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Investigation on DOPO as reactive fumes suppressant to reduce the fumes emission of asphalt

Shangheng Zeng [a], Sanpeng Mao [a,b], Shi Xu [c,d], Yanheng He [a], Jianying Yu [a,*]

[a] *State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, PR China*
[b] *Research Institute of Petro China Fuel Oil Co., Ltd., Beiwucun Road 25, Beijing 100195, PR China*
[c] *Hubei Key Laboratory of Roadway Bridge and Structure Engineering, Wuhan University of Technology, Wuhan 430070, PR China*
[d] *Faculty of Civil Engineering and Geosciences, Delft University of Technology, 2628 CN Delft, the Netherlands*

HIGHLIGHTS

- DOPO can significantly reduce the VOCs and H_2S in the fume of asphalt.
- Effect of DOPO on the chemical structure and composition of asphalt was investigated.
- The reactive fumes suppression mechanism of DOPO on asphalt has been explored.

GRAPHICAL ABSTRACT
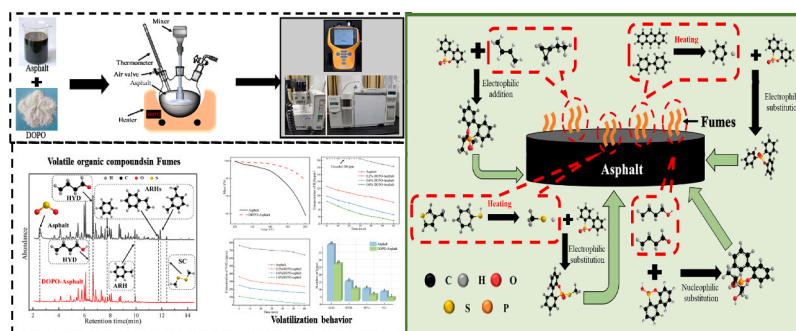
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ABSTRACT

Asphalt fumes released during pavement construction posed a threat to human health and environment. In this study, 9,10-dihydro-9-oxa-10-phosphorophenanthrene-10-oxide (DOPO) was used as a reactive fumes suppressant to reduce the asphalt fumes emission. The volatilization behavior of DOPO modified asphalt (DOPO-Asphalt) was investigated through thermogravimetric analysis, volatility test and thermal destruction gas chromatography mass spectrometry, and effect of DOPO on the chemical structure and composition of asphalt was explored through nuclear magnetic resonance hydrogen spectroscopy, Fourier transform infrared spectroscopy, and asphalt component testing. The results indicated that 1.0 wt% DOPO reduced the fume content of control asphalt by 1.1% from 120 °C − 200 °C and the H_2S and VOC content by 96.9% and 84.2%, respectively, at 180 °C. Moreover, 1.0 wt% DOPO reduced the content of aliphatic hydrocarbons, hydrocarbon derivatives, aromatics, and sulfides in control asphalt fumes by 86.8%, 89.7%, 90.7%, and 93.5%, respectively, which may be attributed to electrophilic and nucleophilic reactions between DOPO and volatile substances in asphalt. Chemical structure and composition changing of DOPO-Asphalt confirmed that P-H bond in DOPO was chemically reacted with components in asphalt, generating stable aromatic hydrocarbons and resins. The results provided a novel method for inhibiting the volatilization of harmful substances in asphalt.

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1. Introduction

Asphalt pavement has been widely used in highway construction due to its excellent driving comfort and skid resistance [23,38,40]. In order to meet the flowability of asphalt mixture during paving, the temperature of asphalt in road construction was usually higher than 160 ℃, and asphalt fumes will be generated during continuous heating, transportation and construction under high temperature [2,4,25,34,37]. The main components of asphalt fumes include volatile organic compounds (VOCs), hydrogen sulfide (H_2S), and particulate matter (PM), which not only pollutes the environment but also seriously threatens the health of construction workers [3,10,16]. Therefore, curbing the emission of asphalt fumes is of great significance to human health and environmental protection.

Warm-mix asphalt mixtures technology was one of the methods to reduce the volatilization of asphalt fumes [14]. It was achieved by adding a warm-mix agent to reduce the mixing temperature of asphalt by 20–40 ℃ [18,21]. Mo et al. [13] investigated the effect of temperature on asphalt fumes production and found that the concentration of asphalt fumes will decrease by 3–7 times when the asphalt mixing temperature dropped from 160 ℃ to 140 ℃. Rubio et al. [19] compared the emissions of hot mix asphalt and warm mix asphalt mixtures in production and found that warm mix technology can effectively reduce harmful fumes by 58%. However, warm mixing technology has adverse effects on the high-temperature performance and bonding performance of asphalt mixtures [39]. In addition, the warm-mix asphalt mixture technology cannot eliminate harmful substances in asphalt, making it possible for harmful substances to evaporate during the service process of asphalt mixture pavement.

Asphalt fumes suppressant, as a novel additive, can effectively reduce the volatilization of harmful fumes from asphalt. Some of existing fume suppressants as well as their dosages and inhibition effects were shown in Table 1 [36]. Currently, most asphalt fumes suppressants are inorganic porous materials, which reduce the harmful fumes volatilization of asphalt through physical adsorption [12,42]. Cui et al. [5] evaluated the inhibitory effect of activated carbon on VOCs in asphalt, and the results showed that 5% activated carbon can reduce the fumes of asphalt by 33%. Sharma and Lee [22] prepared a nanocomposite of Ca(OH)$_2$-zeolite for reducing fumes emissions and found that the nanocomposite can effectively reduce the emissions of VOCs and PM during asphalt mixture production. Yu et al. [41] noted that carbon nanotubes can suppress 65% of asphalt fumes volatilization. Mousavi et al. [15] studied the adsorption mechanism of biochar on the VOCs in asphalt, and the results indicated that biochar can selectively adsorb VOCs released from asphalt. However, the limited adsorption capacity of inorganic adsorbents restricts their inhibitory effect on asphalt fumes. In addition, inorganic adsorbents have poor compatibility with asphalt, are prone to sedimentation, and would reduce the cracking resistance of asphalt at low temperature.

Reactive fumes suppressant diminished the production of asphalt fumes by reacting with toxic substances in asphalt to generate non-volatile or non-toxic derivatives. Cao et al. [1] found that high-octanol can react with sulfur-containing substances in rubber asphalt, thereby reducing the generation of hydrogen sulfide of rubber asphalt. However, there are few reports on the use of reactive fumes suppressant to reduce the fumes of asphalt, and its fume reduction mechanism is still unknown. 9,10-dihydro-9-oxa-10-phosphorophenanthrene-10-oxide (DOPO) is an H-phosphonate compound that can be converted into tautomerism containing P-OH at high temperatures [24,27]. Therefore, the phosphorus atoms in DOPO can react with nucleophilic and electrophilic reagents [26,28,33]. The harmful volatiles in the asphalt were mostly unsaturated alkanes, aromatic hydrocarbons, and sulfides, which are prone to electrophilic reagent reactions. Therefore, DOPO has the potential of reacting with harmful substances in asphalt to generate non-volatile or non-toxic derivatives.

