Physicochemical Characteristics of Particulate Matter Emitted from the Oxygenated Fuel/Diesel Blend Engine

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ABSTRACT

The physicochemical characteristics of particulate matter (PM) produced by polyoxymethylene dimethyl ethers (PODE₂₋₄)/diesel blended fuel at different blend ratios was characterized using transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). TEM analysis indicated that the overall size of PM decreased with an increasing PODE₂₋₄ concentration. TEM images using fractal theory showed that the fractal dimension of PM increased as the PODE₂₋₄ blending ratio increased. These trends increased the oxidation activity. FTIR was used to analyze the aliphatic C-H on the surface of PM and found that the ratio $I_{C-H}/I_{C=C}$ and the aliphatic C-H functional group on the surface of PM decreased with an increasing PODE₂₋₄ blending ratio. According to XPS data, with increments of the PODE₂₋₄ blending ratio, the contents of O/C, sp^3/sp^2 , C-OH, C=O and total oxygen-containing functional groups of the PM increased, demonstrating that the oxygen-containing functional group and disorder of the PM nanostructure was correlated with a faster oxidation rate. Results thus demonstrated that the addition of PODE₂₋₄ can affect the nanostructure and oxidation activity of PM, making it easier to oxidize to reduce environmental pollution.

Keywords: Particulate matter, Physicochemical characteristics, Transmission electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy

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1 INTRODUCTION

The particulate matter (PM) emitted by diesel engines is one of the primary factors that lead to hazy weather, which can cause serious environmental pollution and harm human health (Rouleau *et al.*, 2013; Shi *et al.*, 2019; Xian *et al.*, 2019; Yan *et al.*, 2021). Most PM consists of fine particles, and fine particles (especially PM_{2.5}) can pose a serious threat to health. Many epidemiological studies have shown that long-term exposure to PM_{2.5} can increase the risk of respiratory and cardiovascular diseases (Chen *et al.*, 2015; Di *et al.*, 2017; Li *et al.*, 2017; Yitshak-Sade *et al.*, 2017). Therefore, the PM emitted from diesel engines has always been an important research topic.

To reduce environmental pollution and harm to public health caused by diesel engines, oxygenated fuel has become a prospective solution because it can improve the combustion condition of engines and decrease PM emissions (Awad *et al.*, 2018; Nayyar *et al.*, 2019). As a new type of renewable oxygen-containing fuel, polyoxymethylene dimethyl ethers (PODE_n) is actually a low molecular weight acetal-based polymer that is synthesized by dimethyl ether, methanol and paraformaldehyde as raw materials (Ren *et al.*, 2019). PODE_n has a high cetane number and excellent ignition performance, which can reduce engine noise and yield gentle operation. PODE_n is a liquid fuel under standard conditions, which is simpler than dimethyl ether storage. In addition, due to the absence of C-C bonds and high oxygen content in the PODE_n molecule, the engine achieves

fine combustion performance and reduces harmful PM emissions (Liu *et al.*, 2015; Yang *et al.*, 2016). As an additive to diesel, PODE_n has excellent application prospects (Wang *et al.*, 2018).

TEM can be used to observe the nanomorphology of diesel exhaust particles. Li and Wang (2018) produced photos of diesel and five different biodiesel particles, and discovered that the primary carbon particles were primarily spherical, and the arrangement of biodiesel PM was relatively compact, while the arrangement of diesel particles was relatively loose. Qu *et al.* (2016) viewed the nanostructure of biodiesel exhaust particles in gutter oil and suggested that PM was distributed in a chain shape. With the increase of biodiesel blending proportion, the primary particles became more compact, and the average diameter of the PM decreased. Zhu *et al.* (2016) reported an image of biodiesel-pentanol blended fuel and showed that the diameter of primary particles decreased with increasing pentanol proportion in a blended fuel.

