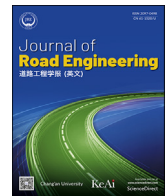




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Review Article

Review of ultraviolet ageing mechanisms and anti-ageing methods for asphalt binders



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HIGHLIGHTS

- The UV ageing mechanisms and sensitive wavelength theory of asphalt are revised.
- UV ageing effects on the chemical and technical properties of asphalt are illustrated.
- The effects and mechanisms of commonly used anti-ageing methods are investigated.
- Multi-functional composite LDHs/UVA anti-ageing agents are suggested.
- Gaps related to the UV ageing of asphalt are pointed out.

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SUMMARY

Asphalt binder is inevitably aged by ultraviolet (UV) light during its service period. UV ageing can significantly decrease the technical properties of asphalt binder. The sensitivity of asphalt to UV ageing and thermal-oxidative ageing differs, such that the UV ageing performance cannot be determined based on the thermal-oxidative ageing performance. Previous researches mainly focused on the chemical composition and technical performance changes of asphalt binder during UV ageing, and the UV light parameters effect on the ageing rate of asphalt binder. However, the theory for characterizing and explaining the development of UV ageing depth does not get too much attentions, and the UV ageing mechanism of asphalt binder is not very clear. Therefore, it cannot guide to develop or select the good methods or anti-UV ageing additives for asphalt binders. This paper focuses on the latest researches of the mechanisms and anti-ageing methods of asphalt binders. With the increase of UV ageing time, the UV ageing of asphalt binder develops gradually from the surface to inner part. There are various methods, such as low-penetration grade asphalt, less air void ratio, UV stabilizers and UV light absorbers, that can improve the UV ageing resistance of asphalt binders. A new theory of sensitive wavelengths of asphalt UV ageing is proposed, which can enrich the basic theory of asphalt UV ageing. Depending on this theory, different wavelengths of UV light have different ageing effects on asphalt binder. The composite anti-UV ageing additives with barrier and

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specific absorption effects on UV light is proposed, and may have better improvement effect on the anti-UV ageing performance of asphalt binder.

1. Introduction

Asphalt pavement has the advantages of good driving comfort, ease of maintenance, noise reduction, and no dust (Liu and Cao, 2009); as such, it has become the main construction material for highways and urban roads. The design service life of a highway pavement is 8–15 years, while the design base period for urban asphalt pavement is 10–15 years. Theoretically, asphalt pavement should be in service until the end of its design life before serious disease occurs and structural overhaul is required; however, the actual service life of asphalt pavement is much shorter than its design life.

Asphalt concrete is an asphalt pavement material, which consists of asphalt, aggregate, and filler. The asphalt acts as the binder to bond the loose aggregates (with suitable particle size distribution) and filler into a whole, and provides mechanical properties allowing for the fulfillment of load-bearing capacity, traffic safety (Bekheet et al., 2001), and comfort requirements. The viscoelasticity of the asphalt binder has a typical temperature (or time) dependence (Li et al., 2019a). In order to ensure that it has excellent mechanical and road properties, the asphalt binder should have good elasticity at high temperatures to meet rutting resistance requirements (Motamedi et al., 2021), and good adhesion at low temperatures to meet cracking resistance requirements. The asphalt binder is an organic material and, in the process of asphalt production, storage, and the service period (Yu et al., 2019), it will be subject to the action of environmental factors such as heat, ultraviolet (UV) light, oxygen, and water (Huang et al., 1996; Li et al., 2020b; Zou et al., 2021). Thus, the asphalt binder will inevitably be aged. After ageing, asphalt becomes brittle and hard; its water stability, low-temperature crack resistance, and fatigue resistance are deteriorated; and the occurrence and development of asphalt pavement distress are accelerated. Coupled with the repeated action of vehicle loads, the pavement structure is gradually destroyed, leading the service life of asphalt pavement to be much shorter than the design life. During the use of asphalt pavement, it is subjected to multiple complex service environment factors and vehicle loads, and the decay and deterioration of road performance occurs too quickly, which is an important reason for the occurrence of pavement distress and reduction of service life.

Such service life reduction leads to significant road maintenance and repair tasks. In 2020, the maintenance expenditures for only the 179,200 km of toll roads in China amounted to 74.41 billion yuan, comprising more than 50% of the total annual investment in water transport construction. At the same time, these maintenance and repair processes require additional new raw materials (Pan et al., 2021), leading to an increase in the extraction of natural resources, such as stone and asphalt, and causing a huge environmental burden. The anti-ageing performance of asphalt pavement materials is a key factor affecting the quality and life of asphalt pavements; therefore, improving the anti-ageing performance of asphalt pavement materials can effectively reduce asphalt pavement diseases and extend the service life of pavements, leading to significant economic and environmental protection benefits (Zhang, 2021).

The ageing modes of asphalt binders include thermal-oxidative ageing (Chen et al., 2018) and UV ageing (Xiao and Fan, 2022). UV ageing refers to the ageing that occurs in the open traffic phase of asphalt pavement under the action of external environmental factors, such as UV light, oxygen, and temperature. Short-term thermal-oxidative ageing refers to the ageing of asphalt that occurs during the production, storage, and transportation of the asphalt binder, and in the mixing, transportation, and paving stages of asphalt mixtures. Long-term thermal-oxidative ageing testing is carried out to simulate the thermal-oxidative ageing that occurs during the asphalt pavement service period.

A lot of researches have been carried out regarding the thermal-oxidative ageing behavior of asphalt and asphalt mixtures. On one hand, considering thermal-oxidative ageing (whether short- or long-term), a unified simulation test standard has been established, as well as technical standards for the performance indicators of asphalt after ageing. For instance, the rolling thin film oven test (RTFOT, EN 12607–1, ASTM D 2872 (Lu and Isacsson, 2002) or AASHTO T240) or thin film oven test (TFOT, ASTM D 1754) can be applied to simulate the short-term thermal-oxidative ageing of asphalt binders, and a pressure ageing vessel (PAV, ASTM D 6521) can be used to simulate the long-term thermal-oxidative ageing of asphalt binders. However, thermal-oxidative ageing simulation is mainly used to evaluate the oxidation resistance of asphalt under experimental temperature and oxygen (or pressure) conditions, but cannot account for the effects of multiple factors or the actual use conditions on the ageing of asphalt; for example, UV light is not considered. The polymer photochemical theory states that the mechanism of asphalt UV ageing is completely different from the mechanism of thermal-oxidative ageing (Wu, 2003), and the sensitivity of asphalt to thermal-oxidative ageing and photo-oxidative ageing differs, such that asphalt thermal-oxidative ageing resistance testing cannot be used to evaluate or replace UV ageing resistance.

Compared to researches on the thermal-oxidative ageing of asphalt, studies focused on its anti-UV ageing performance are relatively few and there are still many shortcomings. In recent years, researches on the mechanisms of UV ageing of asphalt have focused on the changes of elemental content, chemical structure, microscopic morphology, and components of asphalt during UV ageing, as well as the effects of UV light intensity, ageing time, and test temperature on the ageing state. Other factors, such as the effect of the wavelength range of UV light on the ageing rate of asphalt and the growth mechanism of asphalt ageing depth are still unclear, and cannot reveal the UV ageing mechanisms of asphalt perfectly. In this paper, we analyze the effects of UV ageing on the chemical properties and technical performance of asphalt. Based on a summary of the research results on the UV ageing mechanisms of asphalt, we detail the deficiencies of the existing basic theory of UV ageing mechanisms and propose research ideas for the improvement of the basic theory of UV ageing of asphalt, thus providing theoretical support for the development of UV ageing methods based on the UV ageing mechanisms of asphalt.

2. UV ageing process of asphalt

The whole life cycle of asphalt consists of production, storage, construction, and service process, where the environmental conditions differ at each stage, and the influencing factors of ageing also differ in different stages. The ageing process of asphalt, throughout its whole life cycle, is shown in Fig. 1.

During the production and storage phases of asphalt, it undergoes hot storage, hot transportation, storage tank pre-heating, and blending kettle development processes. In these stages, the light components in the asphalt volatilize and the asphalt at the surface in the storage tank reacts with oxygen in the air, resulting in asphalt ageing.

In the construction phase, during the asphalt mixing process, the heating temperature of the aggregates is generally in the range of 170 °C–180 °C, or even up to 190 °C. Asphalt is wrapped on the surface of the high-temperature aggregate. The thickness of the asphalt film is very thin, and the surface area of asphalt is large. For example, open-graded asphalt mixture is about 14 µm thick, while dense-graded asphalt mixture is about 6–10 µm thick. Therefore, the light components in the film-like asphalt evaporate rapidly, and chemical reactions occur under the coupling effects of temperature and oxygen. The thermal-oxidative

ageing in the asphalt mixing stage is much more serious than that in the asphalt binder production and storage stages. During the production, storage, transportation, and paving phases of asphalt mixtures, the mixtures are aged by oxygen. After the paving of asphalt mixtures, the thermal-oxidative ageing effect is relatively weak.

The main factors of above process on the asphalt ageing factors are mainly temperature and oxygen, mainly contributing to thermal-oxidative ageing. In the service phase of asphalt pavement, ageing of the asphalt mixture occurs under the action of external environmental factors, such as oxygen, UV light, temperature, and water. In the service process, as the asphalt mixture has already been through the high-temperature mixing process, the service temperature is much less than the construction temperature. The volatilization of low molecular components is no longer the main reason for asphalt ageing (Jemison et al., 1992), and photo-oxidative ageing under the action of UV light and oxygen is the main reason for the long-term ageing of asphalt pavement. Ageing of the asphalt binder causes the road performance to deteriorate, resulting in serious early disease of the road (Fig. 2) (Sun et al., 2020).

Therefore, the ageing of asphalt binder go through the whole life cycle of asphalt pavement, and the UV ageing is mainly occurred in the service period of asphalt pavement.

3. UV ageing effects on chemical properties and technical performance of asphalt

3.1. UV ageing effects on chemical properties of asphalt

The main elements in asphalt are carbon (80%–88%), hydrogen (8%–12%), sulfur (0–9%), oxygen (0–2%), and nitrogen (0–2%), as well as trace amounts of heteroatoms (Fernández-Gómez et al., 2013; Speight, 2006; Zhang et al., 2021). These elements make up the asphalt molecules, where different molecules have different chemical bonds, chemical functional groups, activities, and polarities (Pan et al., 2012). The macroscopic technical properties of asphalt are determined by the elemental composition, elemental binding states, and chemical structure of the asphalt molecules (Sultana and Bhasin, 2014). Wei et al. (2014) studied the correlation between the component ratios and elemental

contents of 23 asphalts and their surface energies. The results showed that there exists a significant correlation between the component ratios and elemental contents of asphalt and its surface energy. Yut and Zofka (2014) studied the relationship between the chemical composition and physical properties of asphalt, and showed that the colloidal dispersion state, molecular polarity, hydrogen bonding, and π - π intermolecular interactions (Hunter and Sanders, 1990) of asphalt significantly affect the physical properties, as well as the rheological properties, of asphalt. Michalica et al. (2008) studied the chemical composition and rheological properties of two types of asphalt aged for short and long periods. It was found that the molecular weight of the asphalt and, especially, the polarity of the components had the most significant effect on the rheological properties of asphalt.