In this study, DOPO was used as a reactive fumes suppressant to reduce the fumes emission of asphalt. The effect of DOPO on the volatilization behavior of asphalt fumes was explored by thermogravimetric analysis (TGA) and H_2S and VOCs gas detector. Thermal desorption gas chromatography mass spectrometry (TD-GC-MS) was used to determine the composition of asphalt fumes., and the inhibition mechanism of asphalt fumes by DOPO was discussed by the compositional changes before and after the modification of asphalt. The chemical reaction mechanism between DOPO and asphalt was revealed through nuclear magnetic resonance (NMR), Fourier transform infrared spectrometer (FTIR).

2. Methodology

2.1. Materials

The primary properties of Pen 60/80 asphalt, which was created by Shandong Haiyun Asphalt Co., Ltd, China, were listed in Table 2. 9,10-dihydro-9-oxa-10-phosphorophenanthrene-10-oxide (purity 98%) was bought from Aladin Biochemical Technology Co., Ltd, China.

2.2. Preparation of DOPO-Asphalt

DOPO modified asphalt (DOPO-Asphalt) was prepared by the melt blending method. The three necked flasks were filled with 200 g asphalt at 180 °C. DOPO with different dosages (virgin asphalt, 0.2 wt%, 0.6 wt% and 1.0 wt% of asphalt) was added and mixed at 180 °C for 1 h, 1000 rpm to obtain DOPO-Asphalt.

2.3. Release behavior analysis of DOPO-Asphalt fumes

2.3.1. Fume content of DOPO-Asphalt

In this study, the mass loss of asphalt was used to evaluate the fume content of DOPO-Asphalt of asphalt. TGA (NETZSCH, STA449F3, Germany) was used to analyze the mass loss of asphalt and 1.0 wt% DOPO-Asphalt form 120 ℃ to 200 ℃. For control asphalt and DOPO-Asphalt, an alumina crucible was filled with a sample with 5 mg. The mass change was observed in two stages. The sample was heated from 30 °C to

Table1
Some of existing fume suppressants as well as their dosages and inhibition effects.

Fume suppressant	Dosages (wt%)	Inhibitory effect (%)
MoO$_3$	3.0	50.0
Sasobit	3.0	50.0
Ca(OH)$_2$	5.0	33.0
Ca(OH)$_2$-zeolite	6.0	93.0
Geopolymer	6.0	66.7
Activated carbon	5.0	33.5
CNTs	3.0	65.0
OMMT	5.0	53.0
LDHs	4.0	60.0
Tourmaline	17.0	58.9

Table 2
Primary properties of the asphalt.

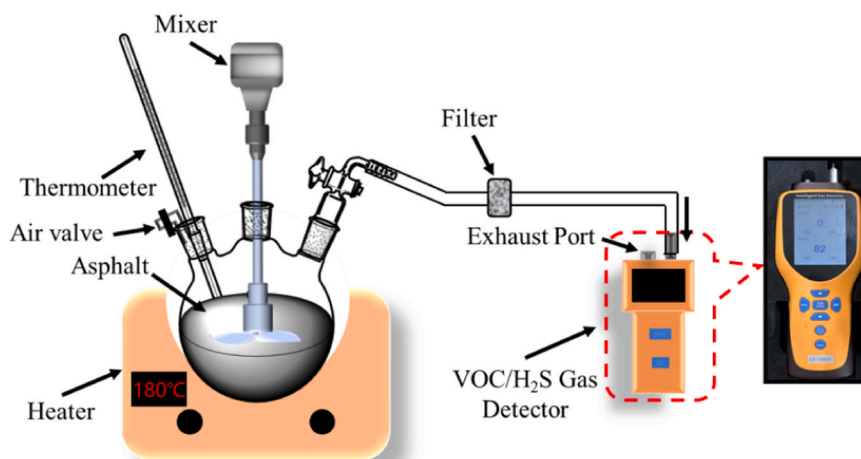| Physical properties		Test value
Penetration (25 °C, 0.1 mm)		74
Softening point (℃)		48.5
Ductility (10 °C, cm)		26.3
Viscosity (60 °C, Pa·s)		331
Flash point (℃)		274
Solubility (%)		99.9
Wax content (%)		2.0
After thin film oven test (163 ℃, 5 h)	Mass loss (%)	-0.3
	Penetration ratio (%)	74.3
	Ductility (15 °C, cm)	18

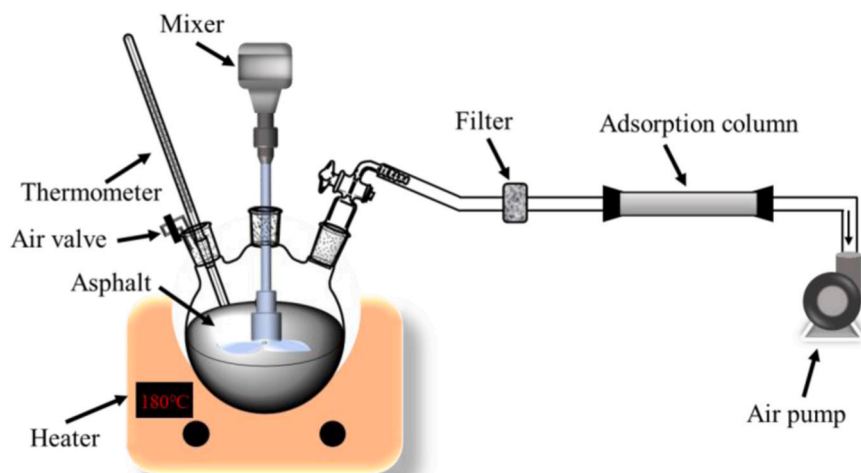**Fig. 1.** Fume-generation and detection device for asphalt.

Fig. 2. Asphalt fume generation and collection system.

120 °C at a rate of 10 °C/min in stage one. The sample was heated at a rate of 5 °C/min between 120 °C and 200 °C in stage two. Due to the small mass loss of asphalt from 30 ℃ − 120 ℃, only the mass loss of asphalt from 120 ℃ − 200 ℃ was analyzed in the research. To avoid any potential oxidation processes during temperature rise, pure N_2 was used at a flow rate of 20 ml/min.

2.3.2. H_2S and VOCs content in fumes of DOPO-Asphalt

In this study, the H_2S and VOCs content in the asphalt fumes were measured. The setup for H_2S and VOC was created as depicted in Fig. 1. The H_2S and VOC emission characteristics of the asphalt were monitored during the heating process using a pump-suction H_2S and VOC detector (JA908-TVOC, China) with a photoionization detector sensor. 200 g of the asphalt sample was placed in a flask and the volatilization of H_2S and VOCs was measured every 10 min during heating at 180 ℃ for 1 h. During the test, after the instrument displayed the stabilized value, it was recorded three times at 3 s intervals and the average of the three values was taken. Four samples (virgin asphalt, 0.2 wt% DOPO-Asphalt, 0.6 wt% DOPO-Asphalt, 1.0 wt% DOPO-Asphalt) were tested. Thus, the effects of DOPO dosages on the content of H_2S and VOCs in asphalt fumes were investigated.