FTIR can be applied to study the composition of functional groups on the surface of diesel particles. Omidvarborna *et al.* (2016) compared the surface functional groups of soybean methyl ester, tallow oil, waste cooking oil and diesel emission particles, and results showed that aliphatic C-H functional groups were an important part of the surface functional groups of biodiesel particles. Salamanca *et al.* (2012) studied the surface functional groups of palm oil biodiesel particles with different blending ratios and found that the blending ratio of biodiesel increased and the content of aliphatic functional groups on the surface of PM decreased. The authors believed that the increase in oxygen content made the oxidation of PM easier, which led to a lower content of aliphatic functional groups. Wang *et al.* (2019) investigated the surface functional groups of diesel particles under different loads and found that with increasing engine load, the relative content of aliphatic C-H functional groups of diesel particles decreased, while the engine speed had no significant effect on C-H functional groups.

XPS is the most commonly used technique for PM surface analysis (Atzei *et al.*, 2014; Guascito *et al.*, 2015). XPS can determine the composition of the elements in a sample by determining electron binding energy and can be used to analyze the functional group distribution of the elements and the degree of carbon atom hybridization. Savic *et al.* (2016) analyzed the microstructure of microalgae B50 and B5 particles and discovered that there were three elements on the surface of exhaust PM, oxygen, carbon and silicon. As the proportion of biodiesel increased in a blended fuel, the oxygen content of the fuel surface increased, and the arrangement of PM became more disordered. Lapuerta *et al.* (2019) studied the functional groups on the surface of butanol mixed fuel particles and found that with the increase of butanol content in the fuel, the oxygen-containing functional groups on the surface of exhaust PM increased.

Few studies have investigated the PM emissions of diesel engines fueled with PODE_n/diesel blends. In this paper, TEM, FTIR, XPS experiments and fractal theory were used to study the variation regularity of organic functional groups, the hybridization ratio of carbon and nanostructures on the surface of diesel particles fueled with different blending ratios of PODE_n/diesel blended fuel; volume ratios of 0/100, 10/90, 20/80, which are referred to as P0, P10 and P20. TEM experiments and fractal theory primarily investigated the particle size to describe the effect of the PODE_n blending ratio on the oxidation reactivity of blended fuel particles. FTIR and XPS experiments primarily focused on the surface functional group content of PM. The results of the XPS experiment on the surface oxygen-containing functional groups of PM supported the conclusion that the content of C-H aliphatic functional groups on the surface of PM decreased in the FTIR experiment. In contrast, results also verified the accuracy of the XPS test conclusion. The purpose of those experiments was to study the oxidation activity of blended fuel exhaust particulates under different blending proportions, and to explore the difficulty of regeneration of the particulate filter.

2 METHODS

2.1 PM Sampling Procedure and Preparation

The engine used in this experiment was the single-cylinder four-stroke R180 diesel engine produced by the Changchai Company. The primary parameters of the engine are shown in Table 1. The fuel oxygenating additive used in this paper was PODE₂₋₄, which was made by blending PODE₂, PODE₃ and PODE₄ according to mass distributions of 2.55%, 88.9% and 8.48%, with diesel as the base fuel. Sampling was performed under 5% and 100% working conditions at 1800 r min⁻¹.

Table 1. Main specifications of diesel engine.

Model	Changchai R180
Number of cylinders	Single-cylinder
Rated power (kW)	5.67 (2600 r min ⁻¹)
Rated torque (N·m)	23.4 (1800 r min ⁻¹)
Bore × Stroke (mm × mm)	80 × 80
Displacement volume (mL)	402
Compression ratio	21:1
Injection pressure (MPa)	13.72 ± 0.5

Samples were collected in the exhaust pipe 1.2 m away from the engine exhaust manifold using the metal-filter direct sampling method. In the experiment, the multilayer metal wire mesh was placed in the exhaust pipe, and the diesel exhaust particles were filtered by the metal filter, achieving a similar effect to that of DPF, thus obtaining PM samples similar to those of DPF. Diesel blends' exhaust particles were collected at different concentrations in sample bottles and then sealed. Before each test, the engine was preheated for 20 minutes.