Studies on the chemical properties of asphalt during thermal-oxidative ageing have shown that, in the absence of oxygen, the asphalt molecules are thermally impacted, and certain high molecular weight asphalt molecules are degraded to lower molecular weight molecules, while certain long chains and unsaturated bonds are broken. Subsequently, under the catalytic effect of the very small amount of heteroatoms contained in the asphalt, the small molecules can re-polymerize with each other and increase the molecular weight. This process is relatively slow without the oxidation of oxygen molecules. In addition, under the coupling actions of high temperature and oxygen, the ageing rate increases significantly (Bowers et al., 2014; Li et al., 2016, 2018b; Petersen, 2009; Siddiqui and Ali, 1999b). Wu et al. (2009a) performed the RTFOT and PAV on a styrene-butadiene-styrene (SBS)-modified asphalt. The results showed that, after thermal-oxidative ageing, the relative content of carbonyl and sulfoxide groups in the SBS asphalt increased, while the relative content of butadiene functional groups of the SBS modifier decreased. The asphaltene micelle content increased, the asphalt binder was oxidized, and the SBS modifier was degraded. In addition, changes in the chemical properties of asphalt binders were significantly correlated with changes in macroscopic technical properties (i.e., physical and rheological properties) after thermal-oxidative ageing; furthermore, the softening point and complex modulus increased after ageing. Ali et al. (2013) performed the RTFOT and PAV on rubber-modified asphalt, and the complex modulus

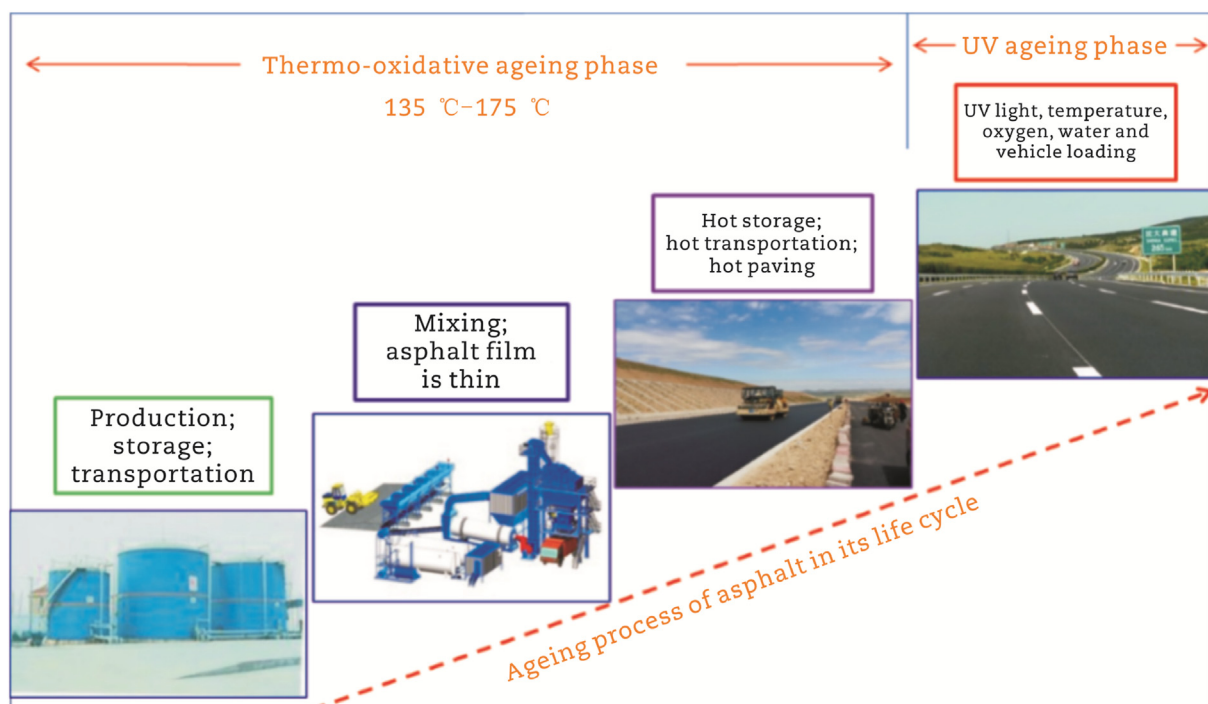


Fig. 1. Ageing process of asphalt throughout its life cycle.

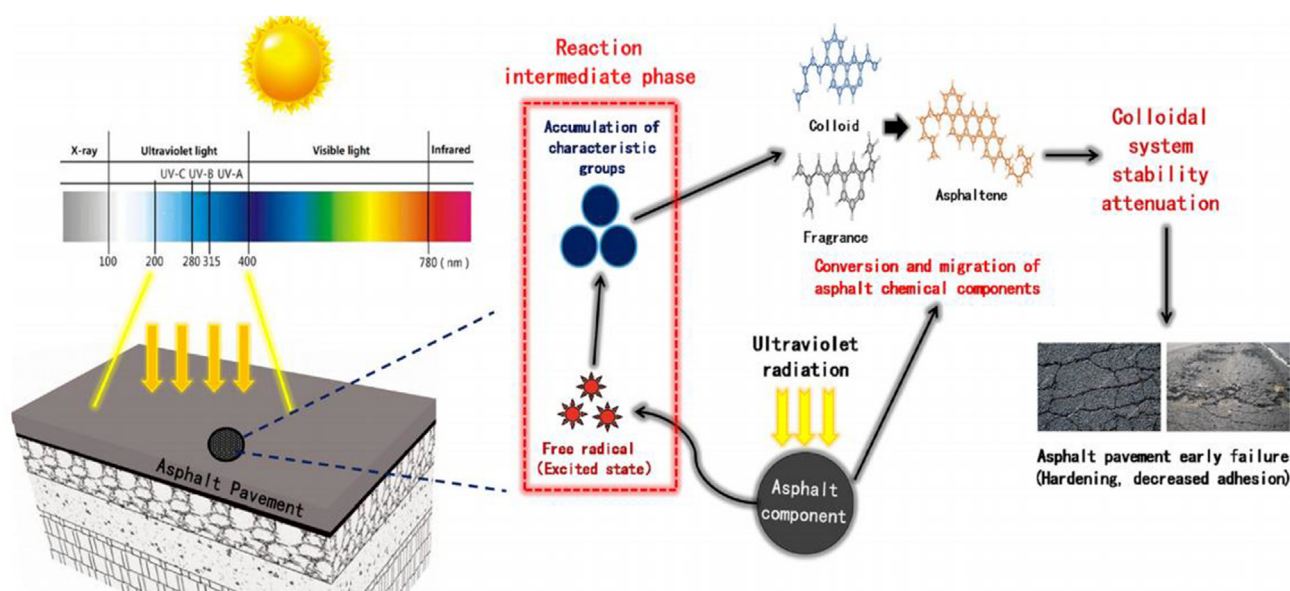


Fig. 2. Formation process of UV ageing of asphalt pavement (Sun et al., 2020).

and phase angle of asphalt were tested, using a dynamic shear rheometer (DSR), after ageing. The results showed that, after thermal-oxidative ageing, the rutting factor of the asphalt increased, the Brookfield viscosity was significantly increased, and the physical properties (e.g., softening point, needle penetration) changed significantly, indicating that the chemical and rheological properties of the asphalt binder were significantly degraded during thermal-oxidative ageing.

Similar to the thermal-oxidative ageing of asphalt, UV ageing can also significantly alter the chemical properties of asphalt binders. Wu et al. (2017a) indicated that, during UV radiation, the active carbon and sulfur in asphalt can absorb oxygen and be oxidized, resulting in an increase in oxygen content and the relative content of oxygen-containing functional groups (e.g., carbonyl and sulfoxide groups) in asphalt. Yu et al. (2019) showed that, after UV ageing, C=C bonds in unsaturated olefins in asphalt were broken to form C-H bonds, resulting in gradual increases in the relative contents of methyl and methylene; C-O was oxidized to C=O; and C-O and C-S bonds were broken to form S=O bonds. At the same time, UV ageing can break the cross-linked structure of SBS-modified asphalt binders and the chemical structure of SBS modifiers. The relative contents of polybutadiene (PB) C=C and polystyrene (PS) C-H in SBS are decreased by UV ageing. Mouillet et al. (2008) used RTFO to simulate short-term thermal-oxidative ageing of a rubber-modified asphalt binder, followed by indoor UV irradiation tests using asphalt films approximately 10 μm thick. The results showed that carbonyl functional groups were observed in the aged asphalt binder. Wu et al. (2010) investigated the effect of UV irradiation on the chemical structure of asphalt binders. The results showed that the relative content of carbonyl functional groups in the asphalt binders increased after UV irradiation. Furthermore, the viscosity of the SBS-modified asphalt binder was reduced, as the SBS modifier was also degraded during ageing, which weakened its modification effect. The technical properties of the asphalt decayed significantly after UV irradiation, and the ageing effect was more pronounced when the thickness of the asphalt film was less than 150 μm .

The effects of oxidation on the structure of the asphalt binder are mainly due to dehydrogenation, oxidation of alkyl sulfur to sulfoxide, oxidation of benzyl carbon to ketones, and oxidation of ketones to dicarboxylic anhydride and carboxylic acids (other carbonyl compounds) (Petersen, 2009). Under UV light irradiation and the action of oxygen, asphalt molecules undergo photo-oxidative degradation reactions, such as asphalt molecule isomerization, condensation, increases in the relative content of oxygen-containing functional groups, and dehydrogenation. Oxygen causes the removal of hydrogen atoms from carbon atoms,

resulting in an increase in the proportion of asphaltenes in the asphalt binder and a decrease in the proportion of resins and most aromatic compounds. These processes also lead to increases in polarity, acidity, and condensation of asphalt constituent molecules. Feng et al. (2016a) pointed out that, due to the complex chemical composition and structure of asphalt binders, a series of complex chemical reactions occur in the UV ageing phase. UV irradiation tests were conducted on the base asphalt, as well as saturated, aromatic fraction, resin, and asphaltene (SARA) fractions, respectively. The results showed that oxidation and aromatization reactions occurred in all four components of the asphalt binder and its SARA components. The single components separated from asphalt binder were more severely oxidized and more susceptible to UV ageing than the base asphalt. In contrast, the saturated fraction of asphalt was the least stable under UV irradiation conditions. Liu et al. (2015) indicated that the light fraction in asphalt volatilizes during UV ageing, which reduces the stability of the colloidal structure. Li et al. (2020c) showed that the proportion of saturated and aromatic fractions in asphalt decreased and the relative proportion of resin and asphaltene fractions increased after UV ageing; thus, the colloid structure index, colloid stability index, and the colloid stability were decreased. Siddiqui and Ali (1999a) studied the structural parameters of asphalt using C-spectrum nuclear magnetic resonance (NMR). The results demonstrated that the molecular structure of asphalt is significantly changed by isomerization, internal cross-linking, and dehydrogenation during UV ageing.

In addition to indoor tests, pavement field asphalt samples have been considered, in order to study the chemical composition and chemical structure changes of asphalt binders during the service phase. Wang et al. (2019) sampled *in situ* asphalt concrete under different pavement conditions, including bridge decks, ramps, and normal sections, and showed that the ageing of asphalt binders varied in different pavement structures. The asphalt in the surface layer was aged significantly more than asphalt in the middle layer, while the asphalt in the lower surface layer was aged the least. The ageing of asphalt at the pavement site is caused by oxidation and oxygen absorption. Large molecules in asphalt are broken down into lower molecular weight molecules, such that the proportion of small- and medium-sized molecules increases. The SBS modifier contained in the asphalt becomes granular and relatively separates from the asphalt. Li et al. (2019c) collected asphalt concrete cylindrical specimens from an asphalt pavement field test in Sichuan Province, China, from normal sections and tunnels. A study of the chemical structure and elemental content of the reclaimed asphalt binder showed that there were different levels of ageing in the asphalt concrete 0.5–1.0 cm below

the pavement after four years of service. The relative proportions of carbonyl and sulfoxide oxygen-containing functional groups in the aged asphalt binder were increased. At the same time, the relative content of oxygen was also increased. In addition, asphalt pavements in Inner Mongolia, China, have been investigated after one year of service (Li et al., 2018a). The results indicated that the relative contents of carbonyl and sulfoxide functional groups in the asphalt binder were increased after service, while the SBS index of SBS polymer modifier decreased. Wu et al. (2017b) analyzed the SARA components and oxygen-containing functional groups of recycled asphalt binders from asphalt pavement after 10 years of service. The results showed that the ratio of SARA components and the content of oxygen-containing functional groups (e.g., C=O and S=O) changed significantly, while C=C was degraded during service. Vehicle loading can accelerate this decay process. The surface layer of asphalt concrete can protect the underlying asphalt concrete but, after 10 years of service, the underlying concrete may also be significantly deteriorated. In order to develop a predictive model for the rheological properties of asphalt binder during field service, Qin et al. (2014) sampled asphalt concrete from three roads in Arizona and Virginia, USA. The chemical functional groups and rheological properties of the asphalt binders were studied. The results indicated that the asphalt binder tends to become harder after ageing, where the observed rheological hardening effect is closely related to the compositional changes in the asphalt at the pavement site, including the conversion of aromatic hydrocarbons to toluene-soluble asphaltene and increases in the relative contents of total aromatic, carbonyl, and sulfoxide functional groups.