2.3.3. VOCs composition analysis in DOPO-Asphalt

The content of VOCs composition in control asphalt and 1.0 wt% DOPO-Asphalt was investigated. The collection device of fumes was presented in Fig. 2. The method was as follows: 1) the asphalt sample was placed in a sealed three-necked flask and heated to 180 °C. 2) the valve of the three necked flask was opened and a sampling pump was used to collect fumes at a pumping rate of 500 ml/min for a total of 10 s 3) the valve of the three-necked flask was opened and the fumes was collected by a sampling pump at a pumping rate of 500 ml/min. 4) the adsorption column, which had completed the collection of fumes, was placed in a GC-MS (Agilent, 7890B −5977B, USA) equipment for compositional analysis of the collected fumes.

Thermal desorption gas chromatography mass spectrometry (TD-GC-MS) worked as follows: 1) The fume adsorbed in the adsorption column was frozen and captured at an ultra-low temperature of − 150 °C using high-purity N_2 as a carrier at a flow rate of 60 ml/min, with a capture time of 5 min 2) The captured gas was rapidly warmed up to 120 °C to dissociate the fume, with a dissociation time of 5 min 3) The fume was dissociated by gas chromatography mass spectrometry (GC-MS). The composition and content of different substances in the dissociated gas were analyzed. The temperature programmed for GC-MS was set to 72 °C and held for 4 min. The temperature was then increased to 280 °C for 2 min at a rate of 8.0 °C/min. The model of the capillary adsorption
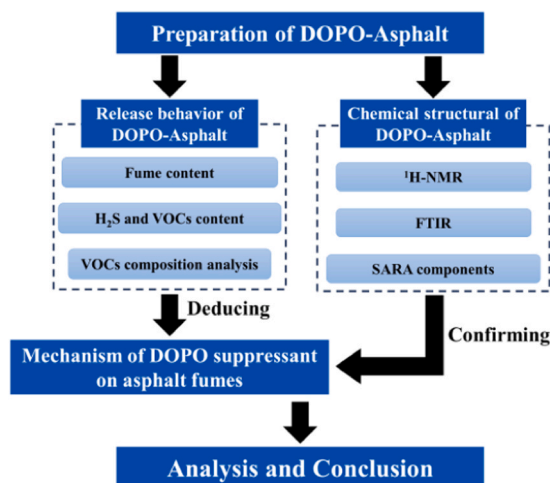
Fig. 3. Research process chart.

column used in this study was Agilent 222–5532LTM capillary adsorption column.

2.4. Chemical structural characterization of DOPO-Asphalt

2.4.1. ^1H NMR

^{1}H NMR (A Bruker AVANCE III HD, Switzerland) was handled to identify the hydrogen atoms in control asphalt, DOPO and 1.0 wt% DOPO-Asphalt. The solvent was deuterated chloroform (CDCl$_3$), and 6 mg of asphalt was dissolved in 6 ml of solvent and allowed to dissolve entirely.

2.4.2. FTIR

The chemical composition of DOPO was examined using FTIR (Nexus, Thermo Nicolet Corporation, America). Before the test, the samples must be dry. The material was then combined with potassium bromide and compacted into slices. The spectrum analysis was applied in the 400–4000 cm^{-1} range with a spectral resolution of 4 cm^{-1}.

FTIR was also used to examine the chemical structure of control asphalt and 1.0 wt% DOPO-Asphalt. In carbon bisulfide, control asphalt and DOPO-Asphalt were dissolved (the consistency of control asphalt and DOPO-Asphalt was 4 wt%). Then, place it on the potassium bromide tablet and expose it to a mercury lamp for two minutes to completely volatilize the carbon bisulfide. The scanning rate was 64/min, the spectral resolution was 4 cm^{-1}, and the measurement range was 400–4000 cm^{-1}.

2.4.3. Asphalt chemical components measurement

Chemical composition of asphalt referred to the components of saturates (S), aromatics (A), resins (R), and asphaltenes (A), known as the SARA components. In this research, the SARA components of control asphalt and DOPO-Asphalt were measured according to ASTM D4124–2001. The method was as follows: 1) dissolve 1 g ± 0.1 g of asphalt with n-heptane, and the insoluble substance separated is asphaltene. 2) place the filtrate separated in a glass chromatographic column containing 50 g activated alumina. The saturated fraction, aromatic fraction, and resin were eluted and separated with n-heptane, toluene, and a 1:1 mixture of saturated toluene and ethanol, respectively. 3) remove the eluent by distillation to obtain the corresponding components. 4) test each sample 2 times and take the average value.

2.5. Flowchart for testing with arrangement

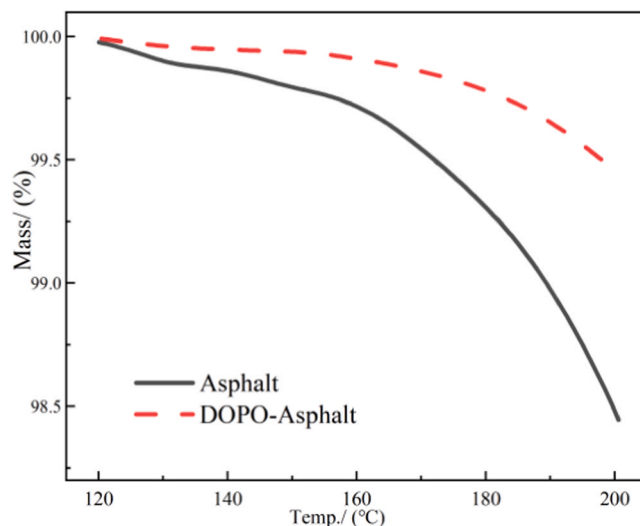The process chart of this experiment arrangement was depicted Fig. 3.

Fig. 4. Thermogravimetry curves of control asphalts and 1.0 wt% DOPO-Asphalt.

3. Result and discussion

3.1. Release behavior of asphalt fumes in DOPO-Asphalt

3.1.1. Fume content of DOPO-Asphalt

Fig. 4 presented the thermogravimetric (TG) curves of control asphalt and DOPO-Asphalt. According to Fig. 4, the mass loss of DOPO-Asphalt from 120 °C to 200 °C was significantly lower than that of control asphalt. When the temperature rose from 120 °C to 160 °C, the mass loss of control asphalt was 0.53%, while the mass loss of DOPO-Asphalt was only 0.12%. As the temperature increased, the mass loss of the control asphalt significantly rose. When the heating temperature reached 160 °C, the mass loss of control asphalt significantly increased. When the temperature reached 200 °C, the mass loss of control asphalt reached 1.61%, while the mass loss of DOPO-Asphalt was only 0.51%, which meant that DOPO reduced the fumes of asphalt from 120 °C to 200 °C.

