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Review Article

Review on the properties and mechanisms of asphalt modified with bio-oil and biochar

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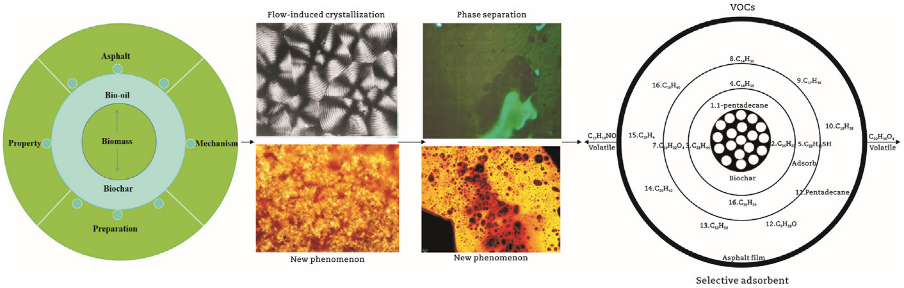
HIGHLIGHTS

- Crystalline wax in bio-oil is the key of flow-induced crystallization of bio-asphalt.
- The surface organic functional groups of biochar are the main inducement of VOCs adsorption.
- Both bio-oil and biochar can lead to the change of four components of asphalt.

GRAPHICAL ABSTRACT



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ABSTRACT

Bio-asphalt has a great application prospect in the replacement of petroleum-based asphalt to pave and maintain asphalt pavement. However, the problems of flow-induced crystallization and phase separation caused by flow-induced crystallization had severely restricted its application. This paper describes the progress of research on preparation, property evaluation and phase separation mechanism of bio-asphalt. The advantages and disadvantages of preparation methods of bio-asphalt are states. The fundamental physical and rheological properties of bio-asphalt are investigated, especially for flow-induced crystallization. There exists obvious flow-induced crystallization because bio-asphalt is rich in waxes that crystallize easily. Owing to the existence of excess biochar, bio-asphalt appears phase separation. A brief review of the effect of bio-oil and biochar on asphalt volatile organic compounds (VOCs) is presented. Research find that bio-oil/biochar are not only replenish the light components of asphalt, but also improve the flow-induced crystallization and phase separation of bio-asphalt. There exists synergistic effect of biochar and bio-oil in asphalt modification. Moreover, biochar can improve the durability of bio-oil modified asphalt, but excessive addition of biochar to bio-oil modified asphalt can cause phase separation.

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Adding an appropriate amount of bio-oil and biochar to asphalt can improve its high-temperature resistance, low-temperature crack resistance, and system compatibility.

1. Introduction

With the rapid development of highway construction and the in-depth promotion of “the Belt and Road Initiative”, the importance of highway construction has become increasingly prominent. As the transportation infrastructure, highways have been vigorously developed. As the main pavement type of highway, asphalt pavement accounts for more than 90%. Asphalt is one of the main raw materials for highway construction, and it is gradually being consumed in an irreversible manner, with an annual consumption of over 33 million tons (China Statistics Press, 2002). Furthermore, asphalt releases a large amount of volatile organic compounds (VOCs) during high-temperature mixing or paving (Fig. 1), which seriously pollutes the environment and endangers human health. With the national strategic goal proposing of “carbon peaking and carbon neutrality”, it is urgent to find green alternative materials for asphalt with low VOCs volatilization (Abdullah et al., 2017).

Bio-oil refers to a liquid fuel obtained by pyrolysis or hydrothermal liquefaction using biomass as raw material (Fig. 2). Moreover, it is a potential substitute for asphalt, with advantages such as renewable, environmentally friendly, and widely available. It can be also mixed with asphalt in a certain proportion to form bio-asphalt, thereby reducing the consumption of asphalt (Deng, 2016; Yan et al., 2022; Zhang, 2013; Zhang et al., 2022). Moreover, bio-oils were used as recycling agents for aged asphalt and it is feasible to the high content bio-oil modified asphalt (Ju et al., 2022, 2023; Kazemi et al., 2022; Peng et al., 2023; Yuan et al., 2024). Currently, the production cost of bio-oil (biomass pyrolysis) is approximately 1500 RMB/ton to 2000 RMB/ton, and the selling price of bio-oil as boiler fuel ranged from 2000 RMB/ton to 2500 RMB/ton, with limited economic benefits. The production cost of bio-oil is less than 50% of the price of domestically produced asphalt (4000–5000 RMB/ton). The cost of biomass raw materials can vary significantly by source and region. So, the source and region can affect significantly the cost of bio-oil. There are 3494 million tons of biomass in China, which is 700 million tons of standard coal (Chen et al., 2024). And the annual asphalt consumptions are 66,992,000 tons. If bio-oil is partially used to replace asphalt, it can significantly reduce the amount of asphalt and the construction cost of asphalt pavement.

Biochar refers to the carbon-rich solid product obtained by pyrolysis or hydrothermal liquefaction or gasification using biomass as raw material (Fig. 2). It is a major by-product during thermochemical processes and is rich in aromatic hydrocarbons and elemental carbon, with a carbon content of up to 60%. Biochar is porous, large surface area, and good adsorption capacity, making it a potential inhibitor for asphalt VOCs (Sheng and Yang, 2022; Xu et al., 2018). The pyrolysis of biomass can simultaneously produce the main product (liquid bio-oil) and by-product (solid biochar), and the products do not need to separate. The bio-oil modified asphalt, biochar modified asphalt, and bio-oil and biochar modified asphalt collectively known as bio-asphalt. Therefore, the pyrolysis is a good method to prepare the bio-oil and biochar.

Fig. 1. VOCs emissions of asphalt during paving process.

China's annual biomass potential for the preparation of bio-oil/biochar is 460 million tons of standard coal, and the efficient utilization of biomass is an important pathway for green development (Zhang, 2017). Currently, the main biomass materials included sawdust, straw, rice husk, and algae, which used for pyrolysis to prepare bio-oil/biochar (Cao et al., 2015; Chen et al., 2016). Among them, sawdust is abundant in resources and has a complete front-end and back-end industrial chain, with a high degree of industrialization, which gives it obvious advantages compared to other biomass materials. The theoretical pyrolysis yield of sawdust-based bio-oil is relatively high, up to 70% (Wang et al., 2020a), and sawdust-based biochar has optimal adsorption characteristics, making it a potential inhibitor for asphalt VOCs. The use of bio-oil to modify asphalt has significant resource advantages, economic benefits, and social and ecological benefits. 20%–30% by-products (biochar) are produced during the pyrolysis process of bio-oil. If biochar was not fully utilized, it will inevitably cause serious environmental pollution. The addition of biochar into bio-oil modified asphalt can inhibit the emissions of VOCs and improve its road performance (Wang et al., 2020b). The addition of rubber or polyphosphoric acid can also improve the road pavement of bio-asphalt.

The main purpose of bio-oil/biochar composite modified asphalt is to obtain a green alternative material for low asphalt VOCs. The addition of bio-oil/biochar can improve the heat resistance and ultraviolet aging resistance of asphalt, reduce the emissions of VOCs, and achieve full-scale utilization of biomass pyrolysis products. It provides a new pathway for the resource utilization of biomass pyrolysis products and is of great significance for the development of renewable resources such as petroleum asphalt substitutes and the comprehensive utilization of biomass resources.

As shown in Fig. 3, this study aimed at reviewing the preparation parameters and properties of bio-oil/biochar, the preparation process of bio-asphalt, the effects of bio-oil/biochar on the composition, structure and properties of asphalt, and the mechanism of bio-oil/biochar on asphalt. It emphatically analyzed the effects of bio-oil/biochar on the composition, structure and properties of asphalt and the mechanism of bio-oil/biochar on asphalt. Finally, the study was summarized and looked forward.