The above discussion indicates that the chemical properties of asphalt binders change significantly, both in the indoor UV ageing simulation tests of asphalt binders (Figs. 3 and 4), as well as in the field service phase of outdoor pavements (Fig. 5). The main manifestations are increases in the relative content of oxygen elements and decreases in the relative contents of C, H, S, and N elements in asphalt (Li et al., 2019d; Mouillet et al., 2008; Petersen, 1998). The relative contents of carbonyl and sulfoxide oxygen-containing functional groups are increased (Liu et al., 1998; Pang et al., 2018; Su et al., 2016; Zeng et al., 2018), with the change rate varying with the different stages of UV ageing (Lamontagne et al., 2001; Mikhailenko et al., 2016). The proportion of the light fraction is decreased due to volatilization, the proportion of the heavy fraction increases due to the polymerization reaction due to the oxidation process (Weigel and Stephan, 2018), and the chemical properties of the saturated fraction are relatively unstable (Wei et al., 2006). The scale of the bee-like structure in the height map of the atomic force microscope (AFM) surface micromorphology increases. The above changes in chemical properties become more significant with increased UV irradiation intensity (Li et al., 2021) and ageing time (Wu et al., 2017a).

According to the previous research work, it can be found that under

high temperature or UV light, asphalt will undergo a series of chemical reactions, resulting in addition, polymerization, oxidative dehydrogenation and other reactions of short-chain compounds, resulting in complex cyclic compounds and carbonyl, carbonyl, polar functional groups such as sulfoxide groups increase the molecular weight of asphalt, and light components (such as the aromatic components) are transformed into heavy components (such as the asphaltene). However, the current research is still in analyzing the change of chemical composition during the ageing process. A unified and effective connection has not been established among various chemical indicators. The interaction mechanism between various indicators and the ageing evolution process is far from clear. Most of the researches on the chemical composition of asphalt focus on the changes of functional groups, chemical bonds, and structures, and the research angle is relatively single, and systematic and in-depth research is still needed at the molecular level of asphalt.

3.2. UV ageing effects on technical performance of asphalt

The chemical composition and structure of a substance is the fundamental basis for its technical properties. The discussion in the previous section indicated that the microscopic chemical properties of asphalt binders change significantly during UV ageing, which inevitably leads to the degradation of the macroscopic technical properties of asphalt (Redeligi and Soenen, 2015).

Li et al. (2020c) conducted UV ageing simulation tests on loose asphalt mixtures and studied the technical properties of reclaimed asphalt binders. The results showed that the physical and rheological properties of the asphalt binders were significantly attenuated after UV ageing. This tendency was verified decreases in penetration, ductility, and phase angle, as well as increases in the softening point and composite modulus of the asphalt binder, while the self-healing properties of asphalt binders were reduced.

Airey et al. (2016), Gama et al. (2016), Godenzoni et al. (2017), Mandula and Olexa (2017), Simnofske and Mollenhauer (2017), Tu et al. (2016), Xiao et al. (2015), and Zhang et al. (2017) have indicated that the rheological properties of asphalt binders change significantly after UV ageing, with the composite modulus (G^*) becoming increased, indicating that the resistance of the asphalt to shear deformation had improved. At the same time, the phase angle (δ) of the asphalt binders decreased, indicating that their viscoelastic properties had shifted to elastic properties. The increase in the composite shear modulus and the decrease in the phase angle resulted in an increase in the rutting factor ($G^*/\sin \delta$) and an increase in the rutting resistance of the asphalt binder, which is mainly due to the hardening and embrittlement of the asphalt binder after UV ageing (Cong et al., 2012; Hu et al., 2017; Xiao et al., 2014). In addition, Li et al. (2020c) and Wu et al. (2019) studied that UV ageing also affects

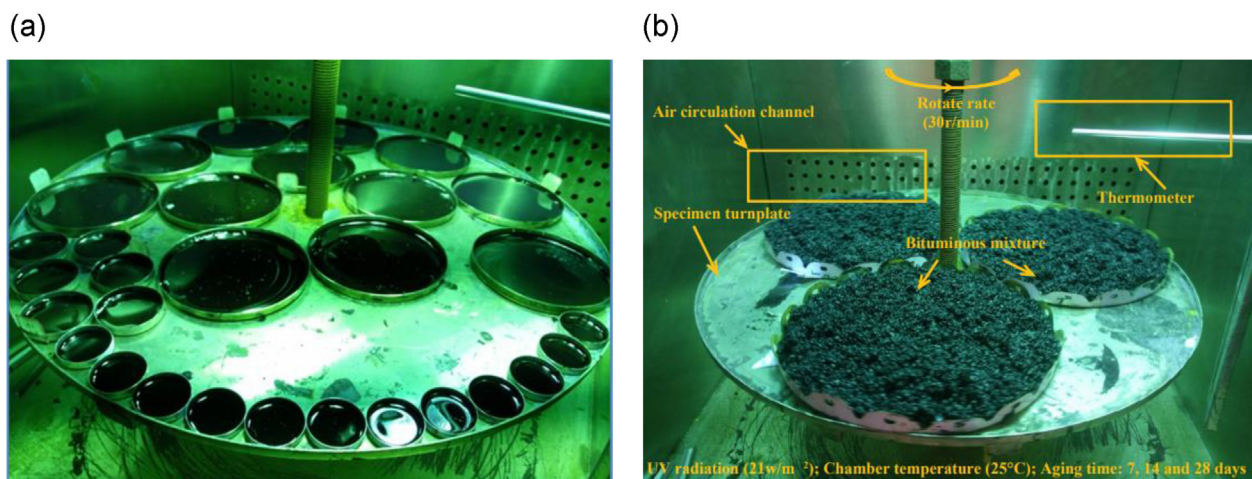


Fig. 3. UV ageing simulation tests (Li et al., 2020c). (a) Asphalt binders. (b) Asphalt mixtures.

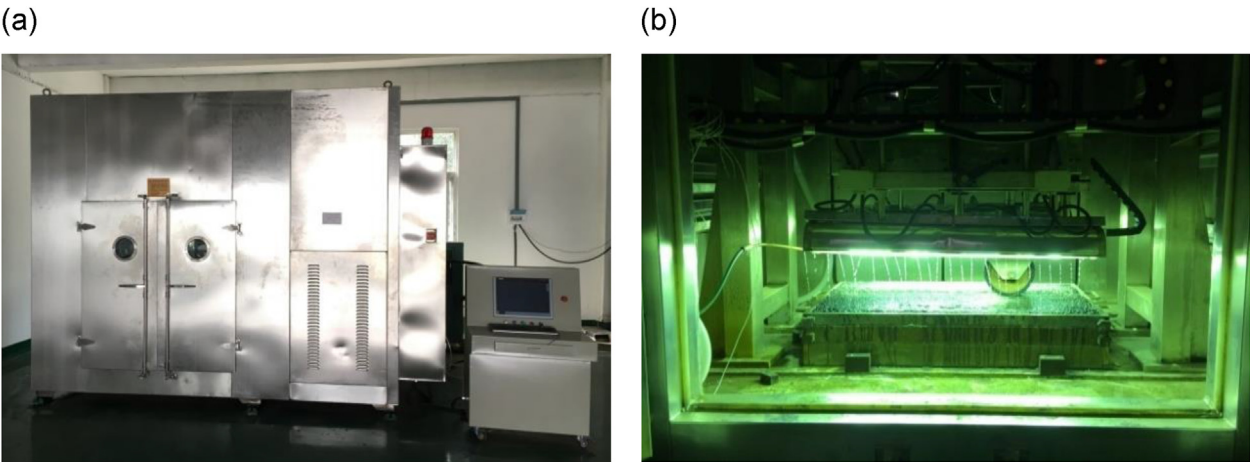


Fig. 4. Multi-functional whole-life analyzer for road materials. (a) Dimension drawing. (b) Simulation testing.



Fig. 5. Appearance of test roads (Li et al., 2018a). (a) SBS MA compared road. (b) LDHs MA test road. (c) SS-LDHs MA test road.

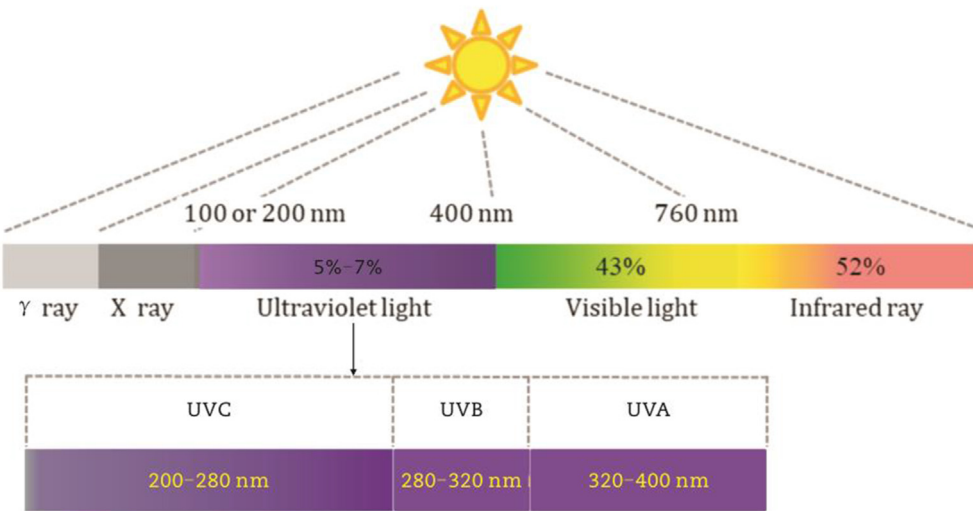


Fig. 6. Wavelength distribution of solar radiation.

the self-healing properties of asphalt and asphalt concrete. Li et al. (2018a, 2019c), Qin et al. (2014), Wang et al. (2019), and Wu et al. (2017b) characterized the ageing degree of reclaimed asphalt

binders in asphalt concrete sampled from asphalt pavements. Their results indicated that the viscoelastic ratio of asphalt changed after coupled ageing due to environmental factors during field service, the elastic ratio

increased, and the asphalt binder became more hardened. The bending tensile strength and bending tensile modulus of the aged asphalt concrete specimens increased, while the bending tensile strain decreased, indicating that its low-temperature crack resistance was reduced. Meanwhile, the semicircular three-point bending and tensile strength of asphalt concrete increased, while the fatigue life decreased significantly. The fatigue resistance of aged asphalt concrete was very fragile, and it was sensitive to the applied loads.

As a result, the macroscopic technical properties of the asphalt binder decay significantly after UV ageing. The physical properties are shifted; for example, the softening point increases, and the penetration and ductility decrease. In addition, rheological properties also change; for example, the viscosity and complex modulus increase, while the phase angle decreases. The asphalt binder becomes harder and more brittle. This is all mainly due to changes in the chemical properties of the asphalt caused by UV ageing.

