

Thermal-oxidation mechanism of dioctyl adipate base oil

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Abstract: The ester base oil of dioctyl adipate (DOA) was oxidized in an oven at 200 °C for 30 h, and variations in the physicochemical and tribological properties were studied. To investigate the thermal-oxidation mechanism, the thermal-oxidation products were analyzed by gas chromatography–mass spectrometry (GC–MS), and the thermal-oxidation process was simulated using visual reactive force field molecular dynamics (ReaxFF MD). The results indicated that the total acid number (TAN) increased significantly because of the presence of 14% carboxylic acids and low molecular weight monoesters. The tribological properties were improved by the formation of the strongly polar carboxylic acids. Additionally, the increase in kinematic viscosity was limited due to the formation of high molecular weight polymerization products and low molecular weight degradation products. Thermal-oxidative degradation and polymerization mechanisms were proposed by combining ReaxFF MD simulations and GC–MS results.

Keywords: dioctyl adipate; GC–MS; physicochemical properties; tribological properties; ReaxFF MD

1 Introduction

Dioctyl adipate (DOA), a synthetic ester oil, is prepared by the esterification of adipic acid and 2-ethyl hexanol [1]. It has been widely used in the aerospace and automotive industries, as well as under extreme working conditions, due to its high thermal-oxidation stability, low production of carbon residue, excellent viscosity index, good thermal conductivity, and large specific heat capacity [2–4]. Currently, the overload and high speed requirements of machinery and equipment result in harsh working conditions in mechanical lubrication systems and elevated working temperatures. Although DOA has good thermal-oxidation stability, it will inevitably undergo oxidation, thereby altering its service performance, especially under conditions of sustained high temperature. However, because of its unique ester bonds, the existing scientific literature

relevant to the thermal-oxidation behavior of hydrocarbon mineral oils cannot be generalized to DOA [5–7]. Additionally, the thermal-oxidation mechanism and the relationship between the change in properties and thermal-oxidation products of DOA have not been elucidated. Therefore, it is important to identify an appropriate method to chemically characterize DOA and determine its thermal-oxidation mechanism during such processes. Methods commonly used to analyze the thermal-oxidation stability and products of synthetic ester oils include thermal analysis [8–10], chemiluminescence [11–13], spectroscopy [14–16], and chromatography–mass spectrometry [17].

Pressure differential scanning calorimetry (PDSC) is a typical thermal analysis method [18, 19] that is widely used to characterize the thermal-oxidation stability of ester oils based on the oxidative onset temperature (OOT) or oxidative induction time (OIT) index. Nadia et al. [20] studied the thermal-oxidation stability of a series of oleic acid-based triester derivatives and found that derivatives with shorter chains had

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better thermal-oxidation stability. However, the chemical components and molecular structures of the thermal-oxidation products could not be identified by PDSC.

Chemiluminescence (CL) analysis is a trace analysis method used to determine the contents of a substance according to the light emitted during a chemical reaction. Richaud et al. [21] calculated the oxidation rate constants and activation energies of three methyl esters by fitting their CL curves from 90 to 150 °C. CL can be used to evaluate the degrees of thermal-oxidation of ester oils at the macro level, but it cannot elucidate the chemical components and molecular structure information of the thermal-oxidation products.

Infrared spectroscopy is a rapid and non-destructive technique used to evaluate chemical oxidation changes based on variations in peak positions and intensities [22, 23]. Hahn et al. [24] studied the ageing behavior of trimethylolpropane esters using infrared spectroscopy. The results showed that the thermal-oxidation products contained hydroxyl and carboxyl functional groups. However, infrared spectroscopy can only characterize changes in some functional groups at the micro level. Similar to PDSC and CL, infrared spectroscopy cannot completely identify the chemical components and molecular structures of thermal-oxidation products.

Gas chromatography–mass spectrometry (GC–MS) [25] is a powerful technique used to analyze thermal-oxidation products. The various components of the thermal-oxidation products can be separated and their corresponding molecular structures identified by GC–MS. Wu et al. [26] studied the chemical components and molecular structures of oxidized diesters. Approximately eleven thermal-oxidative degradation products and their corresponding structures were obtained using this technique, which they then used to propose a thermal-oxidative degradation mechanism.

