol asphalt and sol asphalt tends to suffer slightly from isothermal conditioning. It is surprising to observe that the grade loss declined as the

Gaestel index increased. More research is needed to explain this abnormal trend. The penetration index was calculated to further explore the relationship between the colloidal structure of asphalt and thermoreversible aging (Figure 5). From the point of view of penetration index, the asphalt binders used in this study are all sol-gel or sol type. Similar to the Gaestel index, the colloidal structure characterized by the penetration index showed no obvious correlation with the thermoreversible aging trend of asphalt.

Figure 4. The relationship between thermoreversible aging and asphalt components related indices (a) wax content, (b) asphaltenes content, and (c) Gaestel index.

Figure 5. The relationship between thermoreversible aging and penetration index of asphalt binder.

MDSC results of asphalt binders

The endothermic and exothermic effects of asphalt binder during the heating process can be reflected by irreversible heat flow. The peaks on the irreversible heat flow curve are usually caused by the melting or precipitation of crystalline components in asphalt (Planche *et al.* 1998). As can be seen from Figure 6, there is almost no endothermic peak in samples A, B, and F. Moreover, the size of the endothermic peak did not change with conditioning time, denoting the lower degree of thermoreversible aging in these binders. In contrast, the irreversible heat flow curves changed significantly with conditioning time in some asphalt binders (C, G, H, and I). With no isothermal conditioning, only a single exothermic peak of cold crystallization appears. With the extension of conditioning time, the exothermic peak of cold crystallization gradually transforms into the endothermic peak of melting. However, this study did not find the double-endothermic peak reported in the literature (Frolov *et al.* 2020). Possible reasons could be that the asphalt samples used did not undergo a solid-solid transformation or the distribution of crystal molecular weight was different. It is believed that saturates, which are basically a mixture of various n-alkanes, contribute most to the endothermic effect (Harnsberger and F.Turner 1997). Sample G exhibited the largest endothermic peak after 24h isothermal conditioning while its saturation content is extremely low. The length of linear paraffinic side chains in paraffin-naphthene-aromatic molecules may be the parameter that affects the endothermic behavior of asphalt. Irregular bulky ring structures cannot easily fit into crystal structures. On the contrary, they can disrupt the crystallization process. Only those with enough chain length would be able to form crystallites, as illustrated in Figure 7.

Figure 6. Irreversible heat flow curves of selected asphalt binders.

Figure 7. Schematic illustration of possible crystallites formed by side naphthene aromatics structures and linear paraffin molecules.

The local maximum value of the first derivative curve of the reversible heat capacity usually corresponds to the glass transition temperature. It can be clearly seen from Figure 8 that the binders with a low degree of thermoreversible aging exhibited a Gaussian distribution with a unique maximum and the curves did not shift with conditioning time. On the other hand, for a binder with a high degree of thermoreversible aging, the curve at the low-temperature domain shifted to high temperature which means higher glass transition temperature with the extension of conditioning time. In addition, the signal at around 0℃ increased with isothermal conditioning, indicating that an obvious multiphase structure is formed inside the asphalt.

Figure 8. Reversible heat capacity first derivative curves of selected asphalt binders.

Conclusions

Based on a systematic literature review and a series of experimental works, several conclusions emerged from this research effort. They are as follows:

- Thermoreversible aging is not an inherent characteristic of asphalt, and some binders were not affected by thermoreversible aging. By considering thermoreversible aging as a criterion, one can better distinguish the asphalt binder with good performance from the one with poor performance.

- The relationship between thermoreversible aging and asphalt components related indices indicated that the grade loss showed a high correlation with the wax content in asphalt, but had no obvious relationship with asphaltenes content and colloidal structure indices used (Gaestel index and penetration index).
- The results of the thermal analysis can well explain the degree of thermoreversible aging in asphalt binders. The binder with a low crystallizable fraction was less affected by isothermal conditioning, and the first derivative of reversible heat capacity presented a Gaussian distribution.
- There was an asphalt binder sample that had the largest endothermic peak after 24 h of isothermal conditioning, while its saturation content was extremely low. The endothermic peak and crystallites formed might be due to the long side chains in naphthene aromatic molecules.
- The use of modified asphalt in the pavement is gradually increasing, however, the influence mechanism of various modifiers on the thermoreversible aging in asphalt is still unclear. The thermoreversible aging characteristics of modified asphalt deserve further study.

Disclosure statement

No potential conflict of interest was reported by the authors.

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