2. Preparation and properties of bio-oil/biochar

The main methods for the preparation of bio-oil and biochar include pyrolysis and hydrothermal liquefaction (Huang et al., 2022). The pyrolysis of sawdust is the process of thermally decomposing sawdust under a protective gas to produce the bio-oil, biochar, and gases (CO_2, CO, CH_4, H_2, etc.) (Liu and Wang, 2006). The hydrothermal liquefaction of sawdust is the process of heating and pressurizing sawdust with the aid of super-critical/sub-critical liquids (water, organic acids, etc.) to undergo thermochemical reactions and produce the bio-oil and biochar (Zhang, 2007). Hydrothermal liquefaction produces a mixture of bio-oil and biochar at first, which needs further separation and refining. However, pyrolysis can directly obtain bio-oil and biochar, with high resource utilization efficiency. Therefore, pyrolysis is commonly used for the industrial preparation of bio-oil and biochar.

As shown in Fig. 4, the preparation of bio-oil/biochar is influenced by the composition and type of sawdust, pyrolysis temperature, and the flow rate of protective gas (Guo et al., 2020). Pan et al. (2014) studied the effects of pyrolysis temperature, heating rate, flow rate of protective gas, and particle size on the yield and properties of bio-oil. It was found that the gas yield of yellowhorn tree and torch pine were high, while the bio-oil/biochar yield of mulberry tree and jujube tree were high. The pyrolysis temperature had the greatest impact on the bio-oil yield, with the maximum yield of 52.04% at 500 °C. The effects of heating rate, flow rate of protective gas, and particle size on bio-oil yield were not significant (Fu, 2010). These studies indicated that biomass composition and type, as well as pyrolysis temperature, were key parameters for the preparation of bio-oil/biochar. The type of bio-oil will significantly influence the performance of modified asphalt.

As shown in Fig. 5, water extraction is a classical technology to separate bio-oil into heavy fraction and light fraction. Two fractions can be obtained by adding of water, diethyl ether, and dicholoromethane into bio-oil. Diethyl ether and dicholoromethane extraction are good technologies to separate the heavy fraction and light fraction of bio-oil. Generally, heavy fraction is rich in lignin derived compounds and is composed of acids, sugars, ketones, aldehydes and other poplar carbohydrates. The light fraction is rich in cellulose and hemicellulose derived compounds, and mainly contains phenolics and other aromatic compounds, pyrolytic lignin, and some ketones.

As shown in Table 1, the optimal pyrolysis temperature for sawdust-based bio-oil/biochar preparation is different. For the sawdust-based bio-oil yield, the optimal pyrolysis temperature is 500 °C during the selected temperature interval, while for the sawdust-based biochar yield, the optimal pyrolysis temperature is 550 °C during the selected temperature interval. However, there is limited research on the optimal pyrolysis temperature considering both bio-oil/biochar yield and performance conditions.

The preparation of bio-oil/biochar is also influenced by process parameters such as catalyst and pre-treatment methods. The effect of catalyst on bio-oil was investigated and found that zeolite catalysts contributed to an increase in bio-oil yield and the formation of 3-methoxyphenol in bio-oil (Cai et al., 2017, 2018). The influence of acid pre-treatment on the composition of bio-oil and the effect of composition changes on bio-oil yield were investigated and it was found that acid pre-treatment could increase the content of phenolic compounds in bio-oil, and the variation in ash and lignin content in pine wood significantly affected the yield of bio-oil/biochar (Li et al., 2022; Pagano et al., 2023). The effect of pre-treatment on the composition of bio-oil separation products was investigated and it was found that small molecular compounds such as acids, aldehydes, and furans were easily distilled during the pre-treatment of bio-oil. Moreover, the distillation temperature and vacuum level significantly affected the composition of bio-oil separation products (Liu, 2020; Liu et al., 2020). As shown in Fig. 6, the micromorphology of biochar varies greatly with different pyrolysis temperatures. Biochar is granular with a large number of micelles on the surface, and the agglomeration among particles is serious.

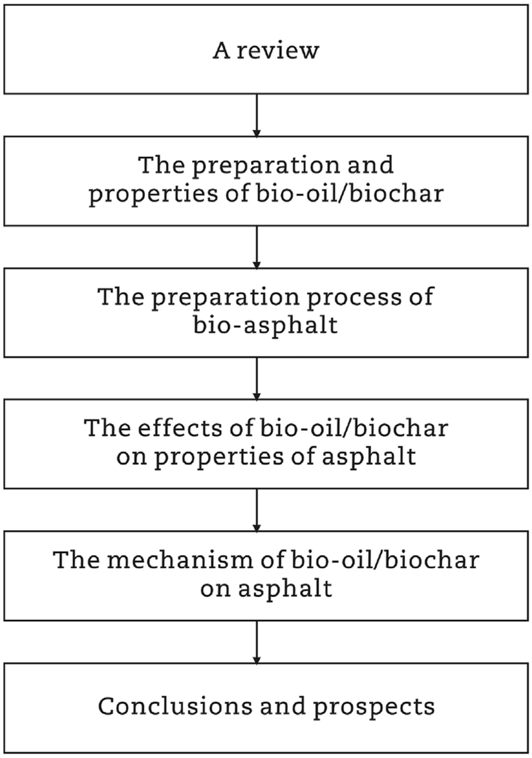

Fig. 3. Technical roadmap.

The physical and chemical characteristics of bio-oil and biochar products under different conditions of origin and preparation temperatures showed in Tables 2 and 3. As shown in this table, the different biomass source and pyrolysis temperature can affect significantly the pyrolyzed bio-oil and biochar properties. In terms of properties characterization of bio-oil/biochar, the optimal yield of bio-oil is 69.3% and its heating value is 13 MJ/kg. Moreover, the main chemical components are furfural, phenol, 3-methyl-1,2-cyclopentanedione, 3-methylphenol, and 4-methylguaiacol (Nhuchhen et al., 2018). The chemical characteristics of bio-oil have a high water content, requiring refining and upgrading through water extraction methods. High temperature condensation can promote the recovery of sugars and phenols, and dew point and water solubility are the main parameters for separating bio-oil and water. Egbosiuba (2022) found that the kinematic viscosity of bio-oil was 3.87 mm^2/s, density was 0.850 g/cm^3, and flash point was 53.5 min. And the yield of biochar reached up to 68.59 wt%. The study also found that bio-oil was a complex acidic mixture with a high oxygen content and low carbon content, containing only a small amount of nitrogen and sulfur, and had minimal environmental impact and almost no pollution (Pan et al., 2014). In summary, bio-oil is an acidic mixture with significant characteristics such as high viscosity, high carboxylic acid content, high water content, and low heating value (Cen et al., 2023; Peng et al., 2010; Wang et al., 2009).

Lan et al. (2016) found that biochar-modified composite membranes have good ethanol permeability and biochar has abundant organic groups, which is easier to chemically modify and form films. Xiang et al. (2022) studied the adsorption of organic pollutants by biochar and found that biochar had the strongest adsorption capacity when the pyrolysis temperature was 600 °C, and residence time was 70 min. As with the

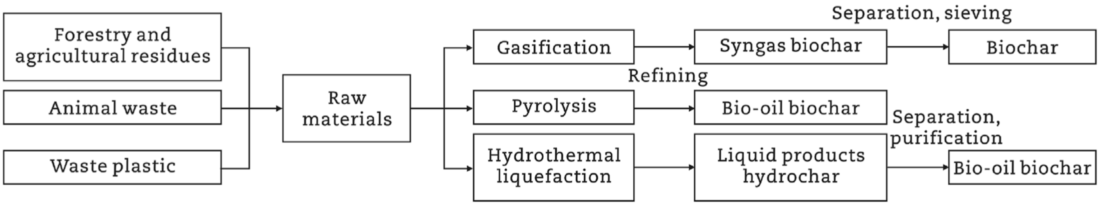

Fig. 2. Schematic representation of bio-oil/biochar preparation.