In addition, the chemical components and molecular structures detected by these methods belong to the final thermal-oxidation products. The transition states formed during the thermal-oxidation process, which are important for determining the thermal-oxidation mechanism, cannot be detected. Proposing thermal-oxidation process intermediates without knowledge of the relevant transition states is not sufficiently rigorous to elucidate the detailed thermal-oxidation mechanism. In recent years, visual reactive force field

molecular dynamics (ReaxFF MD) [27, 28] simulations, which allow for the continuous breakage and formation of bonds [29, 30], have been increasingly applied to the study of chemical mechanisms. ReaxFF MD has great potential for simulating complex reaction systems and visualizing continuous reaction processes. Thus, ReaxFF MD simulations constitute a new research method for exploring the thermal-oxidation mechanisms of ester oils.

In this work, the chemical components and their corresponding contents and structures in oxidized DOA were investigated by GC–MS. The total acid number (TAN), kinematic viscosity, and tribological properties of oxidized DOA were measured, and the relationship between the components, contents, structures, and properties was discussed. The thermal-oxidation mechanism was studied through ReaxFF MD simulations coupled with GC–MS, and could provide important supporting data for the use of DOA base oil.

2 Experimental

2.1 Materials

Commercially available DOA was used as the base oil, which was supplied by the Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China. The typical properties of DOA base oil are shown in Table 1.

2.2 Oven-accelerated thermal-oxidation test

In this test, 150 mL DOA base oil was placed into a 200 mL open glass beaker and heated in an oven at 200 °C for 30 h. The TAN and kinematic viscosity of DOA base oil and oxidized DOA were determined according to ASTM D 974 and ASTM D 445, respectively.

Table 1 Typical properties of DOA base oil.

Property	DOA	Test method
Viscosity at 40 °C (mm ² /s)	7.55	ASTM D 445-86
Viscosity at 100 °C (mm ² /s)	2.32	ASTM D 445-86
Total acid number (mgKOH/g)	0.046	ASTM D 974-97

2.3 Tribological test

The tribological properties were evaluated using a four-ball machine under the following conditions: rotating rate 1450 rev/min, test duration 30 min, load 147 N, and temperature 25 °C.

2.4 GC-MS analysis

DOA base oil and oxidized DOA were analyzed by GC-MS. The column temperature was programmed to increase from 80 °C to 150 °C (held for 5 min) at 10 °C/min, from 150 °C to 230 °C (held for 10 min) at 5 °C/min, and then from 230 °C to 280 °C (held for 20 min) at 5 °C/min. Helium was used as the carrier gas at a flow rate of 1 mL/min. The identification of compounds in DOA base oil and oxidized DOA was performed in full-scan mode (50–500 m/z) using a combination of the National Institute of Standards and Technology (NIST) mass spectral library and the GC retention times of standard compounds.

2.5 ReaxFF MD settings

The thermal-oxidation process of DOA base oil was simulated in Materials Studio software. The simulations were performed with constant N (simulation atom number), V (simulation cell volume), and T (simulation temperature), designated as NVT [31]. The simulation temperature was 900 °C and the simulation time was 200 ps [32]. A thermostat parameter with a 0.1 ps damping constant was employed to control the temperature. The equilibration time was 10 ps.

3 Results and discussion

3.1 Thermal-oxidation product analysis

Figure 1 displays the GC-MS total ion chromatograms (TICs) of DOA base oil and oxidized DOA heated at 200 °C for 30 h. As shown in Fig. 1(a), the peak at 29.73 min is identified as DOA, and the molecular structure of DOA is shown in the inset. Figure 1(b) shows the GC-MS TIC of oxidized DOA heated at 200 °C for 30 h. The strongest peak at 29.73 min corresponds to DOA. The other small peaks correspond to the thermal-oxidation products, including both degradation and polymerization products. The retention