3.1.2. H$_2$S content in the fumes of DOPO-Asphalt

Fig. 5 presented the H$_2$S content of in the fumes of DOPO-Asphalt with different dosages DOPO. From Fig. 5, it can be noted that the H$_2$S content in fumes of asphalt gradually cut down with the increase of
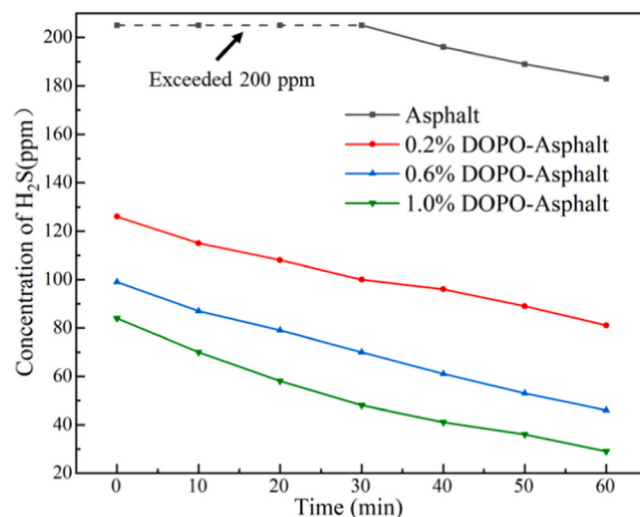
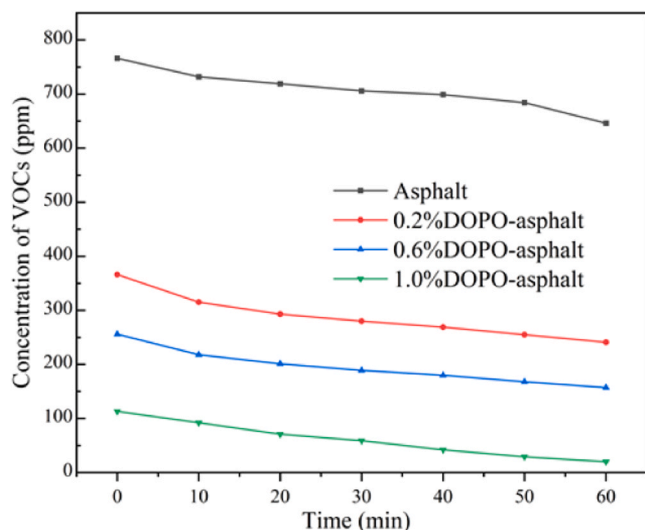**Fig. 5.** Volatile content of H$_2$S in the fumes of DOPO-Asphalts at 180 °C.

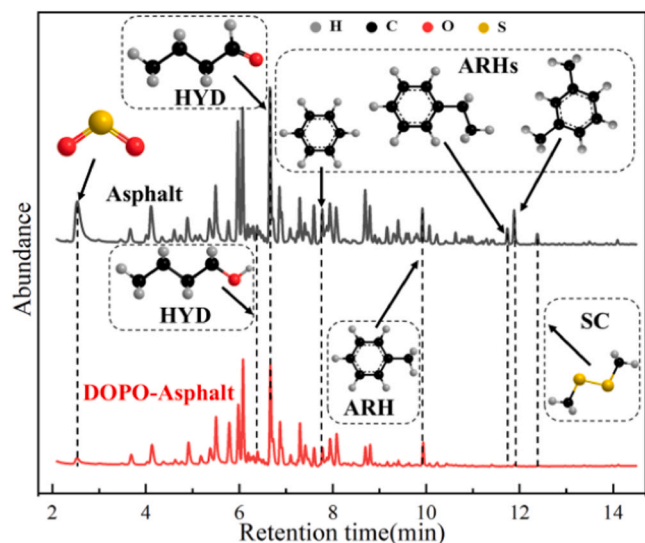**Fig. 6.** VOCs content in the fumes of DOPO-Asphalts at 180 ℃.

Fig. 7. GC-MS chromatograms of control asphalt and 1.0 wt% DOPO-Asphalt.

the dosage of DOPO at 180 ℃. When heated from indoor temperature to 180 ℃, the H_2S content in the control asphalt fumes exceeded the range of the detector (maximum 200 ppm), while the addition of DOPO significantly reduced the H_2S content in the asphalt. When the dosage of DOPO was 1.0 wt%, the H_2S content of DOPO-Asphalt was only 84 ppm. As the heating time increases, the H_2S content in the asphalt fumes gradually decreases. The H_2S content of the control asphalt exceeded 200 ppm for the first 30 min at 180 ℃ but decreased to 183 ppm by 60 min. The H_2S content of DOPO-Asphalt decreased with time, and the H_2S content of DOPO-Asphalt with higher DOPO content decreased more significantly. The H_2S content of 0.2 wt% DOPO-Asphalt heated at 180 ℃ for 60 min is 81 ppm, while the H_2S content of 1.0% DOPO-Asphalt heated at 180 ℃ for 60 min is only 29 ppm, which indicated that DOPO can significantly inhibit the production of H_2S in asphalt.

3.1.3. VOCs content in fumes of DOPO-Asphalt

VOCs content in the fumes of DOPO-Asphalt was shown in Fig. 6. In Fig. 6, when the temperature of asphalt was heated from indoor temperature to 180 ℃, the VOCs content of control asphalt reached 766 ppm. When DOPO was added, the VOCs content of DOPO-Asphalt significantly decreased at 180 ℃, and the decrease in VOCs content

Table 3
The particular components of fumes.

Chemical class	Retention time (min)	Analyte	Asphalt	DOPO-Asphalt
ALHs	3.677	2-methyl-Butane	√	√
	4.122	Pentane	√	√
	4.744	Propanal	√	-
	4.024	Ehyl-Cyclopropane	√	-
	4.367	(E)- 2-Pentene	√	√
	4.620	1,2-dimethyl-Cyclopropane	√	√
	5.499	2-methyl-Pentane	√	√
	5.782	3-methyl-Pentane	√	√
	6.074	n-Hexane	√	√
	6.254	(E)− 3-Hexene	√	√
	6.301	2,3-dimethyl-2-Butene	√	√
	6.563	1,2,3-trimethyl-Cyclopropane	√	-
	6.572	3-methyl-2-Pentene	-	√
	7.250	1-methyl-Cyclopentene	√	√
	7.407	2-methyl-Hexane	√	√
	7.595	3-methyl-Hexane	√	√
	7.875	2,2-dimethyl-Hexane	√	-
	8.076	Heptane	√	√
	8.232	(1-methyl ethylidene)-Cyclobutane	√	√
	8.695	methyl-Cyclohexane	√	√
	8.795	Pentanal	√	√
	8.902	ethyl-Cyclopentane	√	√
	8.993	3-methylene-Heptane	√	-
	9.164	4-methyl-1-Heptene,	√	-
	9.167	2,3,4-trimethyl-Pentane	√	-
	9.306	2,3,3-trimethyl-Pentane	√	-
	9.403	2-methyl-Heptane	√	√
	9.571	3-methyl-Heptane	√	-
	9.757	2,2,4-trimethyl-Hexane	-	√
	9.801	1,3-dimethyl-Cyclohexane	√	-
	10.069	Octane	√	√
	10.229	5-methyl-2-Heptene	√	√
	10.361	1,3-dimethyl-Cyclohexane	√	-
	10.630	2,6-dimethyl-Heptane	√	√
	10.916	ethyl-Cyclohexane	√	-
	10.983	1,1,3-trimethyl-Cyclohexane	√	-
	11.296	2-methyl-Octane	√	-
	13.611	1,3-Cyclopentadiene	√	√
HYDs	4.753	Cyclopropyl methyl carbinol	√	√
	4.900	Acetone	√	√
	5.166	Isopropyl Alcohol	√	√
	6.186	Methacrolein	√	-
	6.383	1-Propanol	√	√
	6.664	Butanal	√	√
	6.870	2-Butanone	√	√
	7.094	2-Butanol	√	√
	7.937	3-methyl-Butanal	√	-
	8.439	Butanol	√	-
	8.683	2-Pentanone	√	-
	8.987	2-methyl-2-Pentenal	√	√
	10.824	Hexanal	√	-
ARHs	7.775	Benzene	√	√
	9.928	Toluene	√	√
	11.738	Ethylbenzene	√	√
	11.886	1,3-dimethyl-Benzene	√	-
	12.381	p-Xylene	√	-
	13.378	propyl-Benzene	√	-
	13.493	1-ethyl-3-methyl-Benzene	√	-
	14.094	1,2,4-trimethyl-Benzene	√	√
SCs	2.512	Sulfur dioxide	√	√
	5.060	Carbon disulfide	√	-
	9.624	Dimethyl disulfide	√	-
	11.399	Methyl ethyl disulfide	√	-
	12.962	Diethyl disulfide	√	√
	13.956	Dimethyl trisulfide	√	-