4. UV ageing mechanism of asphalt binder

4.1. Pathways of asphalt ageing

Asphalt ageing is a complex process of physical and chemical reactions. Both indoor UV ageing simulation tests of asphalt binders and pavement field service tests have shown that UV radiation has significant effects on the chemical properties of the asphalt binder; which, in turn, leads to the degradation of its technical properties. In a broad sense, the generally accepted pathways of asphalt ageing include physical (site-resistant) hardening, evaporation of low molecular weight components, and oxidation (Zaidullin et al., 2013).

The physical hardening of asphalt is a reversible process which changes the macroscopic technical properties of the asphalt binder, but not its chemical composition (Santagata et al., 2016). This process is associated with the formation of ordered waxy structures in the soft asphaltene phase (Frolov et al., 2016) under the influence of straight-chain alkanes (Petersen, 2009) in the asphaltene. This phenomenon—which usually develops slowly at room temperature, but more rapidly as the temperature decreases—is related to the internal re-organization of the molecules in the asphalt binder. It leads to the hardening effect, which is reversible with increasing temperature of the asphalt binders (Dessouky et al., 2015; Shell, 1990). Thus, its effect is weak and can be disregarded.

More significant than physical hardening is the volatilization of volatile components (e.g., saturated and aromatic fractions) of the asphalt binder, which is also considered an ageing pathway. It depends mainly on the temperature of the asphalt binder and the exposure conditions, such as the diffusion rate and the length or thickness of the diffusion path (Shell, 1990). As the temperature increases, the volatilization rate increases. However, the contribution of volatilization to ageing is limited, compared to the oxidation process (Petersen, 1989; Zupanick and Baseline, 1997). It is possible that the proportion of such compounds in asphalt is limited, due to the current control of refining conditions in order to limit the potential toxic soot emissions when heating the asphalt binder. Volatilization is more significant during the thermal-oxidative ageing of asphalt, due to the higher temperatures used (about 90 °C–163 °C for indoor simulation tests and 100 °C–190 °C for the production process), while the UV irradiation process during the service phase involves lower pavement temperatures (lower than 70 °C), compared to thermal-oxidative ageing; therefore, the volatilization rate of light components is relatively slow at this stage.

The third ageing pathway involves the oxidation of the asphalt binder. Oxidation is the most significant pathway for the UV ageing process. Thurston and Knowles (1941) had verified how the components of asphalt—especially asphaltenes and resins—absorb oxygen, and concluded that the ageing of asphalt binder is not only caused by physical hardening, but is also due to oxidation (Yaln et al., 2018). Oxidation is an irreversible, diffusion-driven phenomenon controlled mainly by thermal

reactions between atmospheric oxygen and asphalt components, which alters the chemical properties of the asphalt binder. In the UV ageing phase, this process is influenced by the photo-oxidation ageing reaction at the surface of the asphalt binder. The exposed surface layer of asphalt is capable of photo-oxidative ageing under the conditions of UV irradiation and the presence of oxygen. Asphalt is a good light absorber, and photo-oxidation affects its ageing process, even under low UV light penetration conditions. Especially for some polymer-modified asphalts, such ageing includes not only the ageing of the base asphalt, but also the ageing of the polymer modifier (Durrieu et al., 2007). As oxygen needs to penetrate into the asphalt during oxidation, the whole process is closely related to the diffusion properties of oxygen.

4.2. Influence of UV light wavelength on the ageing of asphalt binders

According to the wavelength range, UV light can be divided into short-wave UVC (200–280 nm), medium-wave UVB (280–320 nm), and long-wave UVA (320–400 nm) ranges (Fig. 6). Before reaching the Earth's surface, sunlight needs to pass through the Earth's atmosphere. Only part of sunlight passes through the atmosphere to reach the ground, while the other part is directly absorbed, scattered, and reflected by the atmospheric molecules, dust, and water vapor. Compared with the original solar radiation, the solar radiation reaching the ground not only has a significantly lower total energy and radiation intensity, but also has significant differences in the wavelength range (Mouillet et al., 2014). After passing through the atmosphere, the wavelength range of UV light that reaches the ground is approximately 280–400 nm, while wavelengths below 280 nm are blocked by the atmosphere from reaching the ground (Diffey, 2002). This part of UV light accounts for only about 5%–7% of the total energy of sunlight (Airey, 2003; Ma et al., 2015), and it is also due to the arrival of this part of UV light that the photochemical reactions produced by organic polymer materials or polymers at the surface can occur. In conditions where there is only the single factor of UV light, the ageing of substances is very slow. However, under conditions where UV light and oxygen are coupled, oxygen is able to exert a catalytic effect that accelerates the photo-oxidative ageing process of the substance, significantly reducing the technical properties of the material.

According to the light quantum theory, the shorter the wavelength of light, the more energy the light quantum has. The energy of one light quantum can be calculated based on quantum theory, which is shown as Eq. (1) (Feldman, 2002). The energies of light quanta in the UV radiation range (280–400 nm) are shown in Table 1.

$$E = h \frac{c}{\lambda} \quad (1)$$

where E expresses the energy of light quantum (J), h expresses Planck's constant ($h = 6.626 \times 10^{-34} \text{ m}^2 \cdot \text{kg/s}$), c expresses the velocity of light ($c = 3 \times 10^8 \text{ m/s}$), and λ is the wavelength (nm).

Asphalt binders may undergo bond breaking upon exposure to UV light, which leads to a series of oxidation processes. The occurrence of this phenomenon depends on the energy of the wavelengths absorbed by the molecular chains and the strength of the chemical bonds. The sensitivities of various polymer structures to different light wavelengths are not the same. The main molecular bonds connected with benzene rings and other stable groups in asphalt are C–H, C–C, C=C, and O–H. Among these, C=C and the carbonyl group contained in ketones are prone to photodegradation or photo-oxidative degradation, where the breaking energy of the first C=C bond is only about 270 kJ/mol. The bond energies of the main chemical bonds in asphalt are shown in Table 2.

It is well-known, from the first law of photochemistry, that different polymer structures have different sensitivities to light wavelengths. In order to produce a photochemical reaction, a molecule has to have a characteristic absorption spectrum for a particular wavelength of UV light. If the wavelength is not the sensitive wavelength of a certain polymer, its photodegradation will be slow (Reyes and Camacho-Tauta,

Table 1

Energies of photons in the UV radiation range with different wavelengths.

Energy of photon in different units	Wavelength of UV light (nm)												
	280	290	300	310	320	330	340	350	360	370	380	390	400
Energy of photon (kJ/mol)	427.4	412.6	398.9	386.0	374.0	362.6	352.0	341.9	332.4	323.4	314.9	306.8	299.2
Energy of photon (kcal/mol)	102.1	98.6	95.3	92.2	89.3	86.6	84.1	81.7	79.4	77.3	75.2	73.3	71.5

Table 2

Bonding energies of main chemical bonds in asphalt molecules.

Chemical bond	C–N	C–C	C–O	N–H	C–H	O–H	C=C
Bonding energy (kJ/mol)	290.9	347.9	351.6	389.3	413.6	463.0	615.3

2022). After light in the sensitive wavelength range is absorbed by the molecule, if the energy of the absorbed photon is higher than the internal bond energy of the molecule, the molecular bond breaking effect will occur, and free radicals will be generated, which allow photo-oxidative chemical reactions to proceed. Free radical theory is the classical theory explaining the ageing of asphalt, and it is believed that the UV ageing of asphalt mainly consists of three stages: chain initiation, chain, growth and chain termination. On the other hand, if the energy of the absorbed photon is lower than the internal bond energy of the molecule, then the energy of the photon cannot meet the energy required for dissociation of the molecular bond, and the bond may only be left in an excited state. If the asphalt contains a small number of heteroatoms or is exposed to air (oxygen), the process of photo-oxidative degradation of organic polymers can then be caused by the action of the heteroatoms or oxygen. Theoretically, many polymers are stable to sunlight, as these polymers do not have chromophores that absorb wavelengths greater than 280 nm under ideal conditions (i.e., absolute purity). For example, C–H cannot absorb light at wavelengths greater than 290 nm, and C–C bonds can only absorb 195 and 230–250 nm UV light.

However, the degradation of polymeric materials in the presence of sunlight is actually quite rapid, as the industrial products of these materials typically contain many impurities which are capable of absorbing UV light, such as residual catalysts, small amounts of oxidation products, and processing aids and colorants. The presence of these impurities (which can all absorb UV light as chromophores) can lead to the rapid oxidation of these polymers in air. In the polymer industry, studies focused on the ageing behavior of polymers take into account the effect of the wavelength range of UV light on their ageing state. Lins et al. (2008) showed that carboxylic acids and esters have little or no sensitivity to UV light at wavelengths greater than 290 nm. Fernández-Gómez et al. (2014) studied the ageing effect of radiation in the wavelength range of 250–500 nm on polymers with ageing times of 1–8 h. The results demonstrated that the yellow index of the samples differed under UV radiation at different wavelengths, indicating that the wavelength of UV light can significantly affect the ageing behavior of polymers. Zeng et al. (2015) investigated the effect of radiation wavelength on the photodegradation behavior of polymethyl methacrylate (PMMA) in the wavelength range of 250–1000 nm, and showed that radiation in the wavelength range of 260–320 nm may lead to main chain breakage of PMMA; however, when the radiation wavelength exceeds 340 nm, the photodegradation phenomenon becomes extremely weak, such that the PMMA photodegradation phenomenon has a significant wavelength dependence. Therefore, the use of UV light with different wavelengths will produce different ageing effects on organic polymers.

Asphalt is an organic binder composed of hydrocarbons of different molecular weights and their non-metallic derivatives, typically containing on the order of 10^5 – 10^6 different molecules, and different wavelengths of UV radiation may cause different ageing effects. During the asphalt binder production phase, certain catalytic components inevitably enter and remain in the asphalt binder, such as metal ions and catalysts

added during the asphalt production phase. Very small amounts of excess metals are present in the asphalt, such as nickel, vanadium, manganese, and iron, in the first transition system. Their d-orbitals are not filled, resulting in chemically unstable and easily shaped complexes. They can play an initiating role in the asphalt binder UV ageing reaction, making it easier to meet the conditions for initiating the photo-oxidative ageing reaction. In addition, the thermal production, storage, and transportation of asphalt binders can lead to the initial thermal-oxidative ageing of the asphalt, producing impurities such as hydroperoxides, C=O compounds, or charge-transfer complexes that absorb UV radiation and trigger UV ageing reactions in the asphalt binder (Wu, 2006).

The central wavelength and wavelength range of UV light are key influencing factors for the ageing state of asphalt. In most asphalt UV ageing simulation tests, various central wavelengths of UV light which are quite different have been used, such as 313 nm (Reyes and Camacho-Tauta, 2022), 340 nm (Fernández-Gómez et al., 2014; Lins et al., 2008), or 365 nm (Zeng et al., 2015). The uncertainty of the wavelength range and central wavelength make the experimental conditions in the literature not uniform, and the associated research results are naturally not comparable. The wavelength range of UV light reaching the Earth's surface is between 280 and 400 nm, which is a relatively wide range, and the random design of UV parameters without considering the influence of the central wavelength or wavelength range may produce the contrasting conclusions.

Based on the above, Airey (2003) argued that UV light with higher irradiance and/or shorter wavelengths is more destructive. Hu et al. (2018a) studied three different central wavelengths of UV light in asphalt UV ageing tests. The wavelength distributions with the three different central wavelengths of UV light are shown in Fig. 7. The results indicated that the three different wavelengths of UV light produced significant ageing effects on the asphalt. In comparison, UV light in the wavelength range of 300–350 nm had the strongest ageing effect on asphalt, followed by that in the wavelength ranges of 260–300 nm and 350–400 nm. However, the central wavelength and wavelength range of the three UVs were different, and the wavelength range of the UVs (40–50 nm) was relatively large, making the results of the study rather ambiguous.