For PM preparation, ultrasonic vibration and centrifugal separation were used. First, the collected diesel exhaust particles were put into ethanol solution and subjected to ultrasonic vibration for 30 minutes to ensure complete dissolution. Then, the mixed solution was transferred directly into the centrifuge tube and centrifuged at 4000 r min⁻¹ for 1 hour. Under the action of centrifugal force, the solid-liquid was stratified, and the separated precipitates were clean PM without a soluble organic fraction (SOF). To completely remove the SOF from the PM surface, ultrasonic vibration and centrifugal separation were repeated three times. Finally, the prepared particles were sealed and stored away from light.

2.2 Experimental Apparatus and Procedure

2.2.1 Transmission electron microscopy

The TEM method was performed with a Tecnai G² 20 field-emission transmission electron microscope produced by FEI Company in the United States to analyze the nanostructure characteristics of PM. Its point resolution was 0.24 nm, a LaB₆ filament was used, the accelerating voltage was 200 kV, and the maximum magnification was 1.03 million times. TEM was used to analyze the prepared samples, and a nanostructure diagram of diesel exhaust particles was obtained.

2.2.2 Fractal dimension

The complex and irregular microstructure of PM had self-similar fractal characteristics. PM's nanostructure was analyzed using fractal dimensions, and the specific number can indicate the density of PM.

Brasil *et al.* (1999) calculated the fractal dimension D_f of diesel engine exhaust PM using Eq. (1):

$$N = k_g \left(\frac{2R_g}{D_p} \right)^{D_f} \quad (1)$$

Taking the logarithm of both sides of Eq. (1) yields:

$$\lg N = D_f \lg(2R_g/D_p) + \lg k_g \quad (2)$$

where N is the number of primary carbon particles; D_p is the diameter of primary carbon particles; and k_g is the pre-exponential factor. For the PM radius of gyration R_g , the following equation can be used

$$R_g = \sqrt{\frac{1}{N} \sum_{i=1}^N r_i^2} \quad (3)$$

where r_i is the distance from the i th primary carbon particle center to the PM centroid.

When Eq. (3) was used to calculate the PM radius of gyration R_g , it was difficult to measure the PM centroid accurately due to stacking and overlapping among the primary carbon particles; thus, it was not realistic to directly measure the PM radius of gyration. Therefore, Brasil *et al.* (1999) discovered that electron microscope images of PM could be analyzed using indirect estimation of the PM radius of gyration. The relationship between the PM radius of gyration and the maximum projected length L is shown in Eq. (4):

$$L/(2R_g) = 1.50 \pm 0.05 \quad (4)$$

The number of primary carbon particles N was also indirectly estimated from the TEM image of PM, and its relationship with the projected area of primary carbon particles A_p and the projected area of particles A_a is shown in Eq. (5):

$$N = k_a \left(\frac{A_a}{A_p} \right)^\alpha \quad (5)$$

Using Image-Pro Plus 6.0 software, the particle projected area A_a and the primary carbon particle diameter D_p can be directly obtained. The projected area A_p of primary carbon particles can be obtained using the equation, where k_a refers to the pre-exponential factor of the projected area, and α refers to the empirical index of the projected area. Based on the results reported by Köylü *et al.* (1995), k_a and α were set equal to 1.16 and 1.10, respectively, and their standard deviations were 0.01 and 0.002, respectively.

2.2.3 Fourier transform infrared spectroscopy

FTIR was performed using a Nicolet 6700 advanced Fourier transform infrared spectroscope that was produced by Thermo Fisher Scientific Company of the United States to analyze the chemical composition of substances of interest. The acquisition resolution was 1 cm^{-1} , the number of scans was 32, and the spectral range was $4000\text{--}400 \text{ cm}^{-1}$. Before analyzing the data, OMNIC software was used for automatic baseline correction and spectral smoothing.