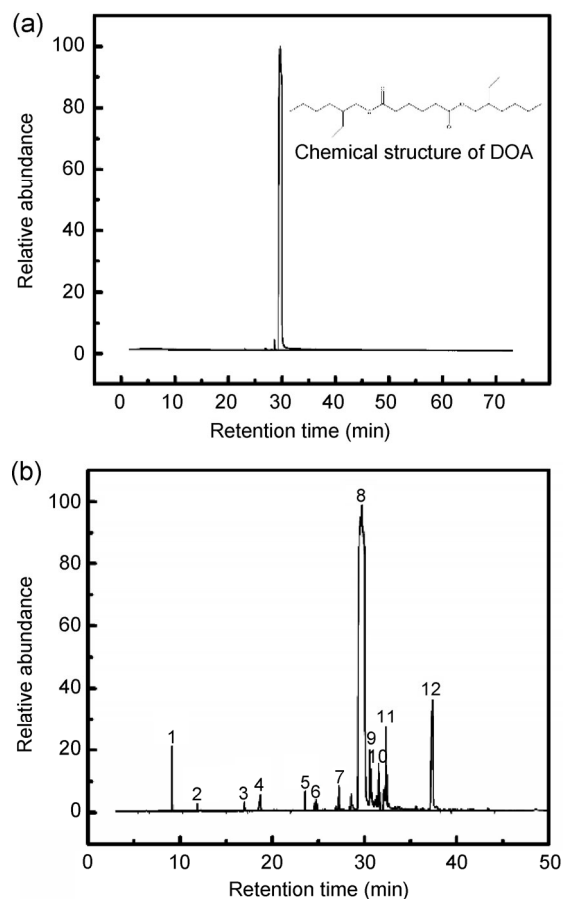


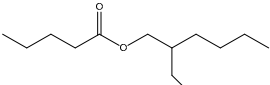
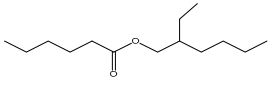
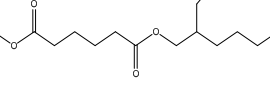
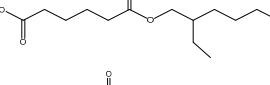
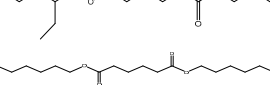
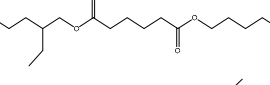
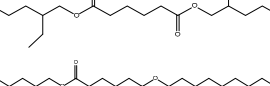
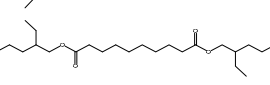
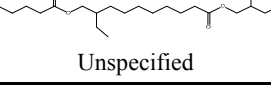
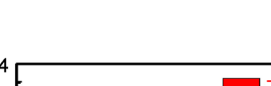

Fig. 1 GC-MS total ion chromatogram (TIC): (a) DOA base oil and (b) oxidized DOA heated at 200 °C for 30 h.

times of the thermal-oxidation products and their corresponding molecular structures are listed in Table 2, except for peak 12. The molecular weight of peak 12 is 497, which is higher than that of DOA base oil. It can be shown that peak 12 represents a thermal-oxidation polymerization product. However, because of the complex structure, the molecular structure of peak 12 product cannot be identified using the NIST mass spectral library and the GC retention times of standard compounds. Based on the relative contents, it can be seen that the thermal-oxidative degradation products mainly consist of low molecular weight carboxylic acids, monoesters, and diesters, whereas the polymerization products mainly consist of carboxylic acids and diesters.

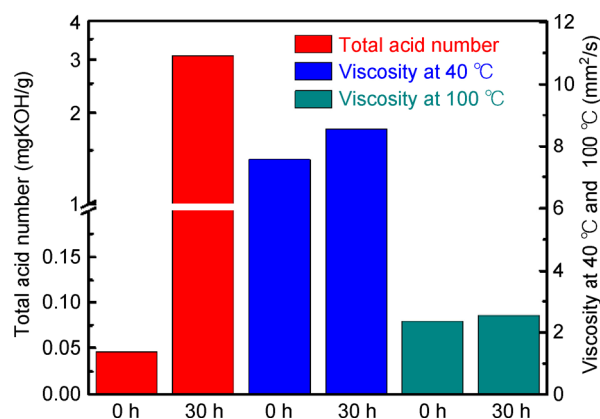
3.2 Effect of thermal-oxidation on physicochemical and tribological properties

As two of the most important factors reflecting

Table 2 The components, contents and structures of oxidized DOA identified by GC-MS.