Li et al. (2019d) conducted experiments using the three UV light

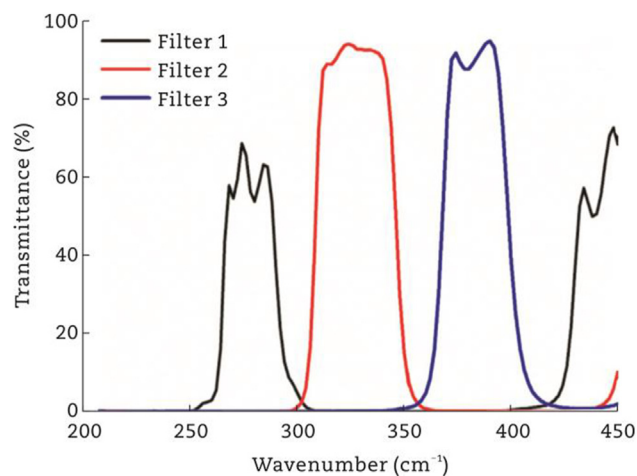


Fig. 7. Transmittance between 200 and 400 nm of different filters used in reference (Hu et al., 2018a).

wavelength ranges of 350–370 nm, 340–380 nm, and 200–400 nm (Fig. 8), all of which had a central wavelength of 360 nm. The specific parameters of the test on the effect of the central wavelength range of UV light on the ageing state of asphalt are shown in Table 3. The results showed that, although the central wavelength and irradiation intensity of the UV light were the same, the ageing effect of UV light on asphalt binders differed with the different wavelength ranges. UV light in the range of 350–370 nm had the most significant ageing effect on asphalt, followed by UV light in the range of 340–380 nm, while the lowest degree of ageing on asphalt binders was observed for UV light in the range of 200–400 nm.

Li et al. (2019b) used five kinds of UV light, with central wavelengths of 300, 320, 340, 360, and 380 nm, in order to conduct accelerated UV ageing tests on asphalt. The UV transmittance of optical filters centered on different wavelengths of UV light is shown in Fig. 9. The wavelength ranges of the five kinds of ultraviolet light were small, only about 20 nm. The specific parameters of the tests considering the effect of the main wavelength of UV light on the ageing state of asphalt are shown in Table 4. The effect of the central wavelength of UV light on the ageing behavior of asphalt was analyzed, in order to determine the sensitive central wavelength of UV radiation for the asphalt. The test results showed that all five kinds of UV light could produce significant ageing effects on asphalt where, under the same conditions, the asphalt irradiated by UV-360 had the highest degree of ageing, followed by UV-340, UV-320, UV-300, and UV-380, respectively.

Therefore, there exists a sensitive wavelength theory for the UV ageing of asphalt. The sensitivity of asphalt molecules to different central wavelengths and wavelength ranges of UV light varies, and the various central wavelengths and wavelength ranges of UV light have significant effects on the ageing-based degradation of asphalt. It is not necessarily the case that a shorter main wavelength of UV light (high photon energy) will have a more severe ageing effect on asphalt. Hu et al. (2018a), and Li et al. (2019b, d) have shown that UV light in the wavelength range close to 360 nm has a more significant ageing effect on asphalt under the same conditions. Therefore, the relative sensitive wavelength range for the UV ageing of asphalt molecules is around 360 nm.

4.3. Research status of UV ageing depth growth law and mechanism

Considering the thermal-oxidative aspect, Omairey et al. (2021) investigated the thermal-oxidative ageing of asphalt by deeply coupling

three physical processes: heat conduction, oxygen diffusion, and oxidation reactions. The results indicated the existence of ageing gradients in the thermal-oxidative ageing of asphalt layers.

For the UV ageing of asphalt, Traxler (1961) pointed out that the ageing effect of UV light on asphalt samples was significant when the thickness of the sample was 3 μm , while the ageing effect became relatively weaker when the thickness of the asphalt sample increased. Kemp and Predoehl (1981) showed that ageing and hardening effects occur in the thickness range of 5–10 μm on the surface of the asphalt binder under the ageing effect of UV light, while the ageing effect of asphalt was significantly reduced when the asphalt thickness was greater than 200 μm . Yamaguchi et al. (2005) conducted UV ageing experiments using asphalt sample thicknesses of 50, 100, 200, 500, and 1000 μm . The results showed that the thinner the asphalt sample, the higher its elastic modulus, and more carbonyl functional groups were generated after UV ageing, indicating a more severe ageing state. In 2007, Durrieu et al. (2007) showed that the UV ageing of 10 μm asphalt reached the level of PAV ageing after several hours. In 2009, Wu et al. (2009b) used sample thicknesses of 50, 100, 200, and 500 μm to investigate the ageing state of asphalt films of different thicknesses under the same UV irradiation conditions. The results showed that the degree of ageing was lower when the sample thickness was thicker. In 2019, Hung et al. (2019) studied the morphological and nanomechanical property changes of asphalt films under the action of UV radiation; however, the transmission depth of UV light in asphalt is shallow. A 600 nm thick asphalt film was prepared by a rotary coating machine and UV-aged in an accelerated UV-ageing tester. The results showed that, as the UV radiation continued from 0 to 400 h, the hydrocarbon content of the films gradually decreased and the relative content of sulfoxide groups and carbonyl groups increased, reducing the solubility of asphalt in organic solvents. After 20 h of UV irradiation, the nanoindentation test showed a significant increase in the hardness and viscoelasticity of the asphalt films, which continued to increase with up to 50 h of irradiation. Therefore, the thickness of asphalt has an effect on its UV ageing state, and the overall ageing degree of asphalt varies with different thicknesses. Under the same UV irradiation conditions, the lower the asphalt thickness, the more obvious the ageing state of the asphalt.

The thickness of the asphalt sample is an extremely important parameter when performing UV ageing simulation tests; however, the thicknesses of asphalt samples used in UV ageing simulation tests conducted by scholars are not consistent, mainly focusing on the range of 10

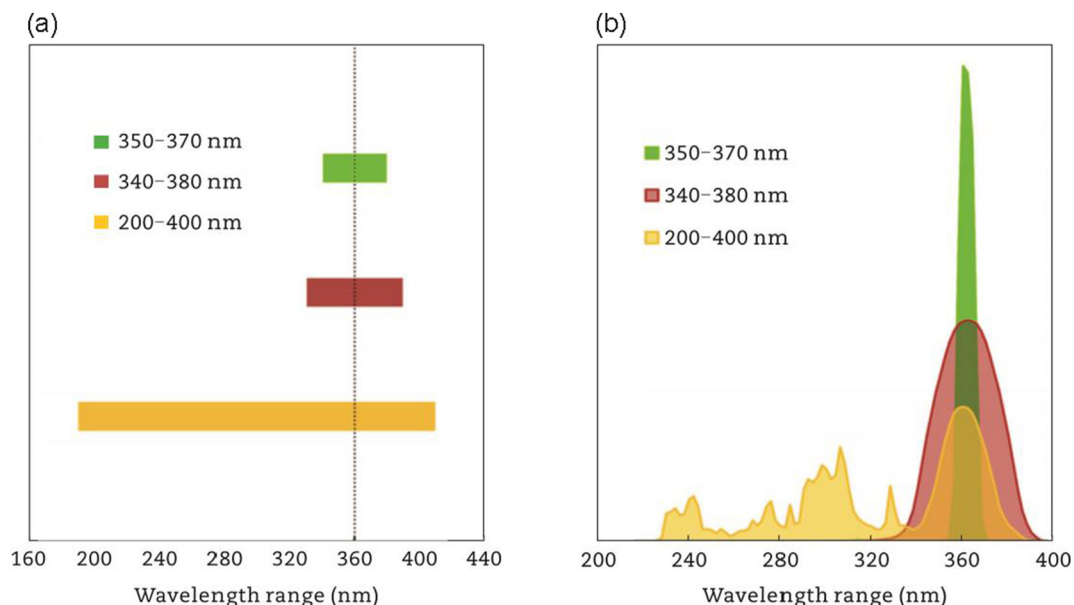
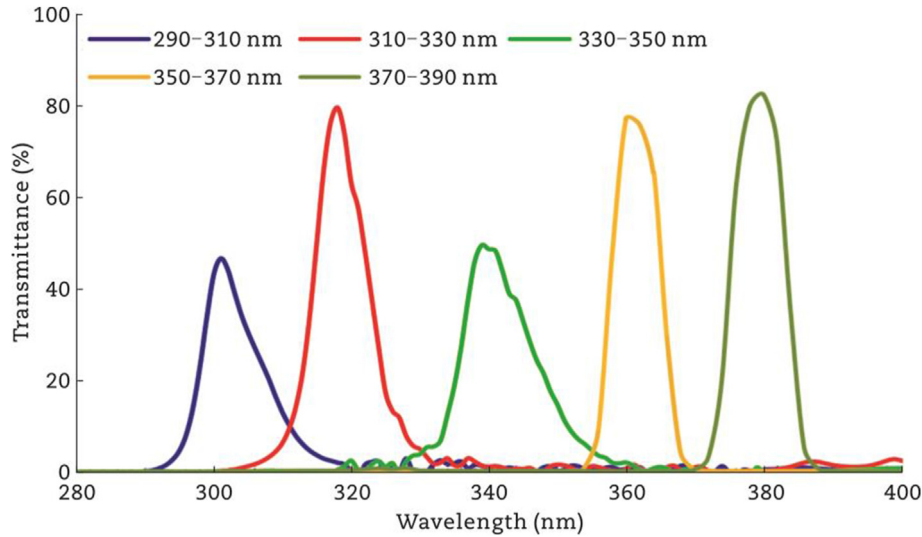


Fig. 8. Schematic figure of the wavelength ranges (Li et al., 2019d). (a) Spectral power distributions. (b) UV light used.

Table 3

Experimental parameters of different UV light wavelength ranges for the testing of asphalt binders (Li et al., 2019d).

UV light	Wavelength range (nm)	Irradiation intensity (W/m ²)	Ageing time (h)	Temperature (°C)
UV-300	350–370	7.0	1, 3, 6, 12, 24, 72, 144, 288	50
UV-320	340–380	7.0	1, 3, 6, 12, 24, 72, 144, 288	50
UV-380	200–400	7.0	1, 3, 6, 12, 24, 72, 144, 288	50

**Fig. 9.** UV transmittance of optical filters centered on different wavelengths of UV light (Li et al., 2019b).**Table 4**

Experimental parameters of different dominant wavelengths of UV light for the testing of bituminous binders (Li et al., 2019b).

UV light	Wavelength (nm)	Irradiation intensity (W/m ²)	Ageing time (h)	Temperature (°C)
UV-300	290–310	7.0	1, 3, 6, 12, 24, 72, 144, 216	50
UV-320	310–330	7.0	1, 3, 6, 12, 24, 72, 144, 216	50
UV-340	330–350	7.0	1, 3, 6, 12, 24, 72, 144, 216	50
UV-360	350–370	7.0	1, 3, 6, 12, 24, 72, 144, 216	50
UV-380	370–390	7.0	1, 3, 6, 12, 24, 72, 144, 216	50

μm to 3.2 mm, where the thickness of 3.2 mm originates from the thermal oxygen ageing test of asphalt. For example, Feng et al. (2016a) have used asphalt films with a thickness of 100 μm; Naskar et al. (2013) and Liu et al. (2014) have used asphalt samples with a thickness of 2.0 mm; while Mouillet et al. (2014), Xiao et al. (2013), and Mollenhauer et al. (2010) have used asphalt specimens with a thickness of 3.2 mm. Using different thicknesses of asphalt samples may lead to the following consequences: the full thickness of small asphalt samples is aged; and, when considering the chemical composition and technical properties of high-thickness asphalt samples after ageing, what is studied is actually a mixture of aged asphalt on the surface and unaged asphalt inside, such that the ageing state of asphalt cannot be accurately characterized. This makes the research results on asphalt samples with different thicknesses non-comparable, which is a major problem in this industry.