Note: "√" demonstrated existence of the substance, and "-" demonstrated absence of the substance.
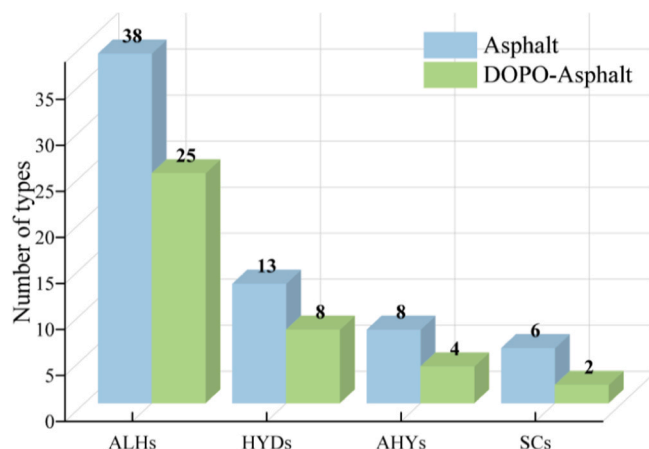
Fig. 8. The number of various substances in asphalt fumes.

became more pronounced with the increase of DOPO content. When the DOPO dosage is 0.2 wt%, the VOCs content of DOPO-Asphalt is 366 ppm, while when the DOPO dosage is 1.0 wt%, the content of DOPO-Asphalt decreases to 157 ppm. As time increased, the VOCs content in DOPO-Asphalt was significantly lower than in control asphalt. When the asphalt was heated at 180 °C for 60 min, the VOCs content of control asphalt was 646 ppm, while the VOCs content of 1.0 wt% DOPO-Asphalt was only 20 ppm. These results indicated that DOPO can also inhibit the production of VOCs in asphalt.

3.2. VOCs composition analysis of DOPO-Asphalt

GC-MS chromatograms of control asphalt and 1.0 wt% DOPO-Asphalt at 180 °C was depicted Fig. 7. The position of the peak correlated to an organic substance, as well as the rise in the number of peaks demonstrated a rise in the number of indicative VOCs in asphalt. The intensity of the peak represented the substance content, and the higher the peak intensity, the more ions were detected and the more intense the signal. The addition of DOPO significantly reduced the content of aliphatic hydrocarbons (ALHs), aromatic hydrocarbons (ARHs), hydrocarbon derivatives (HYDs), and sulphide compounds (SCs) in DOPO-Asphalt, as shown in Fig. 7.

The particular components of fumes were shown in Table 3, and Fig. 8 illustrated the quantity of various substances in fumes of control asphalt and 1.0 wt% DOPO-Asphalt. From Table 2 and Fig. 8, it can be seen that the number of peaks decreased with the addition of DOPO. Compared with control asphalt, the peak number of 1.0 wt% DOPO-Asphalt decreased by 40.0% from 65 to 39, and the peaks number of SCs had the largest reduction, from 6 to 2, a reduction of 66.7%. The peak number of AHYs was reduced from 8 to 4, a reduction of 50.0%, the peak number of HYDs decreased by 38.4%, from 13 to 8 and the peak number of ALHs decreased from 38 to 25, a reduction of 34.2%.

3.2.1. ALHs content in VOCs of DOPO-Asphalt

Harmful substances in ALHs mainly included unsaturated hydrocarbons and cycloalkanes (UHCs), which were generated by free radicals generated by unstable molecules in asphalt at high temperatures [6,8, 17,29], as shown in Formulas (1) and (2).
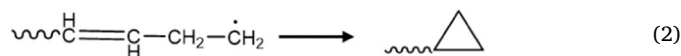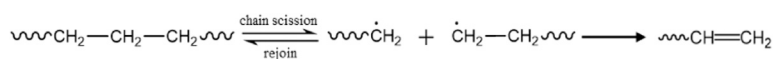
Fig. 9 displayed the content of UHCs in fumes of control asphalt and DOPO-Asphalt. In Fig. 9, the content of UHCs in fumes of DOPO-Asphalt was significantly lower than that of control asphalt. Compared with the fumes content of control asphalt, the pentene content in fumes of DOPO-Asphalt decreased from 22.64 ppm to 3.10 ppm, the heptane content decreased from 19.89 ppm to 2.21 ppm, the butene content decreased from 14.92 ppm to 1.86 ppm, and the cyclopropane content decreased from 32.51 ppm to 5.03 ppm, and the cyclohexane content decreased from 32.51 ppm to 5.03 ppm. These results may be attributed to the formation of stable DOPO derivatives through electrophilic addition of DOPO and UHCs in asphalt, as shown in Eqs. (3) and (4). In addition, that DOPO can capture radicals generated by asphalt at high temperatures during the modification process, reducing the generation of UHCs, as shown in Formulas (5).
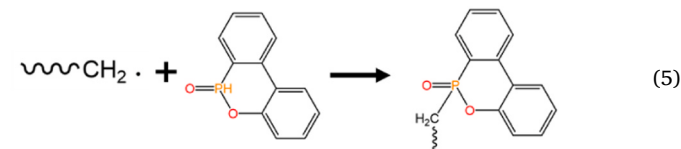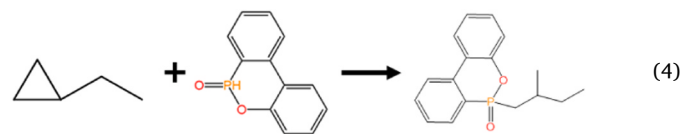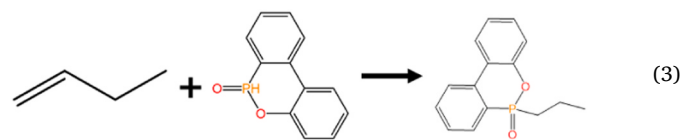
### 3.2.2. HYDs content in VOCs of DOPO-Asphalt