Peak	Retention time (min)	Component name	Component structure	Molecular weight	relative content
1	9.15	Pentanoic acid, 2-ethylhexyl ester		214	8.8%
2	11.87	Hexanoic acid, 2-ethylhexyl ester		228	1.6%
3	16.98	Adipic acid, isohexyl methyl ester		244	2.8%
4	18.71	Hexanedioic acid, mono(2-ethylhexyl) ester		258	3%
5	23.55	Adipic acid, butyl 2-ethylhexyl ester		314	3.1%
6	24.80	Hexanedioic acid, diheptyl ester		342	1.6%
7	27.25	Adipic acid, 2-ethylhexyl hexyl ester		342	3.2%
8	29.73	Diethyl adipate (DOA)		370	37.1%
9	30.5	Adipic acid, decyl 2-ethylhexyl ester		398	7.6%
10	31.53	Bis(2-ethylhexyl)sebacate		426	6.4%
11	32.32	6-((2-ethyl-10-((2-ethylhexyl)oxy)-10-oxodecyl)oxy)-6-oxohexanoic acid		472	10.8%
12	37.33	Unspecified	Unspecified	497	14%

physicochemical properties, changes in TAN and kinematic viscosity directly correlate with a lubricant's thermal-oxidation degree [33]. Figure 2 shows the TAN and kinematic viscosity values of DOA base oil and oxidized DOA heated at 200 °C for 30 h. It can be seen that the TAN of DOA increases rapidly from 0.046 to 3.089 mg KOH/g after thermal-oxidation. The TAN value is determined by the type, content, and molecular weight of the acidic compounds in the thermal-oxidation products. As shown in Table 2, the 3% hexanedioic acid mono(2-ethylhexyl) ester (peak 4) and 10.8% 6-((2-ethyl-10-((2-ethylhexyl)oxy)-10-oxodecyl)oxy)-6-oxohexanoic acid (peak 11) formed during the thermal-oxidation process can significantly increase the TAN. In addition, the 8.8% low molecular weight pentanoic acid 2-ethylhexyl ester (peak 1) can also increase this parameter. Thus, the TAN increases

**Fig. 2** Total acid number and kinematic viscosity of DOA base oil and oxidized DOA heated at 200 °C for 30 h.

rapidly after thermal-oxidation.

The thermal-oxidation of DOA base oil was observed to increase the kinematic viscosity at both 40 °C and

100 °C. These increases could be attributed to the high molecular weight thermal-oxidative polymerization products (peaks 9, 10, 11, and 12 in Table 2). However, the formation of low molecular weight thermal-oxidative degradation products could cause the kinematic viscosity to decrease. Therefore, the extent to which the kinematic viscosity increases during thermal-oxidation is limited by the combined influences of polymerization and degradation products.

The tribological properties are the most important parameters of a lubricant. Figure 3 shows the friction coefficients and wear scar diameters of DOA base oil and oxidized DOA. The friction coefficient of DOA base oil is approximately 0.12, whereas that of oxidized DOA is approximately 0.08. The scar diameters of DOA base oil and oxidized DOA are 0.64 mm and 0.53 mm, respectively. This indicates that the wear-resistant property is also improved after thermal-oxidation. Figure 4 shows the contrast between a worn surface lubricated with DOA base oil and oxidized DOA. It can be observed that the wear mechanism creates grooves and that when oxidized DOA is used, the resulting wear surface is relatively smooth.

carboxylic acids (peaks 4 and 11 in Table 2) in oxidized DOA are polar and tend to migrate to metal surfaces and contribute to the stability of the adsorbed lubricant film. Thus, the tribological properties can be improved after thermal-oxidation. However, the spots in Fig. 4(b) could be corrosion spots resulting from the adsorption of carboxylic acids.