In terms of road verticals, the depth and thickness concepts of asphalt are basically the same. Yamaguchi et al. (2005) showed that the UV ageing of asphalt was more severe in the surface layer than in the interior, indicating that the ageing of asphalt starts from the surface and gradually progresses into the interior. Chen (2017) showed that the ageing depth of

asphalt increased with the extension of UV ageing time, and that the surface layer asphalt composite modulus ratio is linearly related to the ageing time. Li et al. (2021) used the layer-by-layer stripping method to strip asphalt in different ageing states (Fig. 10), in order to test the chemical and rheological properties of asphalt at different depths, to characterize the ageing state of asphalt at different depths, and to reveal the ageing depth growth mechanism. The results showed that, under the same ageing time conditions, the ageing depth of asphalt was greater when using UV light with high UV irradiation intensity than that with low UV irradiation intensity. When the depth of the asphalt is the same, the ageing effect of UV light with higher irradiation intensity is more significant than that of UV light with lower irradiation intensity. The ageing depth of the asphalt binder increased with an increase in UV irradiation time. There was a high correlation between the ageing depth of asphalt after UV irradiation with different irradiation intensity and the UV irradiation time. The growth behavior can be characterized in two phases: using an exponential model and a linear model (Eq. (2)). The rate of the first stage increased faster, mainly in the initial 24 h of UV irradiation, where the ageing depth growth behavior of the asphalt was in accordance with the exponential model, which was a rapid growth stage. The mutation point was at 24 h. When the irradiation time was further extended, the ageing depth growth curve became flatter and the ageing depth growth rate stabilized and decreased, consistent with the linear model.

$$AD = \begin{cases} \alpha t^\beta & 0 < t \leq 24 \text{ h} \\ \alpha t + \beta & t > 24 \text{ h} \end{cases} \quad (2)$$

where AD is the ageing depth of the asphalt binder (μm), t is the UV ageing time of asphalt binder, α and β are the regression coefficients of the exponential and linear equations, respectively.

Therefore, the ageing of asphalt by UV light starts from the surface of the asphalt, and gradually develops to the interior of the asphalt as the ageing time increases, making the ageing depth of asphalt gradually increase. As such, there exists an ageing gradient for the UV ageing of

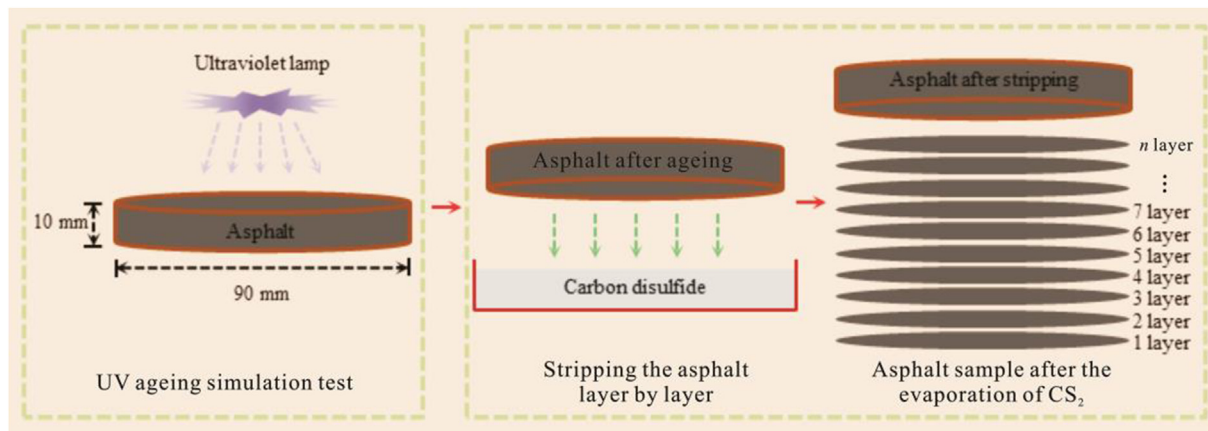


Fig. 10. Layer-by-layer stripping of asphalt binder after UV ageing (Li et al., 2021).

asphalt: ageing in the surface layer is the most serious while, with an increase in depth, the asphalt ageing degree decreases.

So, why does the ageing depth of asphalt gradually increase with the ageing time? Due to the absorption and surface reflection of asphalt molecules, UV light can only reach the surface of asphalt directly, and the penetration depth in asphalt is extremely limited (only a few microns), such that the oxygen transmission depth is only a few millimeters. Hu et al. (2018b), Zeng et al. (2018) and Yu et al. (2021) have used UV spectrophotometry to study the UV light transmission properties of asphalt films of different thicknesses before and after ageing (Fig. 11). The results showed that UV light can only be irradiated directly on the asphalt surface, with an initial penetration depth of about 4.5–13.1 μm (Figs. 12 and 13). In an indoor research process, it was found that the depth of UV light penetration in asphalt increases with an increase in ageing time. The reason for this is that the relative content of the molecular structure and functional groups of asphalt inevitably changes after ageing, which leads to alterations of the UV absorption characteristics of asphalt and affects the penetration depth of UV light in asphalt. Compared to the UV transmission depth, Mouillet et al. (2008) and Petersen (1998) have shown that oxidation can affect the surface layer of pavement to a depth of 1.0 cm during the early years of service. Petersen (2009), Li et al. (2019c), and Reyes and Camacho-Tauta (2008) have shown that UV light can age asphalt mixtures even to a depth of 1 cm to 1 inch; this depth is much greater than the penetration depth of UV light into the asphalt, indicating that the inner asphalt, which cannot be reached by UV light, is also aged. Therefore, with an increased asphalt depth, in addition to an

increase in the UV light transmission depth, there must be another mechanism.

To address this problem, Zeng et al. (2018) has proposed a diffusion mechanism for the UV ageing of asphalt and a model for the UV ageing of asphalt. The asphalt in the UV ageing process is divided into the surface layer part, where the UV light is directly transmitted, and a lower layer part, where the diffusion effect mainly induces ageing (Fig. 14). The increase in asphalt ageing depth is not only due to an increase in UV light transmission depth, but also the mutual expansion of ageing and non-ageing asphalt molecules. Due to molecular diffusion, the surface aged asphalt molecules or products diffuse to the inner asphalt, resulting in the inner asphalt being aged as well. At the same time, the internal un-aged asphalt molecules diffuse to the surface, which are then aged. The diffusion action can have an effect at a depth of nearly 2200 μm after 10 days of UV ageing.

Therefore, both the indoor asphalt binder UV ageing simulation tests and pavement field asphalt pavement tests have shown that the ageing of asphalt by UV light occurs from the surface to the interior of the asphalt, such that the ageing depth gradually increases over time. The increase in ageing depth is based on the combined effect of increased transmission depth and diffusion of UV light into the asphalt. However, in view of the development law of UV penetration depth and asphalt UV ageing depth, as well as the relationship between the two, it is still necessary to carry out quantitative research and establish an asphalt UV ageing model characterizing the molecular diffusion behavior in asphalt. This will be of great significance in determining the development law of asphalt ageing and to reveal the development of asphalt ageing depth.

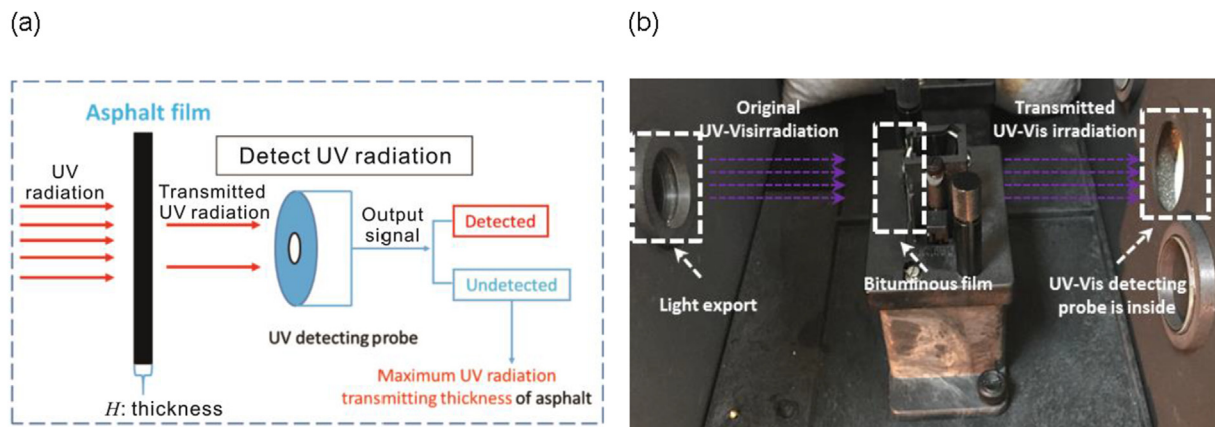


Fig. 11. Ultraviolet transmittance measurement of asphalt film with ultraviolet and visible spectrophotometer. (a) UV spectrophotometry test principle. (b) Schematic diagram of UV spectrophotometric analysis of asphalt films (Zeng et al., 2018).

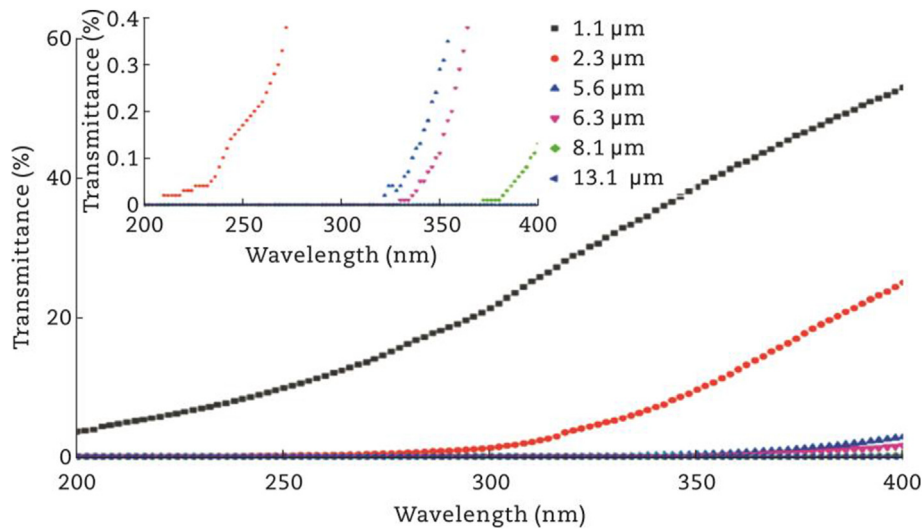


Fig. 12. Transmittance of bitumen with different thicknesses before UV ageing (Hu et al., 2018b).