Asphalt was prone to generating free radicals at high temperatures, which react with oxygen to generate HYDs. The content of HYDs in VOCs of control asphalts and DOPO-Asphalt was shown in Fig. 10. As can be seen in Fig. 10, the content of HYDs in VOCs of DOPO-Asphalt declined dramatically. Compared with the control asphalt, the acetone content in VOCs of DOPO-Asphalt decreased from 31.52 ppm to 3.95 ppm, the methacrolein content decreased from 10.94 ppm to 1.38 ppm, the 1-propanol content decreased from 9.79 ppm to 0.94 ppm, the butanal content decreased from 62.96 ppm to 5.90 ppm, the 2-butanone content decreased from 21.65 ppm to 1.86 ppm, the 2-pentanone content decreased from 8.19 ppm to 0.76 ppm, and the hexanal content decreased from 19.13 ppm to 2.17 ppm. These results may be due to the nucleophilic addition reaction of DOPO and its tautomer with HYDs to produce DOPO derivatives [9,20] and the free radical reaction of DOPO with asphalt, as shown in Formula (6)-(8).

(7)

(8)
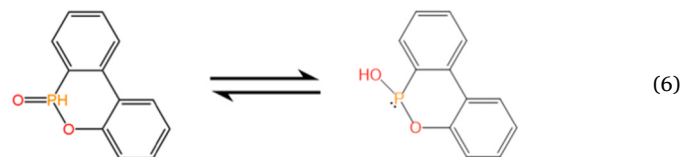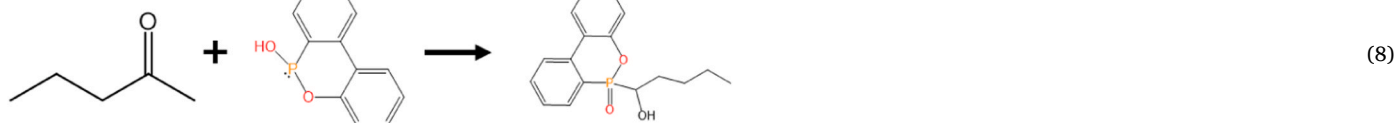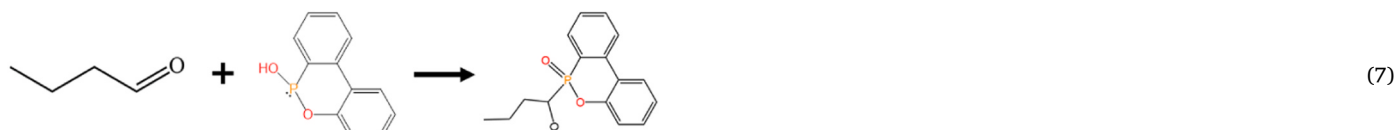
3.2.3. AHYs and SCs content in fumes of DOPO-Asphalt

AHYs and SCs in asphalt fumes were usually formed by the decomposition of polycyclic aromatic hydrocarbons and sulfides in asphalt at high temperatures [11,31,35]. Their decomposition reactions are as follows:

(9)

(10)

(11)
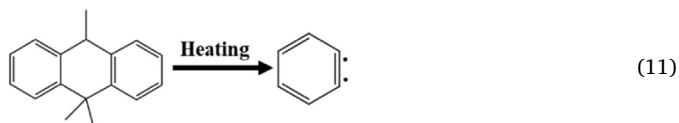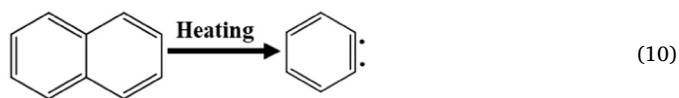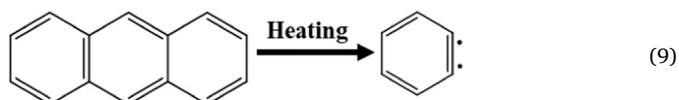
As shown in formulas (9)–(11), polycyclic aromatic hydrocarbons in asphalt would be decomposed into benzene radicals at high temperatures and finally converted into benzene, toluene and other volatile AHYs.

to the electrophilic substitution reaction between DOPO and aromatics and sulfides in asphalt, which prevents the generation of volatile aromatics and sulfides, thus reducing AHYs and SCs in fumes, as shown in Formula (14)-(15).

(14)

(15)
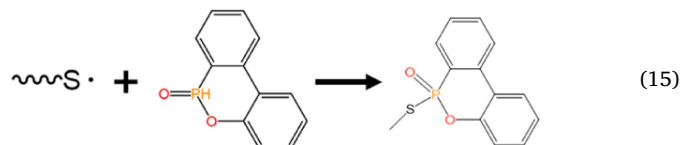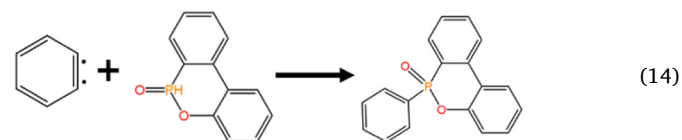
3.3. Effect of DOPO on chemical structure and components of asphalt

3.3.1. ^1H NMR

The chemical shifts of ^1H NMR of control asphalt, 1.0 wt% DOPO-Asphalt, and DOPO were shown in Fig. 12. As illustrated in Fig. 12, the peak b ($\delta = 2.0 -4.0$ ppm) was assigned to H protons located at the α carbon on the aromatic ring in asphalt. The peak c ($\delta = 1.0–2.0$ ppm)

(12)

(13)
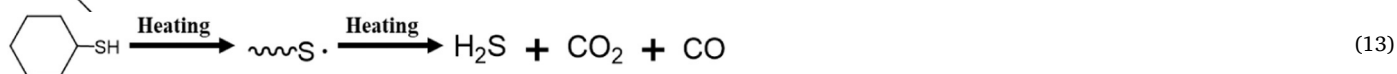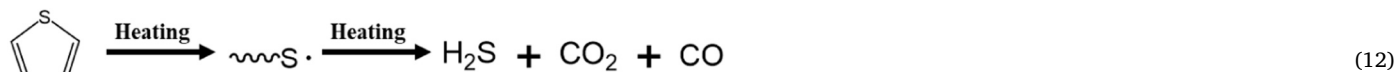
As shown in formulas (12) and (13), sulfides in asphalt will decompose into sulfur radicals at high temperatures. Under further heating, sulfur radicals will decompose into hydrogen sulfide and sulfur dioxide (Cao et al., 2021).