3.3 ReaxFF MD simulation and thermal-oxidation mechanism of DOA

To elucidate the mechanism of the evolution of thermal-oxidation products, the thermal-oxidation process of DOA was simulated by ReaxFF MD. Figure 5(a) shows the 3-D model of DOA and oxygen, and Fig. 5(b) shows the 3-D model of DOA and oxygen at 900 °C for 180 ps. The thermal-oxidative degradation and polymerization mechanism models were determined based on visual images of the thermal-oxidation process. Figures 6 and 7 display the thermal-oxidative degradation (Schemes 1, 2, and 3) and polymerization (Schemes 4, 5, and 6) mechanism models of DOA, respectively. The intermediate products in the mechanism models are transition states

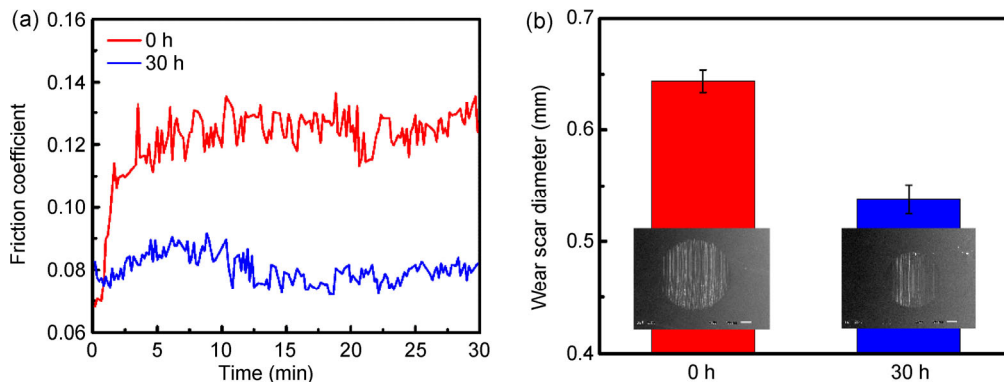


Fig. 3 (a) Friction coefficient and (b) wear scar diameters of DOA and oxidized DOA heated at 200 °C for 30 h.

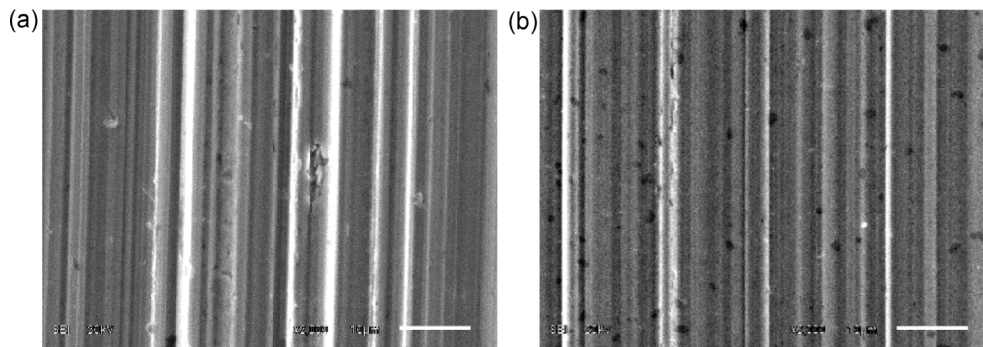


Fig. 4 SEM image of worn surface lubricated with (a) DOA base oil and (b) oxidized DOA.

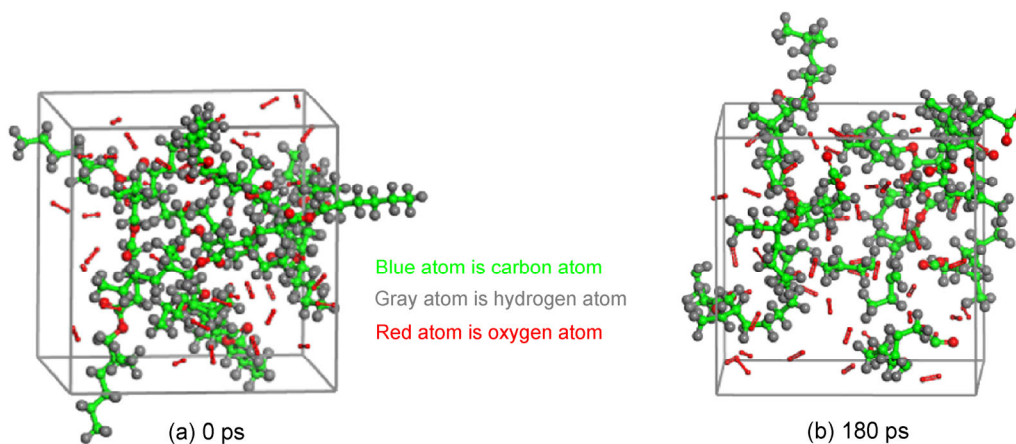


Fig. 5 The 3-D model of DOA and oxygen at 0 ps and 180 ps under 900 °C.