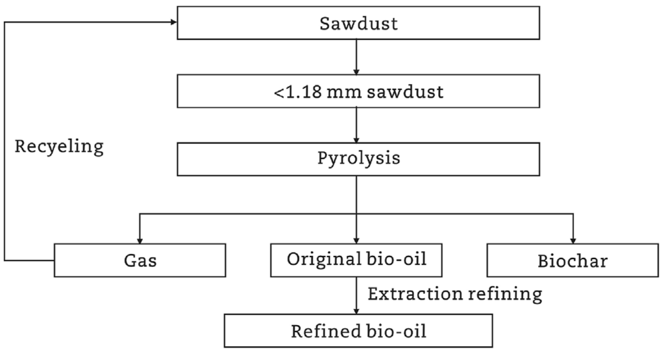

Fig. 4. Preparation process of bio-oil/biochar.

increasing of pyrolysis temperature, the carbon content in the biochar increased, which could enhance its adsorption and removal ability (Chang et al., 2020; Du et al., 2023; Huang et al., 2023; Khan et al., 2023), and increase the specific surface area of biochar (Zhang et al., 2023).

Chang et al. (2018) found that biochar has excellent adsorption properties for water purification and organic pollutants in water due to its rich functional groups and pore structure. Chen et al. (2018) found that biochar samples have well-developed pore structures, with a maximum specific surface area of 214.60 m^2/g; most of the pores in the biochar samples are mesopores, with pore sizes ranging from 2 to 10 nm. He et al. (2021) found that longer pyrolysis time (>60 min) can increase the pore volume of biochar, and the activated biochar has a pore volume 2.1 to 2.9 times that of the original biochar. Bentley et al. (2022) found that alkali metal pre-treatment could alter the pore structure of biochar, increase the micro-pore surface area, promote micro-pore development, and enhance the adsorption of trace organic pollutants by biochar. In summary, biochar has excellent thermal stability and adsorption properties, and can remove organic pollutants and volatile organic compounds, making it an excellent adsorbent.

Current research often focuses on the preparation and properties characterization of bio-oil/biochar, and the properties study of bio-oil modified asphalt or biochar modified asphalt, usually using only one of bio-oil or biochar (Zhou, 2023). The research on bio-oil often focuses on improving its quality for use in engine fuels, biodiesel, etc. (Geng et al., 2021; Huang et al., 2022; Xiong et al., 2021). The utilization of biochar often focuses on improving soil and crop quality, and ultimately applying it to agricultural fertilizers, catalysts, adsorbents, fuel cell materials, etc. (Dang, 2017; Rangarajan et al., 2022; Zhang et al., 2020). Although domestic and foreign scholars have conducted a large amount of research on the preparation and properties characterization of bio-oil/biochar, including the feedstock, pyrolysis process, pyrolysis equipment, and their environmental impacts, there is little research on the property of bio-oil or biochar modified asphalt, especially the physicochemical properties of bio-oil/biochar applied in asphalt. Therefore, the preparation and properties study of bio-oil/biochar composite asphalt is of great significance for the resource utilization of solid waste, the full-scale

Table 1
Elemental composite of biochar with different pyrolysis temperature (Zhou, 2023).

Element composite (%)	Temperature (°C)		
	450	500	550
C	81.14	81.83	81.89
N	1.75	4.01	4.08
O	16.29	12.31	11.95
H	0.39	1.32	1.38
S	0.43	0.53	0.70

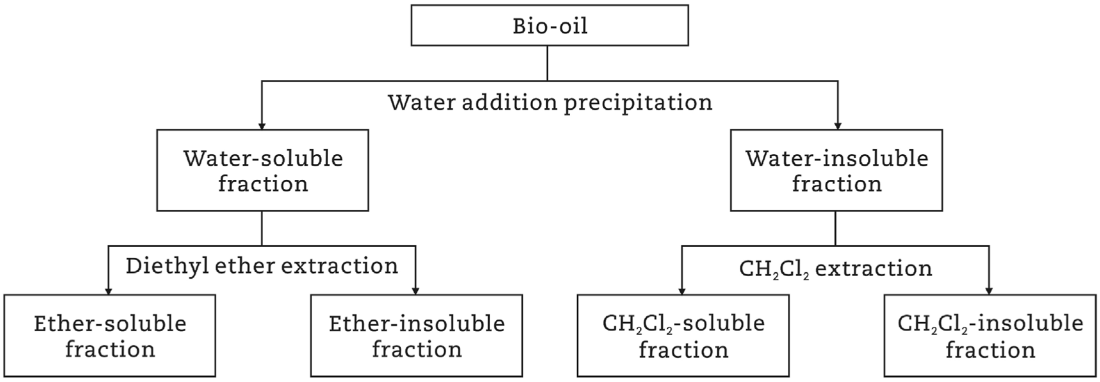

Fig. 5. Separate technology of heavy fraction and light fraction of bio-oil.

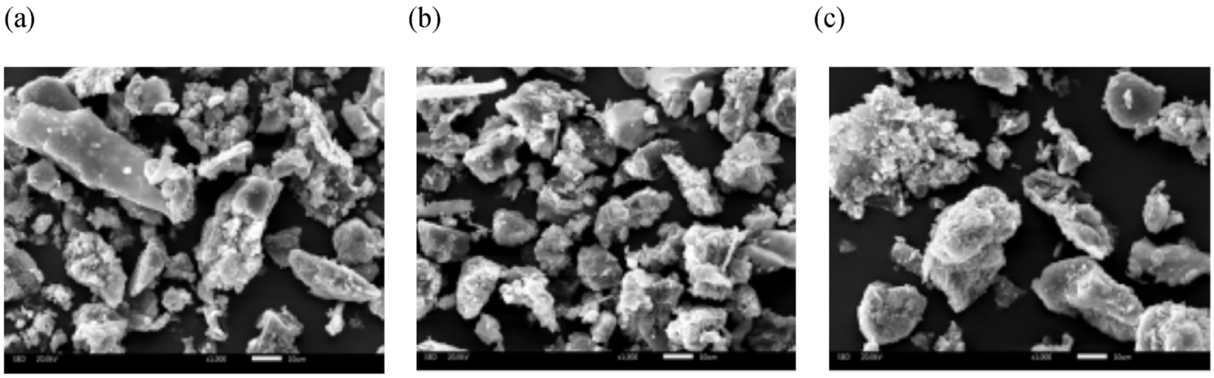

Fig. 6. Micromorphology of biochar at different pyrolysis temperatures. (a) 450 °C. (b) 500 °C. (c) 550 °C.

Table 2
Physical and chemical characteristics of bio-oil and biochar products with different raw materials.

Type	Density (g/cm^3)	Viscosity (cSt)	Heating value (MJ/kg)	Reference
Cassava bio-oil/biochar	1.00–1.50	2.9–1520.0	18.2–20.3	Tangsathitkulchai et al. (2012)
Plam shell bio-oil/biochar	1.10–1.60	23.4–327.0	25.6–33.2	Tangsathitkulchai et al. (2012)
Pine wood bio-oil/biochar	1.21	656.0	21.2	Gao et al. (2017)
Mallee bio-oil/biochar	1.20–1.30	453.0	21.5–25.2	Abdullah et al. (2010)

Table 3
Physical and chemical characteristics of bio-oil and biochar products with different pyrolysis tempertatures.

Feedstock	Temperature (°C)	Heating rate (°C/min)	Heating value (MJ/kg)	Reference
Cassave	300–600	10–30	22.1–28.7	Egbosiuba (2022)
Plam shell	500	10	27.5	Lee et al. (2017)
Pine wood	400–600	10–50	11.8–32.1	AlDayyat et al. (2021)
Mallee	550–750	15	17.9–18.8	Chen et al. (2024)

utilization of wood biomass, and the conservation of non-renewable resources such as petroleum asphalt.

3. Preparation process of bio-asphalt

The preparation of bio-asphalt is not only related to the content of the modifier, but also to the preparation parameters, such as shear rate, shear temperature and shear time. It is found that there is only a small amount of VOCs and without smoke, when the shear temperature is 120 °C and 135 °C. The asphalt sampler will produce heavy smoke after the shear time exceeds 60 min, when the shear temperature is 145 °C. The main reason is that the saturates and aromatics in the bio-oil are high, and the high temperature will make asphalt volatile a lot of VOCs and produce heavy smoke.