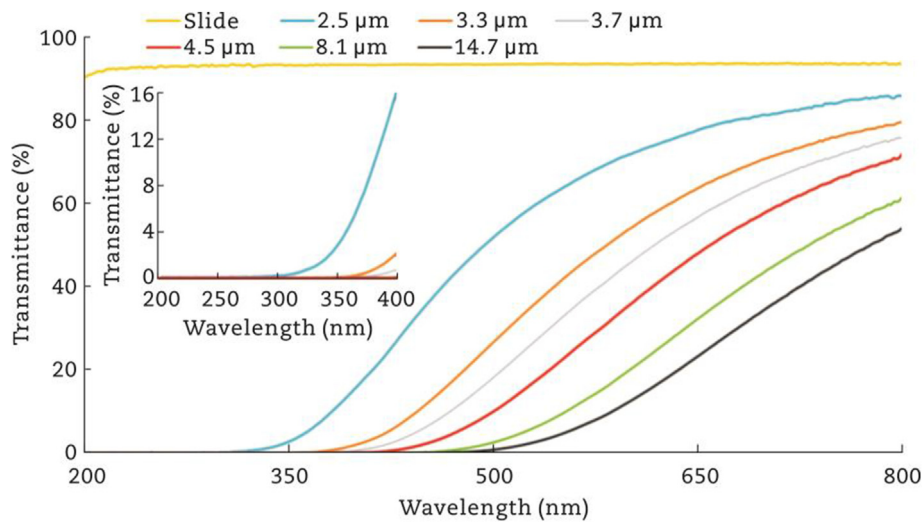


Fig. 13. Transmittance of 70A film with different thickness (Yu et al., 2021).

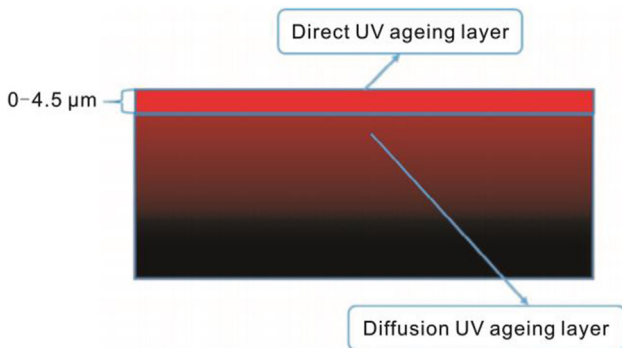


Fig. 14. The UV ageing model of asphalt (Zeng et al., 2018).

5. Research on anti-UV ageing methods for asphalt binders

Based on the three ageing pathways of asphalt, in order to improve the resistance of asphalt binders to UV ageing, many researchers have carried out a lot of research work. By adding various types of modifiers into the asphalt binder, different modification mechanisms can be exploited to reduce the harmful effects of UV ageing on the technical

performance of asphalt binders. According to the mechanism of each anti-UV ageing agent, they can be roughly divided into: UV absorbers, antioxidants, light stabilizers, inorganic fillers, and inorganic nano-materials, among others.

5.1. Composition and structure of the asphalt mixtures

Generally speaking, low-penetration grade asphalt has better resistance to photo-oxidative ageing than high-penetration grade asphalt. Lu and Huang (2009) has studied the physical performance and viscosity before and after the photo-oxidative ageing testing of pen 60/80 and pen 80/100 asphalt binders, and indicated that the photo-oxidative ageing resistance of the pen 60/80 asphalt binder was better than that of the pen 80/100 asphalt binder under the same conditions.

Conventional fillers, such as mineral powder (Lesueur, 2008), with particle size below 0.075 or 0.063 mm, have open microvoids on their surface that can partially absorb the polar molecules-such as ketones, anhydrides, and carboxylic acids-in the asphalt binder that can be oxidized (Li et al., 2020a), thus preventing their oxidation and providing a protective effect (Lesueur, 2008).

Charrié-Duhaut et al. (2000) considered that the residual air void in an asphalt pavement is the key influencing factor for the UV ageing of the

asphalt binder: when the residual air void ratio is less than 5%, the ageing degree of the asphalt pavement is light; when the void ratio is more than 7%, the asphalt binder ageing degree is intensified; and, when the void ratio is between 8% and 12%, the asphalt pavement will suffer from serious water penetration and the ageing of the binder will be serious. The anti-UV ageing performance of an asphalt mixture with fine gradation is better than that of one with coarse gradation. Meanwhile, the anti-UV ageing performance of an asphalt mixture with a smaller air void is better than that of one with larger air voids; the reason for this is that smaller voids can prevent the infiltration of direct sunlight into the deeper part of the pavement, while also reducing the contact area between oxygen and the asphalt mixture, thereby reducing the ageing rate of the asphalt binder.

5.2. UV stabilizers

UV stabilizers can shield or absorb the energy of UV light, burst the single-linear state of oxygen, and decompose hydroperoxide into inactive substances, among other functions. Therefore, under the effect of UV light, the asphalt binder can exclude or slow down the possibility of photochemical reactions, thus stopping or delaying the process of photo-oxidative ageing. For example, Tinuvin 770 is a hindered amine stabilizer, which can improve the heat resistance when combined with anti-oxidants (Feng et al., 2016b). It also has a synergistic effect with UVA, and can further improve the light stabilization effect.

5.3. UV light absorbers (UVA)

UV light absorbers (UVAs) have a strong absorption effect on UV light, and convert the energy of UV light into vibrational energy or secondary radiation, such as the fluorescence or phosphorescence (Ching et al., 2019), thus reducing damage to the structure of asphalt and improving the anti-UV ageing performance.

UVAs can selectively absorb UV light wavelengths that are harmful to polymers, and the wavelength range of UV light absorbed by different UV absorbers varies. For example, the UV absorber octabenzene can absorb UV light in the range 240–340 nm, while bumetrizole can absorb UV light in the range 270–380 nm (Feng, 2013; Zhao et al., 2016). Linking the specific UV absorption wavelength range of UV light with the sensitive wavelength range of asphalt can guide the selection of a UVA and improve the compatibility and anti-ageing effect of the UVA and asphalt binder. The specific absorption wavelength ranges of some UVAs are listed in Table 5.

5.4. Inorganic UV-blocking materials

Inorganic powdered barrier materials, such as zinc oxide (He et al., 2021; Xu et al., 2019), titanium dioxide (Liao et al., 2021; Xie et al., 2020), and silica (Cheraghian et al., 2022; Qian et al., 2020), have a large specific surface area. Their interfaces can diffusely scatter or reflect some of the UV light entering the asphalt, or emit it by converting light energy

to heat.

Multi-layered structure barrier materials include layered double hydroxyl metal hydroxides (LDHs) (Lin and Wang, 2012), montmorillonite (MMT) (Liao et al., 2021; Yu et al., 2009), graphene oxide (Wang et al., 2020; Wu et al., 2017a), and carbon black (Yamaguchi et al., 2004). The whole process is closely related to the diffusion properties of oxygen, as oxygen needs to penetrate into the asphalt during the oxidation process. The multi-layer structure of multi-layered structure barrier materials can form homogeneous hybrid, intercalated, or exfoliated structures with asphalt molecules (or their branched chains). The multi-layered structures of the barrier materials can increase the path length that the oxygen must travel through (zigzag path) to penetrate into the asphalt binder (Zhang et al., 2016), thus reducing the penetration rate of oxygen and significantly improving the ageing resistance of the asphalt binder. Due to the high dispersion and barrier effect of multi-layered structure barrier materials, they can have a blocking effect, slowing down the diffusion of oxygen in the asphalt binder and, thus, the volatilization of lighter components in the asphalt binder.

5.5. Development trend of composite multi-functional ageing-resistant additives

According to the previous discussion, on one hand, the ageing of asphalt binder by UV light occurs from the surface to the interior. There exists an ageing gradient with increasing depth, and the ageing products of the surface-aged asphalt and the internal non-aged asphalt molecules exhibit dynamic diffusion behavior. On the other hand, asphalt has different sensitivities to different wavelengths of UV lights, and the ageing rate of an asphalt binder differs with respect to different wavelengths of UV light.

The most widely used layered inorganic UV barrier materials are LDHs and MMTs, both of which have good physical shielding effects. However, compared to MMT, LDHs have unique chemical structure and technical characteristics. The structure of an LDHs is schematically shown in Fig. 15, where LDHs are inorganic UV-blocking materials consisting of a main bi-metallic hydroxide laminate and an interlayer guest anion. The anti-UV ageing mechanism of LDHs-modified asphalt is shown in Fig. 16. The inorganic laminate acts as a physical shield against UV light, reflecting and refracting UV light several times at the laminate interface, thus attenuating the UV energy reaching the interior of the asphalt; meanwhile, the metal elements on the laminate and the interlayer anion also have a certain chemical absorption role against UV light. This multi-level multiple-chemical absorption and physical shielding effect gives LDHs good UV-blocking abilities (Pan, 2013). On the other hand, the physical barrier effect of LDHs can bend and prolong the diffusion path of oxygen and volatile components, thus reducing the oxygen penetration rate and volatile component volatilization rate.

In addition, LDHs have a unique layered structure with adjustable composition of the lamellae; this structural feature enables the interlayer anions to be exchanged with various anions (Wang et al., 2012). As such, the intercalable nature of LDHs can be used to introduce anionic guests with UV absorption properties into the interlayer (Xu et al., 2015). In addition, LDHs have good thermal stability and structural memory benefit, and their thermal decomposition process is reversible at temperatures not exceeding 600 °C. Therefore, in the construction temperature range of asphalt (within 200 °C), no irreversible structural damage occurs (Tang, 2011), and LDHs can safely be used as carriers of functional anions to form new intercalation-type UV-ageing resistant modifiers with composite functions.

The purpose of preparing LDHs/UVAs composite materials is to use the UVA to selectively absorb the UV light penetrating into the interior of asphalt binder and weaken the ageing effect of UV light on the asphalt. The composite use of LDHs and UVAs not only facilitates the UV-blocking effect of LDHs, but organic UVAs can organically modify the LDHs and improve the overall compatibility with asphalt. Zhao et al. (2013) used UV-284 and LDHs intercalation to prepare an LDHs/UV-284 composite

Table 5
Specific absorption wavelength ranges of different UVAs.

UV light absorber (UVA)	Specific absorption wavelength range (nm)
Octabenzene (Feng, 2013; Zhao et al., 2016)	240–340
2-hydroxy-4-(octyloxy) benzophenone (UV-531)	240–340
Substituted acrylonitrile (Shankar et al., 2019)	240–340
2, 3-dihydroxynaphthalene-6-sulfonic acid sodium salt	240–360
Bumetrizole	270–380
2-(2'-hydroxy-5'-meth-phenyl) benzotriazole	270–380
Benzophenone-4 (Zhao et al., 2013)	270–380
2-hydroxy-4-methoxybenzophenone-5-sulfonic acid	290–400

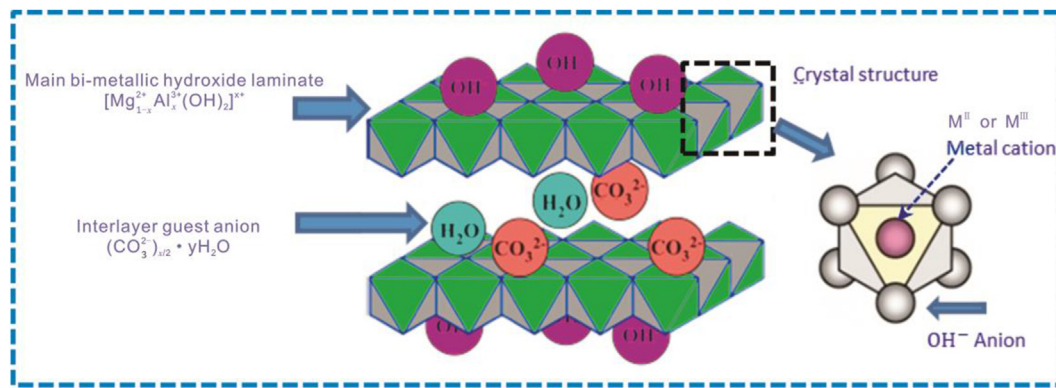


Fig. 15. Structural figure of LDHs.