The content of AHYs and SCs in fumes of control asphalts and DOPO-Asphalt was presented in Fig. 11. From Fig. 11, the content of AHYs and SCs in fumes of asphalt significantly fall with adding of DOPO. Compared with the control asphalt, the benzene content in fumes of DOPO-Asphalt decreased from 30.98 ppm to 3.46 ppm, the toluene content decreased from 17.75 ppm to 1.83 ppm, the ethylbenzene content decreased from 7.50 ppm to 0.31 ppm, the 1,2,4-trimethyl-Benzene content decreased from 6.50 ppm to 0.22 ppm, the sulfur dioxide content decreased from 32.36 ppm to 2.28 ppm, and the diethyl disulfide content decreased from 6.50 ppm to 0.20 ppm. These results may be due

was assigned to the H proton located at the β carbon on the aromatic ring as well as the peak d ($\delta = 0.5–1.0$ ppm) was assigned to the H proton located at the γ carbon on the aromatic ring in asphalt. The peak a ($\delta = 7.0 -8.0$ ppm) was assigned to H protons located at the biphenyl ring in asphalt and DOPO. The peak e ($\delta = 8.7$ ppm) was assigned to H protons located at the P in DOPO [30,32]. Table 3 presented the different hydrogen atom content of control asphalt, DOPO-Asphalt and DOPO. From Table 3, it can be seen that the content of H_{ar} in DOPO-Asphalt had significantly increased from 3.8% to 7.5%, which was due to the presence of a large amount of H_{ar} in DOPO, resulting in an increase in H_{ar} in DOPO-Asphalt. Moreover, the H_α content in DOPO-Asphalt was significantly higher, which may be attributed to the reaction of DOPO with the asphalt, resulting in a decrease in the unsaturated functional groups in the asphalt and an increase in the
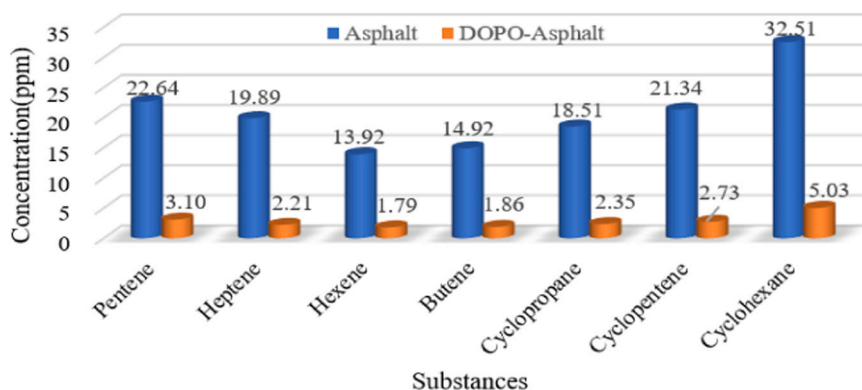
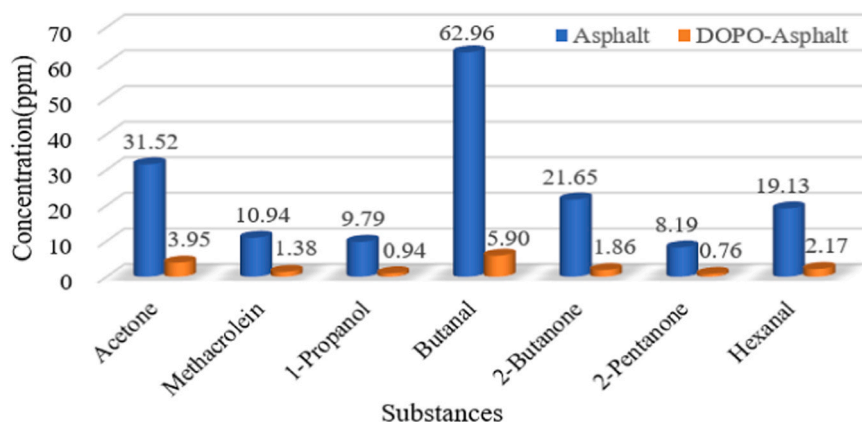**Fig. 9.** UHCs content in fumes of control asphalt and 1.0 wt% DOPO-Asphalt.

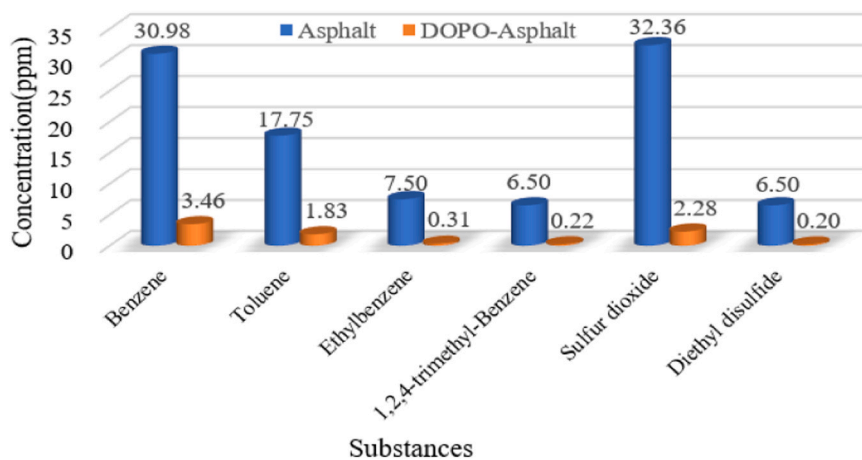**Fig. 10.** HYDs content in fumes of control asphalt and 1.0 wt% DOPO-Asphalt.

Fig. 11. AHYs and SCs content in fumes of control asphalt and 1.0 wt% DOPO-Asphalt.

saturation of the asphalt. In addition, there are almost no P-H bonds in DOPO-Asphalt, which was due to the occurrence of P-H bonds in DOPO reacting with substance in asphalt. Table 4.

3.3.2. FTIR

The FTIR spectra of DOPO, control asphalt and 1.0 wt% DOPO-Asphalt were displayed in Fig. 13. In the spectrums of control asphalts and DOPO-Asphalt, characteristic peaks appeared at 750 cm^{-1}, 812 cm^{-1}, and 865 cm^{-1}, belonged to the absorption peaks of benzene series compounds in asphalt. In addition, the absorption peaks at 1374

and 1453 cm^{-1} belonged to the bending vibration of -CH$_2$- and asymmetric bending vibration of -CH$_3$. Compared to the spectrum of control asphalt, the range characteristic peaks of DOPO-Asphalt at 1200 cm^{-1} and 1057 cm^{-1} became wider and the absorption intensity increased, which may be attributed to the stretching vibration peaks of P $=$ O and P-O in DOPO, respectively. The absorbing peak at 2385 cm^{-1} in the spectra of DOPO belonged to the stretching vibration peaks of the P-H bond [7], which was not noted in the spectra of DOPO-Asphalt, which was because of the chemical reaction between P-H bond in DOPO and the chemical bond in asphalt. In addition, it was noteworthy that the
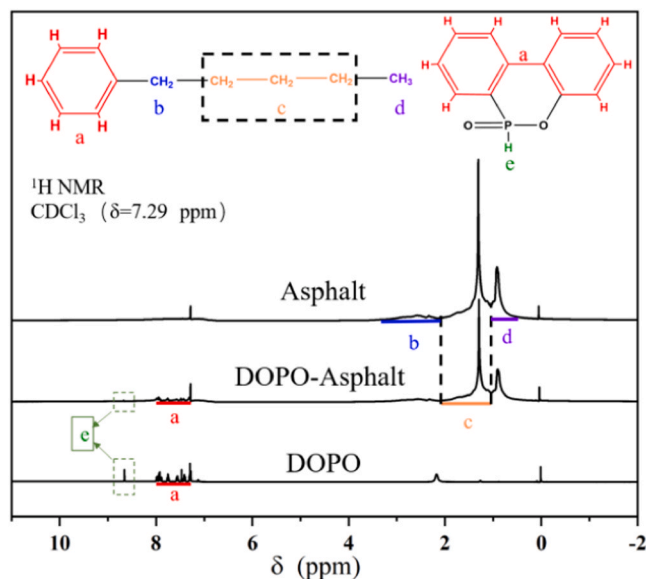
Fig. 12. ¹H NMR spectra of control asphalt, 1.0 wt% DOPO-Asphalt and DOPO.