Increasing shear temperature will increase the softening point of bio-oil modified asphalt and decrease the penetration and ductility of bio-oil modified asphalt. Increasing the shearing time will reduce the softening point of bio-oil modified asphalt, and increase the penetration and ductility of bio-oil modified asphalt. The shearing temperature has a significant effect on the basic physical properties of bio-oil modified asphalt, the shearing time has a weak effect on the basic physical properties of bio-oil modified asphalt, and the shearing rate has almost no effect on the basic physical properties of bio-oil modified asphalt.

With the increase of shear temperature, the softening point of bio-oil/biochar composite modified asphalt increases, while the penetration and ductility decrease gradually. With the increase of shear time, the softening point of bio-oil/biochar composite modified asphalt decreases, while the penetration and ductility increase. However, the basic physical properties of bio-oil/biochar composite modified asphalt are relatively stable, when the shear time is extended from 60 to 120 min. The basic physical properties of bio-oil/biochar modified asphalt changes little with the change of shear rate. Specifically, with the increase of shear rate, the penetration and 10 °C ductility of bio-oil/biochar composite modified asphalt gradually increases, and the softening point slightly decreases.

4. Effects of bio-oil/biochar on the composition, structure and properties of asphalt

As shown in Table 4, the addition of bio-oil can increase the penetration of asphalt, reduce the softening point of asphalt, prepare high grade asphalt, and the content of bio-oil is preferred to choose 15%–20%. This conclusion was also verified by previous researches (Kabir et al., 2020; Mousavi and Fini, 2019; Zhou, 2023; Zhou et al., 2022). The influence of bio-oil on the composition and structure of asphalt was investigated and it was found that the main components of bio-oil were furfural, phenol, 3-methyl-1,2-cyclopentanedione, 3-methylphenol, and 4-methylguaiacol, etc. (Xiong et al., 2021). It can be divided into aromatic fraction (light fraction), oxygen-containing compounds (medium fraction), and phenolic compounds (heavy fraction), which completely fall into the four components of asphalt (saturates, aromatics, resins, and asphaltenes) (Wang et al., 2020b). Therefore, it can be inferred that the composition of bio-oil is similar to that of petroleum asphalt, and it can be partially substituted by asphalt. The influence of bio-oil on the asphalt structure was investigated and it was found that the characteristic functional groups numbers of C═O and O–H, and increase the content of crystalline wax and the molecular weight of oxygen-containing compounds in the system after the addition of bio-oil (Huang et al., 2022; Liu and Wang., 2006; Wang et al., 2020b). Bio-oil belongs to acidic compounds and it has the high oxygen content and viscosity. The addition of bio-oil will change the acid value and colloid structure, promoting the transformation of asphalt into a high-gel state.

As shown in Fig. 7, bio-oil can reduce the complex modulus of asphalt and increase the phase angle of asphalt during the temperature range of 30 °C–80 °C, indicating that bio-oil can reduce the high temperature shear deformation resistance of asphalt and increase the high temperature viscosity of asphalt. The influence of bio-oil on the property of asphalt and the rheological properties of bio-oil were investigated, and it was concluded that complete substitution of asphalt with bio-oil was feasible (Raouf and Williams, 2009). Later, Fini et al. (2011) studied the effects of ultraviolet aging on the rheological properties of bio-oil modified asphalt, and found that ultraviolet aging significantly affected the rheological properties of bio-oil modified asphalt, improving its resistance to rutting and fatigue life (Deng, 2016; Zhu, 2014). Yang et al. (2014) investigated the fundamental physicochemical and rheological properties of bio-oil modified aged asphalt, and found that bio-oil reduced the viscosity and softening point of aged asphalt, enhanced its temperature sensitivity, and promoted the rejuvenation of aged asphalt.

Wang et al. (2014) investigated the effects of the water-oil ratio on the properties of emulsified bio-oil modified asphalt and they recommended using a water-oil ratio of 55:45 to extract bio-oil. It was found that the addition of bio-oil reduced the resistance to rutting of the asphalt (Wang et al., 2015). Ma et al. (2015) reviewed the preparation and road properties of bio-oil modified asphalt, and found that bio-oil modified asphalt was an excellent alternative material to petroleum asphalt. Ding et al. (2018) studied the road property and action mechanism of bio-oil modified asphalt, and found that bio-oil could replenish the saturates and aromatics. Moreover, bio-oil could also form a network structure with asphalt, improving the aging resistance of asphalt. Lu et al. (2017) reviewed the road property of bio-oil modified asphalt, and found that bio-oil could be used as a modifier for asphalt. The soften point of asphalt, bio-oil modified asphalt, and bio-oil and biochar modified asphalt is 45 °C, 48 °C, 53 °C, respectively. It indicated that there exists synergistic effect of biochar and bio-oil in asphalt modification.

The road property of bio-oil modified asphalt was investigated and found that it had good road property and could be used as a road material (Song et al., 2014, 2018). The road property and storage stability of bio-oil modified asphalt was studied, pointing out that excellent storage stability was a prerequisite for the application of bio-oil modified asphalt (Tu, 2016; Tu et al., 2016). Lei (2019) studied the road property and adhesion characteristics of bio-oil modified asphalt and found that the addition of bio-oil significantly affected the three major indicators of

Table 4
Fundamental properties of bio-oil modified asphalt (Zhou, 2023).

Oil content	Penetration (0.1 mm)	Softening point (°C)	15 °C ductility (cm)	10 °C ductility (cm)	Grade
0%	62	49	>150	52	AH-70
5%	82	45	>150	78	AH-90
10%	95	44	>150	89	AH-90
15%	102	43	>150	103	AH-110
20%	124	41	>150	104	AH-130
25%	84	36	>150	55	–
4% biochar	98	44	>150	92	–
SBS asphalt	102	48	>150	115	–

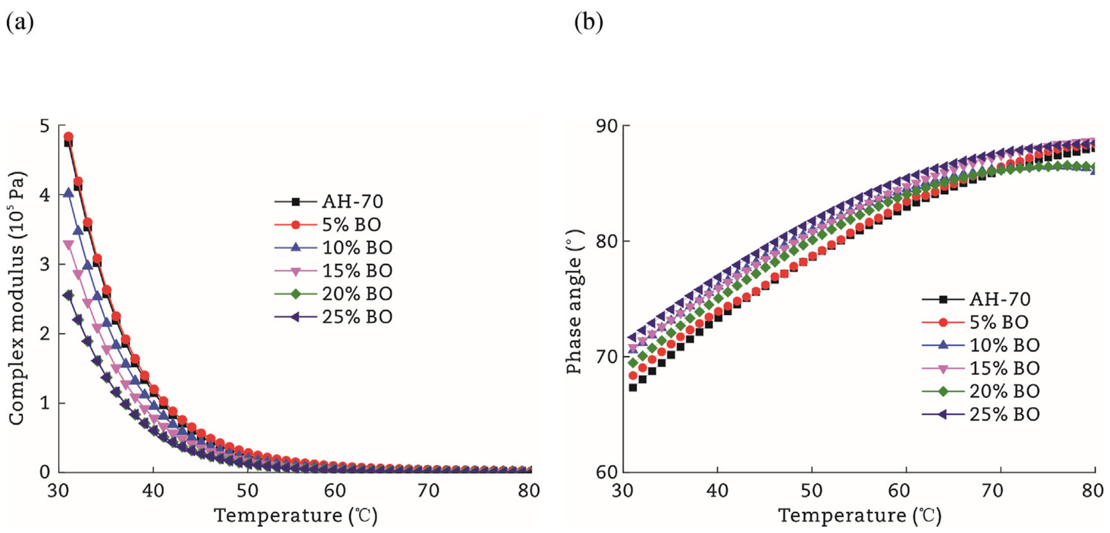

Fig. 7. Temperature scanning curve of bio-oil modified asphalt (Zhou, 2023). (a) Complex modulus. (b) Phase angle.

asphalt, namely penetration, softening point, and ductility. Specifically, the addition of bio-oil increased the penetration and ductility of asphalt while reduced the softening point. Many researchers also got the same experimental conclusions (Xia, 2019). Bio-oil, as a modifier, can effectively improve the rutting resistance of asphalt at high temperatures, but it has a certain negative impact on the low-temperature cracking resistance of asphalt. It can improve the dynamic stability of ATB-25 asphalt mixture, and other road performance indicators such as Marshall stability and residual stability meet the standard requirements. Bio-oil, as a component regulator, can improve the high-temperature stability, fatigue durability, freeze-thaw durability, and self-healing ability of aged asphalt mixtures (Gao and Liu, 2019; Liu et al., 2021; Yan and Zhang, 2020). Currently, the research on bio-oil modified asphalt focuses on property improvement and functional application. However, there are some drawbacks in the application of bio-oil modified asphalt, such as high oxygen content, susceptibility to aging and oxidation, poor durability, and inability to withstand large plastic deformation (Gao et al., 2018; Ingrassia et al., 2020; Kabir et al., 2020; Lyu et al., 2022).