To study the surface functional groups of diesel emission particles, FTIR technology was used to detect and analyze the hydrocarbon functional groups of different fuel PM.

2.2.4 X-ray photoelectron spectroscopy

XPS was performed using a ESCALAB 250Xi multifunctional high-performance X-ray photoelectron spectroscope that was produced by Thermo Fisher Scientific Company of the United States to analyze the elements, functional group distribution and the degree of carbon atom hybridization on the sample surface. The charge effect correction used C1s (284.60 eV). The number of energy steps of PM full spectrum scanning was 1371, the number of scans was 1, the energy step size was 1.000 eV, and the pass energy was 100.0 eV. When conducting fine spectral scanning of carbon elements, the energy step size was 0.100 eV, the pass energy was 30.0 eV, the number of scans was 5 times, the sample analysis area was $0.7 \times 0.3 \text{ mm}^2$, the working voltage was 15 kV, and the power was 400 W.

In this XPS experiment, the elemental composition on the surface of PM, the sp^3/sp^2 hybridization ratio of carbon atoms, and the C-OH and C=O functional groups were analyzed. The C-OH, C=O functional groups and the hybridization information of carbon atoms on the surface were determined by splitting and resolving the C1s peak in the XPS full-spectrum scanning image.

3 RESULTS AND DISCUSSION

3.1 Nanomorphology of PM Samples

Fig. 1 shows that some regions of exhaust PM are darker in color, which is caused by the stacking of several primary carbon particles, thus blurring the outline of a single primary carbon particle. According to the TEM images and the PM density, and the PM in the exhaust gas of P0

Fig. 1. TEM images of PM samples: (a) P0, (b) P10, (c) P20 at low load and (d) P0, (e) P10, (f) P20 at high load (magnification of 50,000 $\times$).

is the loosest. As the blending ratio of PODE₂₋₄ increases, PM becomes smaller and more compactly arranged in terms of overall size. The quantities of branched chains and primary carbon particles also decrease significantly, and the chain length decreases gradually. PODE₂₋₄ is a type of oxygenated fuel that can encourage complete fuel combustion, reducing PM generation. Less PM will lower the probability of collision between primary carbon particles, thus reducing the number of PM required to form a chain shape, which is difficult to combine into large-size PM (Gao *et al.*, 2019). Smaller PM is known to be more easily oxidized, which is conducive to DPF regeneration.

3.2 Fractal Dimension Fitting and Parameter Analysis

Image-Pro Plus 6.0 software is used to manually define each primary carbon particle in the TEM image to determine the primary carbon particle diameter D_p , the maximum projected length L of particles, the projected area A_p of primary carbon particles and the particles projected area A_o , as shown in Fig. 2.

Using the equations above, N and R_g of the PM can be obtained; thus, the $\lg N$ - $\lg (2R_g/D_p)$ coordinate diagram can be drawn, as shown in Fig. 3. Using Origin Software for multipoint fitting, a straight line can be obtained. The particle fractal dimension D_f can be represented by the slope

Fig. 2. Schematic of parameter acquisition.

Fig. 3. Fitting straight line graphs of PM sample fractal dimensions: (a) P0, P10, P20 at low load and (b) P0, P10, P20 at high load.

Table 2. Fractal dimension of PM samples.

	PM	P0	P10	P20
D_f	Low load	1.66	1.71	1.79
	High load	1.58	1.64	1.72

of the straight line, and the pre-exponential factor k_g can be represented by the intercept of the straight line.