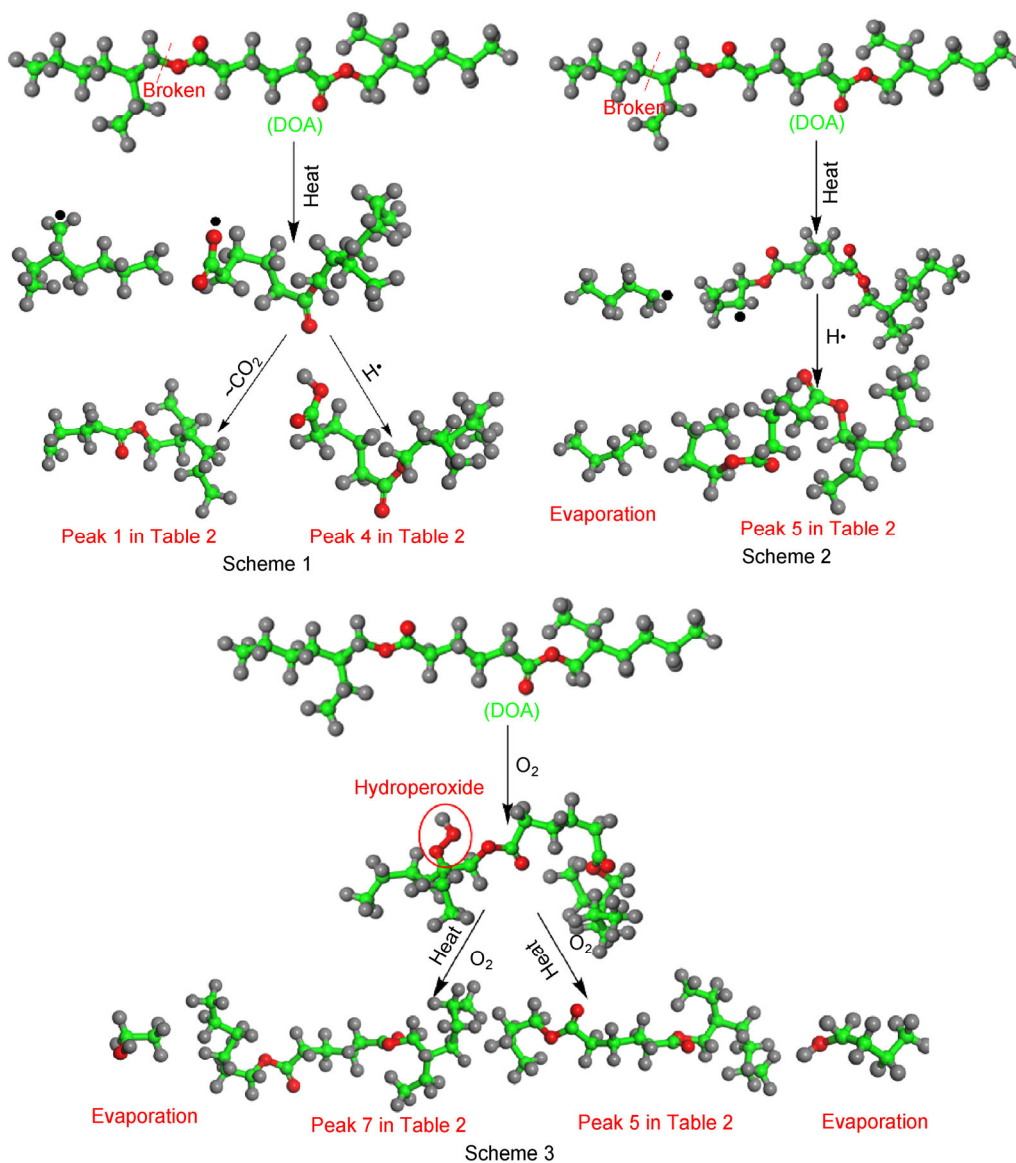


Fig. 6 The thermal-oxidative degradation mechanism models of DOA.