The influence of biochar on the property of asphalt was investigated widely. Ma et al. (2022) studied the rheological property of biochar modified asphalt and found that using a biochar content of 5%–15% could improve the complex modulus and penetration of asphalt, enhancing its high-temperature performance. Fu et al. (2015) investigated the road property of biochar modified asphalt and found that biochar could improve the aging resistance and resistance to rutting of asphalt at high temperatures. The adsorption property of biochar on volatile organic compounds (VOCs) and found that biochar could remove alkanes, polycyclic aromatic hydrocarbons (PAHs), and sulfur compounds from VOCs. The biochar could improve the adsorption capacity of asphalt, and the adsorption capacity of biochar modified asphalt was increased at the higher temperatures (Fig. 8). It was also found that carbon materials such as carbon black and biochar not only inhibited the photo-oxidative aging of asphalt, but also improved its high-temperature stability, resistance to thermal oxidative aging, and suppress the volatilization of VOCs (Rajib et al., 2021). The research also indicated that owing to the characteristics of biochar such as its high porosity, high carbon content, good stability, large specific surface area, strong adsorption capacity, and good compatibility with organic substances, biochar had a significant thickening effect on asphalt, which could improve the aging resistance and high-temperature stability of asphalt and asphalt mixtures, with little impact on the fatigue resistance and crack resistance of asphalt (Fu et al., 2017).

As shown in Table 5, the incorporation of biochar can reduce the penetration and ductility of bio-oil modified asphalt, improve the softening point and high temperature stability, and the appropriate dosage is

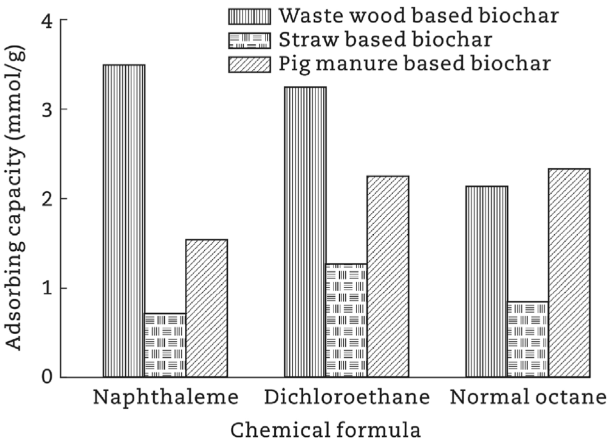

Fig. 8. Adsorption capacity of biochar (Zhou et al., 2022).

4%–6%. Biochar can adsorb the aromatic content and saturation content of bio-oil modified asphalt, change the colloid structure of the asphalt, and has selectivity for the adsorption of four components of bio-oil modified asphalt. The influence of bio-oil/biochar on the composition and property of asphalt were investigated, because both bio-oil and biochar were obtained from the pyrolysis of sawdust, they have good compatibility. The bio-oil and biochar were prepared by pyrolysis of sawdust and used them for modified asphalt. It was found that biochar could improve the high-temperature properties of asphalt, and under shear action, flow-induced crystallization occurred in the bio-oil/biochar composite modified asphalt, which could lead to phase separation when the crystallization exceeded a certain range. Biochar can improve the durability of bio-oil modified asphalt, but excessive addition of biochar to bio-oil modified asphalt can cause phase separation. Adding an appropriate amount of bio-oil and biochar to asphalt can improve its high-temperature resistance, low-temperature crack resistance, and system compatibility (Zhu, 2018).

Current research on the application of bio-oil/biochar modified asphalt is mainly focused on the complete replacement of asphalt with bio-oil, partial replacement of asphalt with bio-oil (15% $\leq$ bio-oil content $<$100%), modification of asphalt with biochar (biochar content $\leq$15%), while the research on bio-oil/biochar composite modified asphalt (i.e., bio-oil and biochar added to asphalt sequentially) is relatively rare. There is also a lack of in-depth research on the composition optimization and structural property design of sawdust-based bio-oil/biochar composite modified asphalt, especially in terms of the influence of sawdust-based bio-oil/biochar on the composition, structure, and property of asphalt.

5. Mechanism of bio-oil/biochar on asphalt

Owing to the high oxygen content and viscosity of bio-oil, as well as the strong adsorption capacity of biochar, the key aspects to focus on regarding the mechanism of action of bio-oil/biochar on asphalt include: the influence of bio-oil/biochar on the flow-induced crystallization of asphalt, the influence of bio-oil/biochar on the phase separation of asphalt, the influence of bio-oil/biochar on the aging and phase separation of asphalt, and the adsorption mechanism of biochar on VOCs in bio-oil modified asphalt.

The flow-induced crystallization refers to the phenomenon where polymers crystallize under shear, stretching, and other flow actions. Owing to its short occurrence time, it is often difficult to observe (Andreev and Rutledge, 2020). Induced crystallization changes the morphology of asphalt by distorting polymer chains, thereby controlling the structure and morphology of the polymer (Jalali et al., 2019; Kané et al., 2003; Lei et al., 2017; Sefiddashti et al., 2020). Asphalt is derived from crude oil and contains a small amount of crystalline wax ($\leq$3.0%) internally, which is the main crystalline phase in asphalt. Crystalline wax mainly consists of C20–C40 normal alkanes, which form a layered crystalline structure with a thickness of about 10 nm on the surface of asphalt (Hung et al., 2017; Norrman et al., 2016; Pahlavan et al., 2016). In order to suppress the low-temperature physical hardening and phase separation caused by flow-induced crystallization of crystalline wax in asphalt, it is necessary to strictly control the wax content in asphalt (Chen, 2005; Zhang, 2006). Moreover, in order to prepare asphalt with excellent road performance, it is important to identify the crystalline compounds and influencing factors related to crystallization in asphalt.

Table 5
Four components of bio-oil/biochar modified asphalt with different biochar content (Zhou, 2023).

Biochar content (%)	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
0	12.45	70.24	10.22	7.09
2	6.42	58.72	21.56	13.30
4	5.85	56.65	23.12	14.38
6	4.69	52.82	28.45	14.04
8	4.52	52.78	28.86	13.84

As shown in Fig. 9, there is no transparent concentric circle in the small angle X-ray scattering pattern of asphalt under shear action, and there is no crystal phase in asphalt. As with the increase of bio-oil content, the small-angle X-ray scattering pattern of bio-oil modified asphalt appears concentric circles under shearing, the scattering pattern of bio-oil modified asphalt has an ordered structure, and there is a local crystalline phase, that is, bio-oil can promote the shear induced crystallization of asphalt. The presence of crystalline wax in bio-oil makes bio-oil modified asphalt prone to flow-induced crystallization (Hung and Fini, 2020; Jeon et al., 2021; Samieadel et al., 2020; Ye et al., 2022). Flow-induced crystallization significantly affects the preparation, processing, and performance of bio-oil modified asphalt (Forestier et al., 2022; Takamatsu and Saito., 2022). It has been found that high-speed shear or vehicle load can cause the aggregation of small crystalline regions in bio-oil modified asphalt, leading to flow-induced crystallization (Forestier et al., 2022). In asphalt materials, a moderate amount of crystallization enhances the rheological properties of asphalt, but excessive or secondary crystallization makes asphalt brittle and reduces impact strength. Therefore, while allowing for a moderate amount of crystallization in the material system, excessive or secondary crystallization should be avoided.