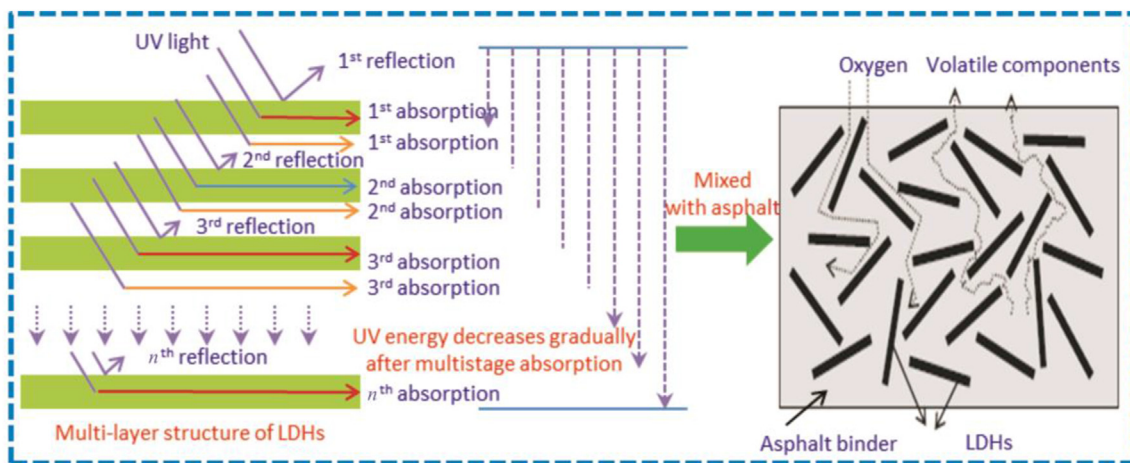


Fig. 16. Anti-UV ageing mechanism of LDHs.

UV-ageing modifier, and studied its effect on the UV-blocking properties of cotton fabrics. The results showed that the LDHs/UV-284 composite UV-ageing modifier significantly improved the UV-blocking properties of cotton fabrics. Chai et al. (2009) prepared 2, 3-dihydroxynaphthalene-6-sulfonate anion-intercalated Zn-Al layered double hydroxides, and showed that the UVA anion and LDHs formed a supramolecular structure through host-guest interaction, the result of which was thermally stable and had a significantly higher absorption capacity for UV light than the UVA or LDHs alone (Fig. 17). Zhao et al. (2016) applied a UVA to modify

LDHs. The UV light reflectance of the modified LDHs was higher than 90% in the wavelength range of 260–400 nm, indicating the excellent UV-blocking ability of the LDHs after modification (Fig. 18). Therefore, it is technically feasible to introduce UVA anions into the interlayer of LDHs. Different UVAs have individual specific absorption wavelength ranges and effects, such that the choice of UVA has a decisive role in the absorption wavelength of the composite material: the key to selecting a UVA relies on its specific wavelength range.

In summary, a conventional filler is one of the necessary components in the asphalt mixture mix design process, which provides a pathway that slows down oxidation by absorbing some of the small molecules of the asphalt binder, shading and protecting them from oxidation. It can have a positive effect on the anti-ageing properties of the asphalt binder, but the improvement may be limited. Antioxidants and light stabilizers mainly reduce the UV ageing reaction rate in asphalt, and achieve the purpose of improving the anti-UV ageing performance of the asphalt binder; similar effects are achieved by slowing down the oxidation pathway. However, if organic antioxidants, UVAs, and light stabilizers are used alone, with the extension of service time, the performance will gradually be reduced, leading to certain limitations in engineering applications. Compared with organic ageing-resistant materials, inorganic UV barrier materials have the advantages of chemical stability and good thermal stability. Inorganic UV-barrier materials can diffusely scatter or reflect through the interface, weakening the UV light reaching the interior of the asphalt and, thus, slowing down the oxidation pathway.

Multi-layered inorganic UV barrier materials have a barrier effect against the free movement of oxygen, UV light, heat, and asphalt molecules. They can slow down the volatilization of the low molecular weight

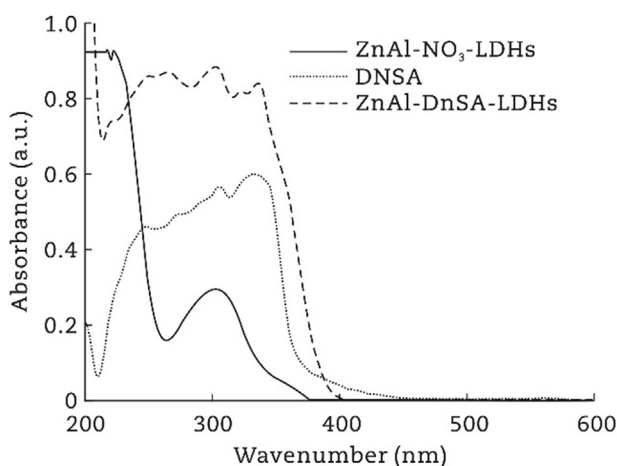


Fig. 17. UV absorbance curves (Chai et al., 2009).

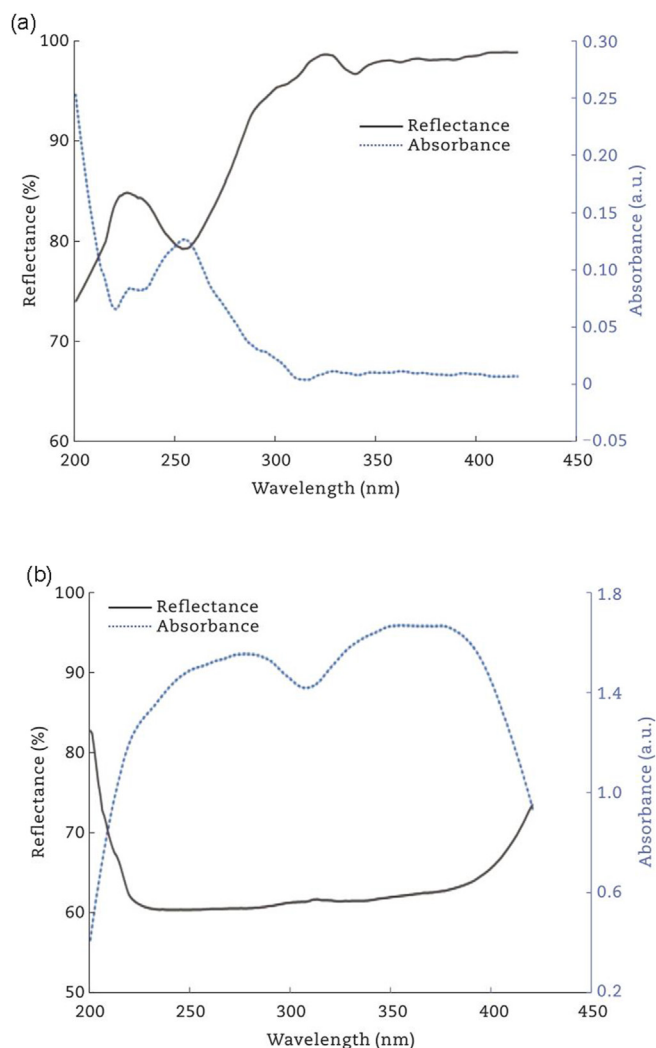


Fig. 18. UV-vis spectra. (a) LDHs. (b) Intercalated LDHs (Zhao et al., 2016).

components and the overall oxidation pathway of the asphalt. Therefore, the anti-UV ageing performance can be significantly improved, and these seem to be a good option as asphalt anti-UV ageing additives. However, although the multi-layered inorganic UV blocking materials have a good blocking effect against UV light, there is still UV light or part of the missed UV light that can enter the asphalt's interior, leading to an ageing effect. If a UV absorber can be applied at the same time, it can be used to absorb the UV light into the asphalt, such that the physical barrier effect of the multi-layered inorganic UV barrier material and the chemical absorption effect of the UVA can be combined to develop a new composite material of multi-layered inorganic UV barrier material/UVA, leading to better anti-ageing effects by exploiting the advantages of both materials.

6. Conclusions

The effects of UV ageing on the chemical properties and technical performance of asphalt binders were analyzed, and the current state of research on UV ageing mechanisms and UV ageing resistance methods for asphalt binders was revealed. The following conclusions were obtained.

- (1) In both indoor asphalt binder UV ageing simulation testing and outdoor pavement service phase testing, the chemical and technical properties of asphalt binders were found to be significantly changed. The chemical properties are mainly manifested by an increase in the

relative content of oxygen elements in asphalt. The main technical property changes are as follows. Considering physical properties, the softening point increases, while penetration and ductility decrease; for the rheological properties, the viscosity and complex modulus increase, while the phase angle decreases; and the asphalt binder becomes harder and more brittle. Overall, the changes in chemical and technical properties are more significant with increases in UV light intensity and ageing time.

- (2) The sensitivity of asphalt molecules varies with respect to the wavelength range of the UV light, where different wavelength ranges have significantly different effects on the ageing degradation effect of the asphalt binder. It is not necessarily the case that UV light with a short central wavelength (i.e., high photon energy) will definitely have a more severe ageing effect on the asphalt binder. Under the same ageing conditions, UV light with a wavelength range close to 360 nm has a more obvious ageing effect on asphalt. Therefore, there exists a sensitive wavelength theory for the UV ageing of asphalt binders, which can improve the basic theory of the asphalt binder UV ageing mechanism. This can be used to guide research into UV ageing resistance methods for asphalt binders, and provides a technical basis for the development and selection of UV ageing resistant modifiers for asphalt binders.
- (3) The ageing of asphalt by UV light occurs from the surface to the interior, and there exists an ageing gradient along the depth direction. With the increase of UV ageing time, the UV ageing depth of asphalt binders increase gradually, and asphalt binders with different depths have different ageing degrees; the penetration depth of the UV light pass through the asphalt binder increases, but the ageing depth of asphalt is much greater than the penetration depth of UV light in asphalt binders. The increase in the UV ageing depth of asphalt is not only due to increased UV transmission depth, but also to the dynamic diffusion behavior of the ageing products in the aged asphalt at the surface and the molecules of the un-aged asphalt in the deeper part, the diffusion of which leads to the increase in the ageing depth of the asphalt binder.
- (4) There are various methods, such as low penetration grade asphalt, less air void ratio, UV stabilizers and UV light absorbers, that can improve the UV-ageing resistance of asphalt binders (including base asphalt and modified asphalt). The LDHs have good physical barrier effect on UV light, and UVAs have specific UV absorption wavelengths. Due to the intercalability of LDHs, it is possible to introduce UVAs into the interlayer of LDHs. This can lead to the development of composite LDHs/UVA anti-UV ageing modifiers for asphalt binders, based on diffusion inhibition and asphalt sensitive wavelength theory.

The future research is also suggested to research the development law of UV penetration depth and asphalt UV ageing depth, as well as the relationship between the two; it is still necessary to carry out quantitative research and establish an asphalt UV ageing model characterizing the molecular diffusion behavior in asphalt. Therefore, reveal the increment mechanism of UV ageing depth, which can be used to guide the development of UV resistance methods for asphalt binder. In addition, depending on the sensitive wavelength theory, the composite functional UV ageing additives (such as LDHs/UVA) should be developed to get a better anti-UV ageing effect.

For the indoor UV ageing simulation testing of asphalt binders, there is still no uniform standard for asphalt sample thickness. Clarification of this issue should be not only based on the UV ageing depth of asphalt binders, but also on the mass of samples required for subsequent tests.

Declaration of Competing Interest

The authors do not have any conflict of interest with other entities or researchers.

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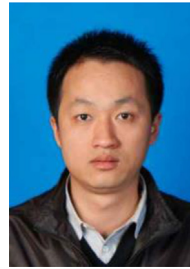
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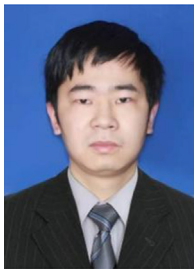
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