Table 4
Different hydrogen atom content of control asphalt, DOPO-Asphalt and DOPO.

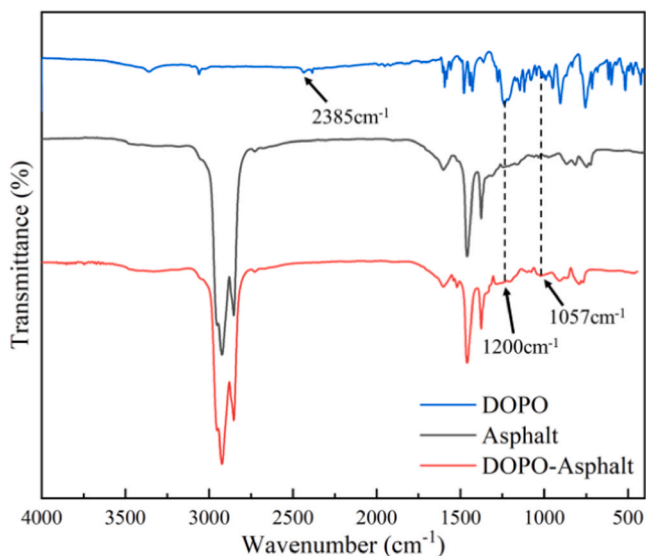|	H_α	H_β	H_γ	H_{ar}	H_P
Control asphalt	0.133	0.536	0.293	0.038	0
DOPO-Asphalt	0.207	0.478	0.239	0.075	0.001
DOPO	-	-	-	0.538	0.083

Fig. 13. FTIR spectra of DOPO, control asphalts and 1.0 wt% DOPO-Asphalt.

absorption peaks at 1310 cm⁻¹, 1030 cm⁻¹ and 966 cm⁻¹, belonging to the C=O, O-S-O stretching absorption peaks and C=C absorption peaks, respectively, in the spectrum of DOPO-Asphalt were significantly weaker than those of control asphalt. These results also may be attributed to the reaction of DOPO with C=C, S-O and C=O in asphalt, resulting in a decrease in the content of these functional groups.
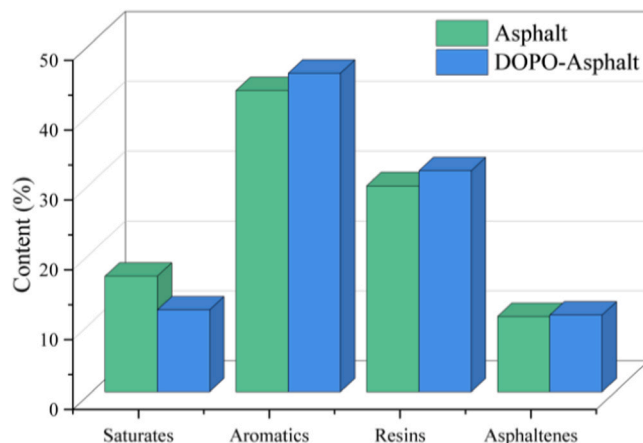

Fig. 14. SARA components of control asphalt and 1.0 wt% DOPO-Asphalt.

3.3.3. Effect of DOPO on SARA components of asphalt

The effect of DOPO on the SASR composition of asphalt was shown in Fig. 14. In the Fig. 14, compared with control asphalt, the content of saturation of DOPO-Asphalt decreased from 16.56% to 11.73%, a decrease of 4.83%, while the content of aromatic increased from 43.14% to 45.62%, and the content of resin rose from 29.51% to 31.66%, an increase of 2.48% and 2.15%, respectively. The content of asphaltene remained almost unchanged. These results implied that DOPO reacted with highly active saturates in asphalt, converting them into stable aromatics and resins, thereby reducing the volatilization of harmful substances in asphalt.

4. Conclusion

In this study, DOPO as a reactive fume suppressant was used to reduce the fumes emission of asphalt. The inhibitory effect of DOPO on asphalt fumes and its influence on the structure and composition of asphalt have been investigated. The following conclusions would be drawn based on the results.

1) TG analysis showed that the mass loss of 1.0 wt% DOPO-Asphalt from 120 ℃ to 200 ℃ was reduced from 1.5% to 0.4% compared to control asphalt. This indicated that DOPO can significantly reduce the mass loss of asphalt during the process of heating from 120–200 ℃, and had a good inhibitory effect on asphalt fumes.

2) DOPO can significantly reduce the content of VOCs and H_2S in fumes of asphalt, and with the increase of DOPO content, the concentration of H_2S and VOCs in asphalt fumes significantly decreased. When the dosage of DOPO was 1.0 wt%, the H_2S and VOCs concentrations in fume of DOPO-Asphalt reduced by 84.2% and 96.9%, respectively, compared to control asphalt at 180 ℃.

3) TD-GC-MS analysis showed that DOPO can significantly reduce the content of ALHs, HYDs, AHYs, and SCs in asphalt fumes. At 180 ℃, compared with control asphalt, the content of UHCs in fumes of 1.0 wt% DOPO-Asphalt decreased by 86.8%, the content of HYDs decreased by 89.7%, and the content of AHYs and SCs decreased by 90.7% and 93.5%, respectively.

4) According to ¹H NMR and FTIR analysis, the P-H bond almost disappeared in DOPO-Asphalt, while the content of S-O bond, C=C bond, and C=O bond significantly decreased, and the content of aromatic carbon and carbon decreased, indicating the presence of reactions between DOPO and ALHs, HYDs, AHYs, and SCs in asphalt through electrophilic reaction and nuclear reaction, respectively, reducing the generation of asphalt fumes. Furthermore, the results of asphalt component analysis confirmed that the addition of DOPO can cause saturate to transform into aromatic and resins.

5) Considering the efficiency of fume suppression and cost of DOPO on asphalt, the optimal dosage of DOPO in asphalt was 1.0 wt%.

CRediT authorship contribution statement

Shangheng Zeng: Writing – original draft, Writing – review & editing. **Sanpeng Mao, Yanheng He**: Investigation, Methodology. **Shi Xu, Jianying Yu**: Data curation, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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