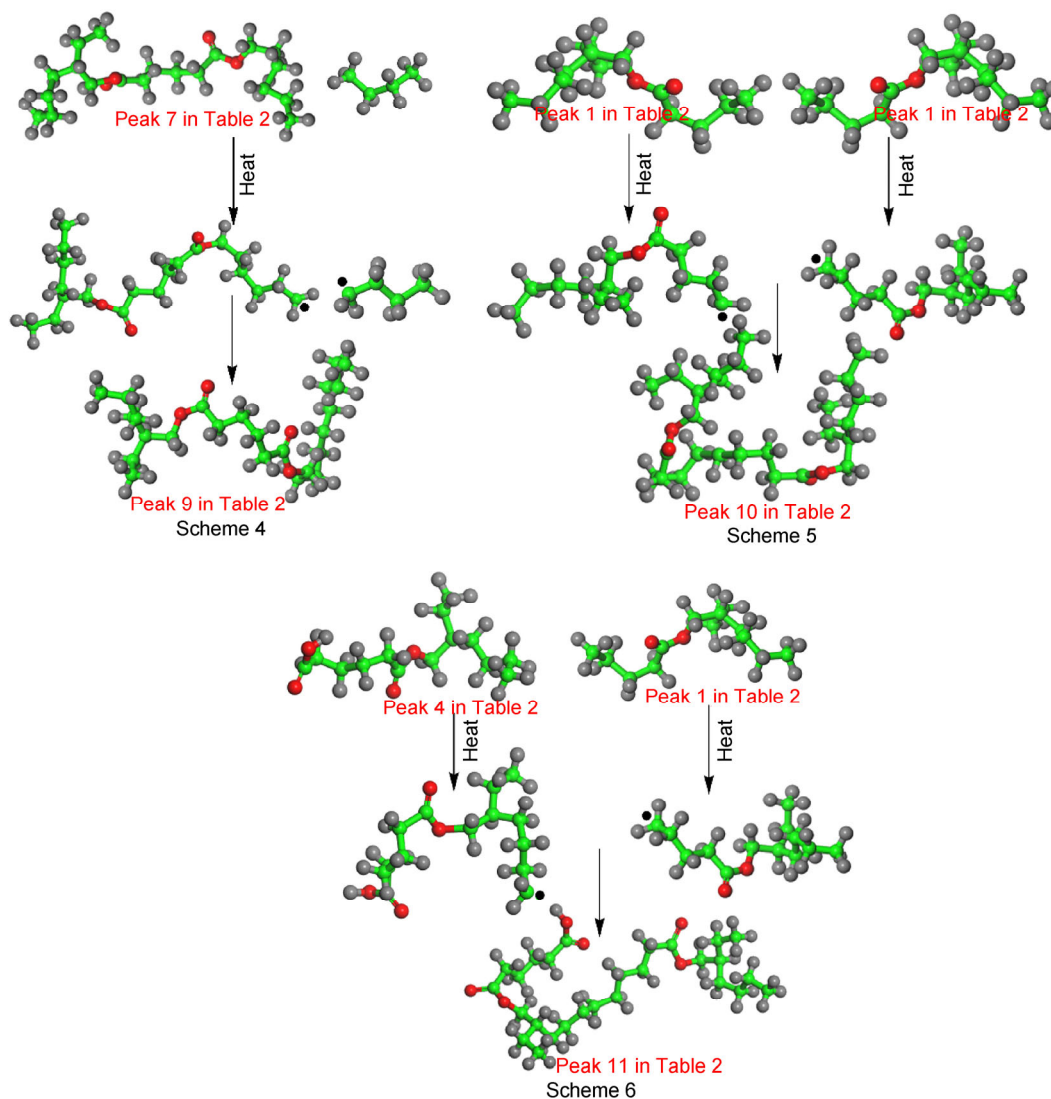


Fig. 7 The thermal-oxidative polymerization mechanism models of DOA.

generated during the thermal-oxidation simulation process.