Figs. 3(a) and 3(b) show the fitting straight line graphs of the exhaust PM fractal dimension of P0, P10 and P20 under low and high loads, respectively. The fractal dimension varies from 1.58 to 1.79, and the specific values are shown in Table 2. Comparison with the data in Table 2 shows that the fractal dimension of PM under high and low loads increases with an increasing PODE₂₋₄ blending ratio. At low load, the fractal dimension of PM emitted from P10 and P20 increases by 0.05 and 0.08 compared with P0, and at high load, the fractal dimension of PM emitted from P10 and P20 increases by 0.06 and 0.08 compared with P0. The fractal dimension can describe the density of PM: the larger the fractal dimension is, the higher the overlapping rate and the closer the arrangement is. This result may occur because PODE₂₋₄ is a type of oxygenated fuel, and with more PODE₂₋₄, the oxygen content of the blended fuel increases, making the fuel burn more completely. Smaller PM will be oxidized, and the amount of PM will decrease. As a result, the probability of collision and combination between primary particles decreases, and it is not easy to connect, merge or agglomerate particles; thus, it is difficult to form a larger PM.

3.3 Results of the FTIR Analysis

Fig. 4 shows the FTIR spectra of the P0, P10 and P20 exhaust PM samples under high and low loads. Generally, the asymmetric methylene peak near 2920 cm^{-1} in the infrared spectrum is attributed to C-H binding, and the aromatic ring peak near 1645 cm^{-1} is attributed to C=C binding. The relative content of aliphatic C-H functional groups is determined by two characteristic peak equivalent peak-height ratios ($I_{\text{C-H}}/I_{\text{C=C}}$) (Santamaría *et al.*, 2010; Cadrusco *et al.*, 2019).

The influence of fuel with different blending ratios on the surface C-H functional groups of exhaust PM is shown in Fig. 5. The ratio of $I_{\text{C-H}}/I_{\text{C=C}}$ of PODE₂₋₄/diesel blends is within the range of 0.13–0.27 at low load and 0.07–0.18 at high load. As the proportion of PODE₂₋₄ additives increases, the ratio of $I_{\text{C-H}}/I_{\text{C=C}}$ decreases, and the aliphatic C-H functional groups on the surface of PM decrease. These results may occur because with increased PODE₂₋₄ concentration, the oxygen content will increase accordingly. More oxygen will make PM oxidize more completely and reduce the content of C-H aliphatic functional groups (Fayad *et al.*, 2020).

3.4 Results of the XPS Analysis

3.4.1 Oxygen-to-carbon elemental ratio

Using survey scans, XPS can obtain the composition and content information of the surface

Fig. 4. FTIR spectrum of P0 exhaust particles under high load.

Fig. 5. $I_{C-H}/I_{C=C}$ ratio of PM samples surface.

elements of PM. The major ingredients of PODE₂₋₄/diesel fuel exhaust PM with different blending proportions collected in this paper are carbon, followed by oxygen, as shown in Fig. 6.

Fig. 7 shows that the O/C ratio of the PODE₂₋₄/diesel blends is 0.246–0.308 at low load and 0.126–0.136 at high load. The O/C ratio increases as the PODE₂₋₄ blending proportion increases, which may be caused by the higher oxygen content of the additive itself.

3.4.2 Different forms of hybrid carbon

The composition information of carbon atoms can be obtained by narrow scans of C. XPS Peak 4.1 software was used to fit the carbon spectrum and Gauss-Lorentz peak fitting method (Mustafi *et al.*, 2010) was used to fit the carbon spectrum into four small peaks, sp^2 , sp^3 , hydroxyl (C-OH) and carbonyl (C=O) groups. The corresponding binding energies are near 284.8 eV, 285.4 eV, 286.6 eV and 288.8 eV, as shown in Fig. 8, which shows that diesel exhaust particles primarily exist in the form of sp^2 and sp^3 hybrids, of which sp^2 is the dominant form. An increase in sp^2 content means a strong order degree of PM, while an increase in sp^3 content means a strong disorder degree of PM. Therefore, with an increase in the sp^3/sp^2 ratio, the disorder degree of PM will also increase (Vander Wal *et al.*, 2010), and the higher the degree of carbon structural disorder is, the easier it is to oxidize.