The crystal growth and nucleation of bio-oil modified asphalt are closely related to its crystallization kinetics. There are mainly two types of crystallization kinetics: isothermal crystallization kinetics and non-isothermal crystallization kinetics. The isothermal crystallization kinetics, mainly proposed by Avrami, is commonly referred to as the Avrami theory (Park et al., 2020). The non-isothermal crystallization kinetics, mainly proposed by Ozawa based on the Avrami theory, is therefore called the Avrami-Ozawa theory (Avrami, 1940). The study of crystallization kinetics mainly involves the determination of crystallization kinetic parameters, including the number of crystal nuclei, nucleation rate, and degree of crystallinity. The Avrami-Ozawa theory can be used to evaluate the non-isothermal crystallization kinetics and its parameters of materials (Ozawa, 1971). The isothermal crystallization kinetic model can be represented by Eq. (1).

$$\ln(-\ln(1 - C(t))) = \ln(Z) + n_1\ln(t) \quad Z = 2\text{–}2.5,\ n_1 = 3.06\text{–}4.17 \tag{1}$$

where $C(t)$ is the crystallinity, Z is a temperature-dependent constant of crystallization kinetics rate, n_1 is Avrami index, and t is time.

The non-isothermal crystallization kinetic model can be represented by Eq. (2).

$$\ln(-\ln(1 - C(t))) = \ln(K(t)) - m\ln(\varphi) \quad K(t) = 2.5\text{–}3.8,\ m = 1\text{–}3 \tag{2}$$

where $K(t)$ is cooling function or crystallization rate, m is the Ozawa index, which reflects the crystal size and nuclei models, φ is the cooling rate.

It can be used to predict the number of crystal nuclei through the critical activation shear rate, relaxation time, and growth function (Guo, 2015; Qiu et al., 2020). It can be also used to calculate the nucleation rate through the Lauritzen-Hoffman model (Jalali et al., 2019; Wei et al., 2021), and determining the degree of crystallinity through the Nakamura crystal model (Shao et al., 2022). Therefore, the crystallization kinetics of bio-oil modified asphalt can be evaluated using the Avrami theory and Avrami-Ozawa theory, with the assistance of the number of crystal nuclei, nucleation rate, and degree of crystallinity. As shown in Fig. 10, the isothermal crystallization kinetics shows that the crystal form is spherulite, when the content of biochar is 0–6%. The crystal form is layered crystal, when the content of biochar is 8%. The crystallization rate constant increased with the increase of biochar content.

The crystalline wax in bio-oil can usually be separated from asphalt and form crystallization (Hung et al., 2019b). And the precipitated crystalline wax usually exists in the interface layer between asphalt and

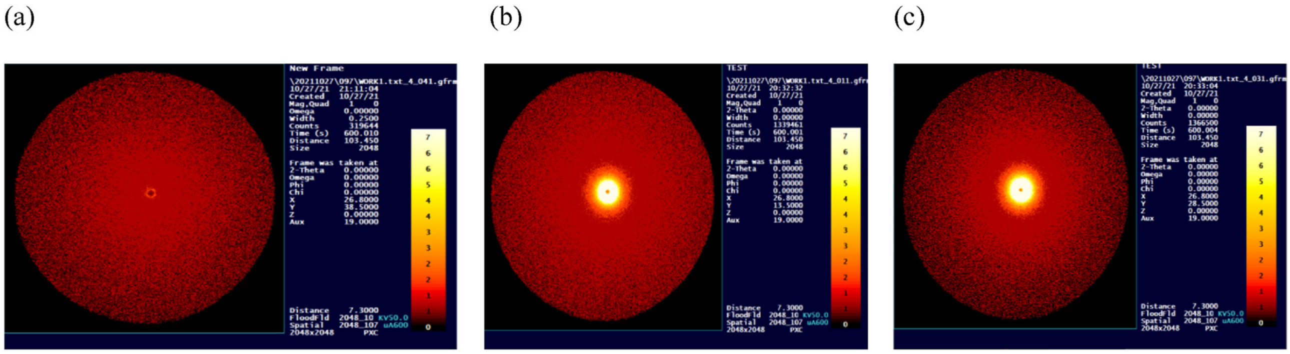

Fig. 9. Small angle X-ray scattering pattern of modified asphalt with different bio-oil contents (Zhou, 2023). (a) AH-70. (b) 10% BO. (c) 20% BO.

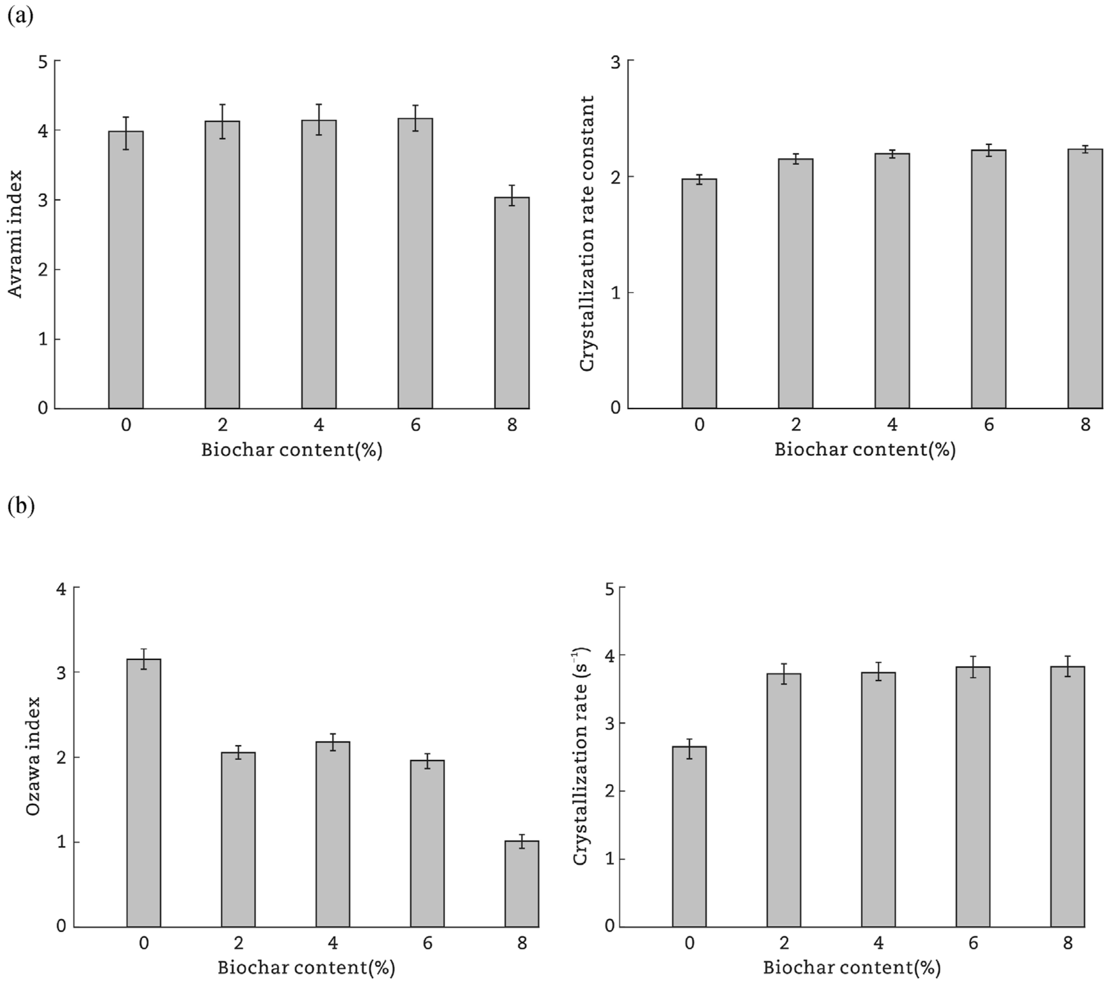

Fig. 10. Isothermal and non-isothermal crystallization kinetics parameters of bio-oil/biochar modified asphalt (Zhou, 2023). (a) Isothermal crystallization kinetics. (b) Non-isothermal crystallization kinetics.