The C–O bonds from the alcohol fragment of DOA are broken to form acyloxy radicals and alkyl free radicals at high temperatures. Acyloxy radicals can then follow two main reaction paths: absorption of a hydrogen free radical to form hexanedioic acid mono(2-ethylhexyl) ester (peak 4 in Table 2), or further oxidation to form pentanoic acid 2-ethylhexyl ester (peak 1 in Table 2) and carbon dioxide. The specific reaction is shown as Scheme 1 in Fig. 6.

Tertiary carbon atoms are active atoms that react easily. The C–C bonds of the tertiary carbon atoms can break to generate free alkyl radicals ($R\bullet$) at high

temperatures. The formed free alkyl radicals can absorb hydrogen free radicals to form adipic acid butyl 2-ethylhexyl ester (peak 5 in Table 2), and *n*-butane. The specific reaction is shown in Scheme 2 in Fig. 6.

Tertiary carbon atoms are also prone to react with oxygen to form hydroperoxides (intermediate product in Scheme 3). Then, the C–C bonds can be broken in one of two ways to generate adipic acid butyl 2-ethylhexyl ester (peak 5 in Table 2) or adipic acid 2-ethylhexyl hexyl ester (peak 7 in Table 2). The resulting small molecular hydroperoxides are further oxidized into small molecular alcohols. The specific reaction is shown in Scheme 3 in Fig. 6.

The terminal active carbons of the thermal-oxidative

degradation products lose a hydrogen atom to form free radicals ($R\bullet$). Two of these free radicals can combine to form polymerization products through electron effective collision and coupling. Scheme 4 shows the reaction of adipic acid 2-ethylhexyl hexyl ester and *n*-butane to form adipic acid decyl 2-ethylhexyl ester (peak 9 in Table 2). Similarly, two molecules of pentanoic acid (2-ethylhexyl ester) can undergo the reaction shown in Scheme 5 to form bis(2-ethylhexyl) sebacate (peak 10 in Table 2). Hexanedioic acid mono(2-ethylhexyl) ester and the pentanoic acid 2-ethylhexyl ester form 6-((2-ethyl-10-((2-ethylhexyl)oxy)-10-oxodecyl)oxy)-6-oxohexanoic acid, as shown in Scheme 6.

From the ReaxFF MD simulations, it can be seen that the thermal-oxidation of DOA began with the breakage of the C–O and C–C bonds from the alcohol fragment and tertiary carbons, respectively, allowing the tertiary carbon atoms to be attacked by oxygen to generate hydroperoxides. Then, the terminal active carbons of the thermal-oxidative degradation products lose a hydrogen atom to form free radicals ($R\bullet$), and the polymerization products are produced by the electron effective collision and coupling of the free radicals. In this work, the oven-accelerated thermal-oxidation test was performed in an open system, and as a result, the small molecules generated during the thermal-oxidation process evaporated. Therefore, small molecules could not be detected in the GC–MS analysis. Conversely, the reaction model used in the ReaxFF MD simulation was a closed system. Hence, the results of the ReaxFF MD simulations and the oven-accelerated thermal-oxidation experiment are somewhat different.

4 Conclusion

The thermal-oxidation products of DOA were analyzed by GC–MS, and the TAN, kinematic viscosity, and tribological properties of oxidized DOA were measured. The thermal-oxidation process was investigated using ReaxFF MD simulations. Based on the above results and discussion, the following conclusions can be drawn:

(1) The thermal-oxidative degradation products mainly consist of low molecular weight carboxylic

acids, monoesters, and diesters, whereas the thermal-oxidative polymerization products mainly consist of carboxylic acids and diesters.

(2) The TAN of DOA increases rapidly during the thermal-oxidation process because of the formation of carboxylic acids and low molecular weight monoesters. The polar nature of the carboxylic acids improved the tribological properties under the test conditions. The combined effects of the thermal-oxidative degradation and polymerization products resulted in a limited increase in viscosity.

(3) The thermal-oxidative degradation mechanism models indicate that the C–O bonds from the alcohol fragment and the tertiary carbon atoms are two susceptible sites at which reaction can occur. The thermal-oxidative polymerization mechanism models suggest that the thermal-oxidative polymerization products of DOA are formed by free radical reactions of the thermal-oxidative degradation products.

Acknowledgments

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