Fig. 9 shows the variation of the hybrid ratio of the P0, P10 and P20 exhaust particles under high and low loads. Considering the variation regularity of sp^3/sp^2 ratio under low load and high load shown in Fig. 9, the sp^3/sp^2 ratio of PODE₂₋₄/diesel blended fuel exhaust PM is 0.607–0.762 and 0.368–0.678, respectively, and the sp^3/sp^2 ratio increases with increasing PODE₂₋₄ concentration.

These results likely occur because as the concentration of PODE₂₋₄ increases, the oxygen content of the blended fuel also increases, and the oxygen component can promote the oxidative decomposition of the exhaust PM, resulting in a shorter length of microcrystalline carbon, and

Fig. 6. XPS survey scans of P0 exhaust particles under high load.

Fig. 7. Variation regularity of PM samples O/C ratio.

Fig. 8. Narrow scans of P0 exhaust particles element C under high load.

enhancing the disorder of the carbon structure. Thus, the increase in the blended fuel oxygen content increases the PM sp^3/sp^2 ratio.

3.4.3 C-OH and C=O oxygen-containing functional groups

Fig. 10 shows the percentage content of oxygen-containing functional groups in the exhaust PM of blended fuel under high and low loads. Results show that the percentage content of C-OH is between 2.21% and 2.52%; the content of C=O is between 1.88% and 2.25%; and the content of total oxygen-containing functional groups is between 4.09% and 4.77% at low load. Under high

Fig. 9. Variation regularity of PM samples sp^3/sp^2 ratio.

Fig. 10. Variation regularity of PM samples oxygen-containing functional groups.

load, the percentage content of C-OH ranged from 1.55% to 1.83%; the content of C=O ranged from 1.35% to 1.73%; and the content of total oxygen-containing functional groups ranged from 2.90% to 3.56%. With increasing PODE₂₋₄ blending proportion, the percentage contents of C-OH, C=O and total oxygen-containing functional groups (C-OH and C=O) of the PM all increased.

These results likely occurred because an increase in oxygen levels can enhance the disorder of PM (Savic *et al.*, 2016). When the disordered degree of PM improves, the surface will have a shorter microcrystalline length and more irregular cross-section, which can increase the number of chemical reaction activation sites. The combination of active oxygen-containing groups and PM in the combustion process becomes easier, making the surface of exhaust PM form a stable oxygen-containing functional group. In addition, the oxygen in the fuel itself more easily participates in the oxidation reaction than the oxygen in air, which increases the number of oxygen-containing groups in the combustion process, thus improving the probability of forming oxygen-containing functional groups on the surface of PM.

4 CONCLUSIONS

- (1) TEM analysis indicated that the overall PM size decreased, and the arrangement of PM became looser with increasing PODE₂₋₄ concentration. In addition, the number of branched chains and primary particles also decreased markedly, and the chain length shortened.
- (2) Fractal theory showed that the fractal dimension was 1.58–1.79 for blended fuel's PM, and the fractal dimension of PM increased as the PODE₂₋₄ blending ratio increased.
- (3) FTIR analysis found that the ratio of $I_{C-H}/I_{C=C}$ of the blended fuel was 0.07–0.27. The ratio $I_{C-H}/I_{C=C}$ and the aliphatic C-H functional group on the surface of PM also decreased with an increasing PODE₂₋₄ blending ratio.

- (4) XPS analysis presented that the O/C ratio of the blended fuel was 0.126–0.308, the sp^3/sp^2 ratio was between 0.368–0.762, and the contents of C–OH, C=O and total oxygen-containing functional groups were 1.55%–2.52%, 1.35%–2.25% and 2.90%–4.77%, respectively. With an increasing PODE₂₋₄ blending ratio, the contents of O/C, sp^3/sp^2 , C–OH, C=O and total oxygen-containing functional groups of the PM increased.

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DISCLAIMER

The authors declare no conflict of interest.

SUPPLEMENTARY MATERIAL

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