siliceous aggregate, thus making asphalt pavement more vulnerable to water damage (Madbou, 2020). The addition of a small amount of biochar can effectively reduce the migration of crystalline wax and the negative effects of flow-induced crystallization on bio-oil modified asphalt, while the introduction of excessive biochar will lead to serious flow-induced crystallization of the system due to the agglomeration of biochar itself (Hung et al., 2019a). Atomic force microscopy (AFM) results showed that the bee structure in the bio-oil/biochar composite modified asphalt was mainly caused by the presence of crystalline wax, and the flow induced crystalline wax to form a lamellar film-bee structure. Moreover, the bee structure in bio-oil/biochar composite modified asphalt can freeze molecules and prevent self-healing of bio-oil/biochar composite modified asphalt (Mousavi et al., 2019). The crystalline wax in the bio-oil/biochar composite modified asphalt will form flow-induced crystal sheets with thickness of 3–30 nm under its own action, and the crystallization characteristic spectrum will appear at 1466 cm^{-1} (Mousavi and Fini, 2019). In the initial phase of flow-induced crystallization, crystalline molecules are crystallized mainly through dynamic structural fluctuations between disordered and crystalline states (Hung et al., 2020). The above research results confirm that in the bio-oil/carbon composite modified asphalt system, the crystalline wax in bio-oil is the key to generate flow-induced crystallization in the system, and the appropriate amount of biochar can effectively reduce the flow-induced crystallization of bio-oil modified asphalt, while excessive biochar can be used as a nucleating agent to induce the crystallization nucleation of bio-oil modified asphalt.

It is generally believed that the nucleus generated by induced crystallization is the key to phase separation, and flow-induced crystallization is closely related to phase separation. Phase separation is the main problem in the preparation and use of bio-oil/biochar composite modified asphalt, and it is the primary problem to be solved in the preparation of bio-oil/biochar composite modified asphalt. In order to inhibit the phase separation of bio-oil/biochar composite modified asphalt and the negative effects of aging on the phase separation of the system, it is urgent to reveal the phase separation mechanism of bio-oil/biochar on the asphalt and the aging phase separation mechanism. The proper amount of bio-oil can be miscible with bitumen without phase separation. Excessive bio-oil will lead to phase separation of the system. Appropriate amount of biochar does not lead to phase separation of bio-oil/biochar composite modified asphalt, while excessive amount of biochar as the core of crystallization nucleation will lead to phase separation of bio-oil/biochar composite modified asphalt (Farjas et al., 2017). The atomic force micro-structure of bio-oil/biochar composite modified asphalt shows that the bee structure is the separation phase of the system (Shehzad and Al-Harthi, 2021). The main reaction is not the oxidation of asphalt molecules during the process of thermal oxygen aging of bio-oil/biochar modified asphalt, but the reaction of condensation dehydrogenation and oxidation to synthesize water. Owing to the oxidation reaction of asphalt, the content of carbonyl (C═O) and sulfoxide (S═O) increases during the ultraviolet aging process, while the content of butadienyl (C═C) decreases, resulting in changes in the colloid structure of asphalt and phase separation (Farjas et al., 2017; Shehzad and Al-Harthi, 2021). The short term aging, pressure aging and ultraviolet aging can accelerate the phase separation of bio-oil/carbon composite modified asphalt. As shown in Fig. 11, compared with short term aging, ultraviolet aging and pressure aging have more serious effects on the phase separation of bio-oil/biochar composite modified asphalt.

The key is to test the change of VOCs components and volatile characteristics of bio-oil/biochar composite modified asphalt during the adsorption mechanism of bio-oil modified asphalt VOCs by biochar. The light components and polycyclic aromatic hydrocarbons in asphalt are easily volatilized by heat to form flue gas, resulting in a large number of toxic VOCs, when asphalt mixture is mixed and spread at high temperature (Wang et al., 2020b). The VOCs of asphalt contain more than 100 components, among which PAHs has the most serious impact on human health (Zhang et al., 2021). Volatilization of VOCs will change the four components of asphalt, pollute the environment, and endanger the health of pavement workers (Wu et al., 2022; Zhao et al., 2022). Since bio-oil is produced by the pyrolysis of biomass at a high temperature of 300 °C–1000 °C, the VOCs content of bio-oil itself is small and difficult to volatilization, coupled with the characteristics of biochar with porous, strong adsorption and adsorption of asphalt VOCs, the inclusion of bio-oil and biochar in asphalt can significantly reduce the volatilization of asphalt VOCs. The main reason for the decrease in VOCs volatilization of bio-oil modified asphalt is that bio-oil replaces part of asphalt, reduces the content of asphalt in the bio-oil/biochar composite modified asphalt system, and bio-oil is more difficult to volatilization VOCs than asphalt, resulting in less VOCs volatilization of bio-oil modified asphalt than asphalt VOCs. The main reason for the decrease in VOCs volatilization of bio-oil/biochar composite modified asphalt is that biochar is very easy to absorb alkane, PAHs and sulfur-containing compounds in VOCs, resulting in less VOCs volatilization of bio-oil/biochar composite modified asphalt than that of bio-oil modified asphalt. As shown in Fig. 12, the developed model shows, firstly, the biochar adsorbs $C_{15}H_{30}$ (1-pentadecane), $C_{16}H_{32}$ and $C_{21}H_{44}$ compounds of the VOCs. Thereafter, $C_{14}H_{10}$, $C_{22}H_{45}SH$, $C_{16}H_{34}$ and $C_{10}H_{22}O_4$ are removed. Lastly, the biochar adsorbs the remaining compounds of $C_{14}H_{30}$, $C_{17}H_{36}$, $C_{18}H_{38}$, $C_{15}H_{30}$ (pentadecane), $C_9H_{18}O$, $C_{13}H_{28}$, $C_{20}H_{42}$, $C_{19}H_{40}$ and $C_{10}H_8$.

At present, the research on asphalt VOCs at home and abroad mainly focuses on the test method, chemical composition, special properties and types of asphalt VOCs (Li et al., 2021). However, whether the existing test method of asphalt VOCs is suitable for the test of VOCs composition change and volatile characteristics of bio-oil/biochar composite modified asphalt remains to be tested. As for the test method of asphalt VOCs, Zhang (2014) studied the inhibition effect of carbon black and layered hydrochar on asphalt VOCs by thermogravimetric mass spectrometry, and found that the dilution effect in the test process could be reduced by thermogravimetric mass spectrometry, and the composition changes of asphalt VOCs were qualitatively analyzed. The thermogravimetric mass spectrometry method is suitable for testing the molecules in the range of 1 amu–300 amu in asphalt VOCs. Li (2017) studied the separation of asphalt VOCs components by gas chromatography-mass spectrometry, quantitatively evaluated the chemical composition of asphalt VOCs, and

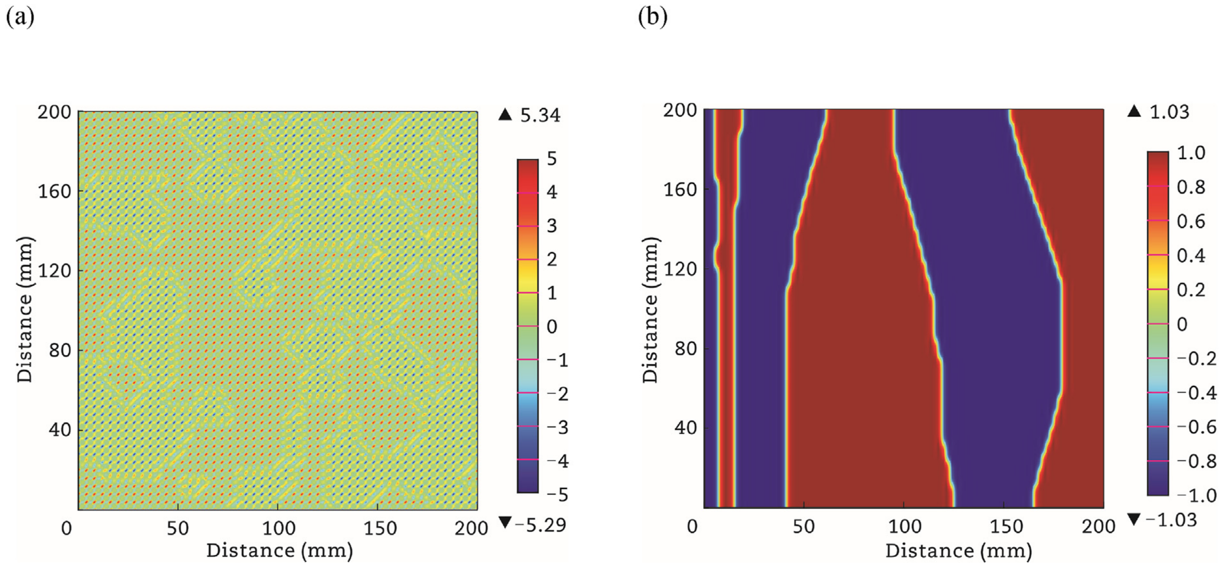

Fig. 11. Simulated morphology of aged bio-oil/biochar modified asphalt (Zhou, 2023). (a) Short-term aging. (b) Ultraviolet aging.

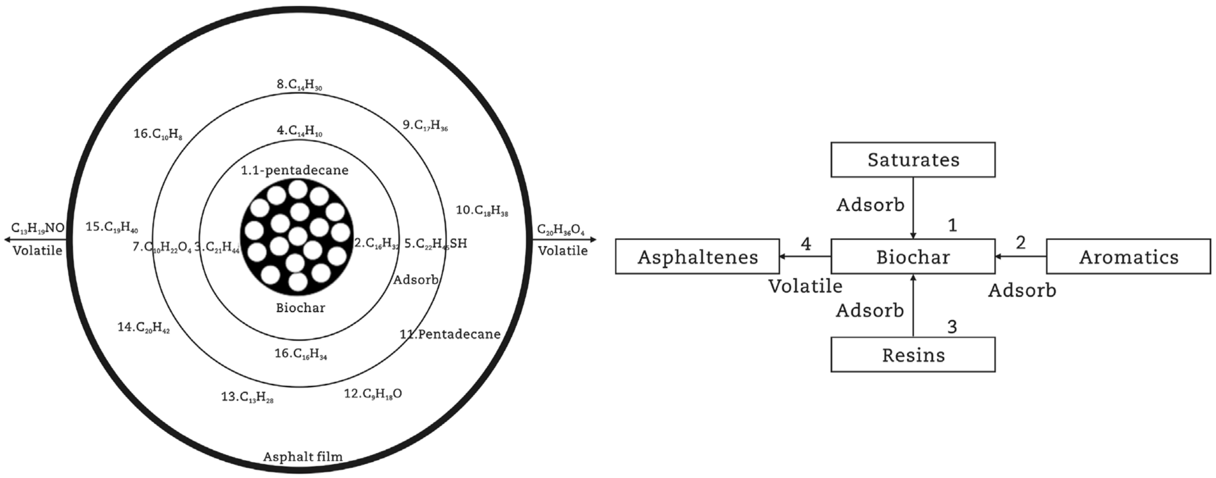

Fig. 12. The “vortex” model of biochar adsorption VOCs (Zhou, 2023).

found that gas chromatography-mass spectrometry was suitable for testing molecules with molecular mass ranging from 30 amu to 1000 amu in asphalt VOCs. Long et al. (2018) found that the combined method of pyrolysis, gas chromatography and mass spectrometry was suitable for qualitative and semi-quantitative evaluation of asphalt VOCs components. Xiao et al. (2019) found that the combined method of pyrolysis, gas chromatography-mass spectrometry was suitable for the test of VOCs components in asphalt. The adsorption of VOCs of bio-oil/biochar composite modified asphalt by gas chromatography and mass spectrometry were investigated, and found that there were 106 main compounds in VOCs, with extremely complex components (Zhou, 2023). Biochar has excellent VOCs adsorption characteristics, and the adsorption capacity can reach 820 mg/g. The method of gas chromatography-mass spectrometry can be used to evaluate the VOCs of bio-oil/biochar composite modified asphalt. In summary, thermogravimetric mass spectrometry, gas chromatography-mass spectrometry and pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) can all be used to evaluate the volatilization rule and component change of asphalt VOCs, but their respective application scenarios are different. Thermogravimetric mass spectrometry is suitable for testing the molecules in the range of 1 amu–300 amu in asphalt VOCs. Gas chromatography-mass spectrometry (GC-MS) is suitable for the determination of the molecules with molecular weight ranging from 30 to 1000 amu in asphalt VOCs, and Py-GC-MS is suitable for the qualitative and semi-quantitative evaluation of asphalt VOCs components. PAHs distributions had special characteristic in biochar and five-membered ring, –COOH, and $-CH_3$ were among the main adsorbed functional groups for PAHs adsorption of biochar. PAHs have the targeted adsorption onto the oxygen-rich biochar. The bio-oil and biochar can reduce VOCs volatility and the findings highlighted the significance of bio-asphalt species and content on VOCs decay pattern in life cycle assessment and global warming potential.

The above reviews confirmed the complexity of the chemical composition of asphalt VOCs, and put forward common solutions and available inhibitors to inhibit VOCs volatilization. However, the adsorption mechanism of biochar on VOCs of bio-oil modified asphalt are not clear, and there is a lack of in-depth and detailed research. At present, the action mechanism of bio-oil/biochar composite modified asphalt is generally understood as follows: the existence of crystalline wax in bio-oil will induce the crystallization of asphalt, and improve the road performance of asphalt by supplementing the light components in asphalt. Biochar adsorbs the VOCs of asphalt through its porous structure and high specific surface area, especially the toxic PAHs in VOCs, and reduces the volatilization of asphalt VOCs. However, the action mechanism of bio-oil/biochar composite modified asphalt has not been studied deeply. Therefore, the key to the application of bio-oil/biochar modified asphalt is to find out the action mechanism of bio-oil/biochar on asphalt.

6. Conclusions and prospects

In this study, the properties and modification mechanism of bio-oil/biochar modified asphalt were investigated. The following conclusions can be derived.

The optimal pyrolysis temperature for bio-oil/biochar preparation is different. The addition of bio-oil can improve the penetration of asphalt, reduce the softening point of asphalt, prepare high grade asphalt, and the content of bio-oil is preferred to choose 15%–20%.

Biochar can improve the durability of bio-oil modified asphalt, but excessive addition of biochar to bio-oil modified asphalt can cause phase separation. Adding an appropriate amount of bio-oil and biochar to asphalt can improve its high-temperature resistance, low-temperature crack resistance, and system compatibility.

In asphalt materials, a moderate amount of crystallization enhances the rheological properties of asphalt, but excessive or secondary crystallization makes asphalt brittle and reduces impact strength. Therefore, excessive or secondary crystallization should be avoided.

Biochar is very easy to absorb alkane, PAHs and sulfur-containing compounds in VOCs. There exists flow-induced crystallization phenomenon and biochar can targeted adsorb the PAHs in bio-oil/biochar modified asphalt.

Declaration of competing interest

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

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