THE TGA-FTIR-GC/MS CHARACTERIZATIONS
OF PYROLYSIS OF POLYURETHANE PAINT SLAGS

by

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Hazardous paint waste from industrial production is an ever-growing concern due to its toxicity and flammability effect. Currently, pyrolysis is one of the promising technologies for paint waste disposal because of its ability to minimize and disinfect waste together with energy recovery. In this study, characterization of pyrolysis of polyurethane paint slags was conducted using TGA-FTIR-GC/MS, and the evolved products were analyzed. The effect of heating rate (10 °C per minute, 20 °C per minute, and 30 °C per minute) were assessed. The TGA results showed that two stages involved in the pyrolysis of waterborne polyurethane paint slag. The first stage was 200~325 °C, while the second stage involved the intense weight loss at 330~500 °C. In addition, the thermal pyrolysis of oily polyurethane included four stages during the pyrolysis reaction. The first three stages were 200~300 °C, 300~435 °C, and 435~640 °C, respectively, which correspond to the volatiles and the decomposition reaction of some organic matter. The fourth stage was the pyrolysis of fixed carbon at 640~790 °C. The increase of heating rate can improve the pyrolysis intensity of two polyurethane paint slags. The FTIR results showed that a large amount of CH_4, CO_2, CO, H_2O, alkanes, olefins, and aromatic compounds were emitted during the pyrolysis of the two paint slags. The GC/MS results concluded that the pyrolysis products of waterborne paint slag were mainly HC and O-compounds, and the pyrolysis products of oily paint slag also included N-compounds. This study provides a theoretical reference for the pyrolysis characteristics and product properties of polyurethane paint slags.

Key words: *waterborne polyurethane paint slag, oily polyurethane paint slag, pyrolysis characteristics, volatile substances, TG-FTIR-GC/MS*

Introduction

In recent years, with the widespread utilization of spray-painting technology in the field of painting, the demand for paint coatings in industries such as automobiles, ships, and decoration has increased, and the production of paint waste has also increased year by year [1, 2]. Paint slag has strong viscosity properties. When the ambient temperature exceeds 10 °C, the paint slag becomes viscous and not easily broken. When the ambient temperature is above 35 °C, paint slag can flow slowly and has a high viscosity [3]. In addition, the moisture

in the paint slag is wrapped in the paint film, making it difficult to evaporate. Even being left for several months, large paint blocks are not easy to harden. In the composition of paint waste, aromatic HC account for 60%, and various alcohol ethers and benzene account for more than 20% [4]. In addition, paint slag also contains various heavy metal ions, such as zinc, iron, lead, *etc.* Paint slag is highly toxic, difficult to treat, contains a large number of organic compounds, has a high calorific value, and is flammable. According to the description of *HW12 dye and coating waste* in the National Hazardous Waste List (2021 edition), except for waterborne paint which is not a hazardous solid waste, all other paints are classified as hazardous solid waste [5]. However, the treatment capacity for paint waste at home and abroad is limited.

The main types of paint include waterborne paint and oily paint. Waterborne paint uses water as a diluent, which is environmentally friendly. It does not contain a series of harmful substances such as formaldehyde, benzene, and xylene, and has a low VOC emission [6]. Waterborne coatings can reduce VOC emissions by 60~70% compared to oily coatings. Oily paint uses banana water and tena water as diluents, containing a large amount of carcinogenic substances such as benzene and xylene that are harmful to the human body. It also has a strong pungent odour [7]. In some developed countries, waterborne paint has basically replaced oily paint, with a usage rate of over 90% [8].

At present, the treatment methods for paint waste mainly include incineration, landfill, cement kiln collaborative disposal, and recycling technology [9-13]. Chang [14] investigated the temperature changes in the secondary combustion chamber during co-pyrolysis of papermaking waste and paint waste slag. The results showed that the addition of paint waste slag was very beneficial for increasing the temperature of the secondary combustion chamber. The reduction effect of pyrolysis gasification after mixing was significant, reaching over 95%. Jiang *et al.* [15] proposed a method of using paint slag to prepare cement as an alternative fuel. By utilizing the calorific value of organic matter in paint slag, a cement kiln alternative fuel with single property and stable calorific value was prepared. Zhang *et al.* [16] investigated the chemical chain gasification characteristics and kinetic behavior of paint waste using Fe_2O_3 as the O_2 carrier using a thermogravimetric analyser and a tube furnace. They found that the addition of Fe_2O_3 can increase the reduction capacity of the pyrolysis products of paint waste. Mudakavi *et al.* [17] found that the use of paint slag in the composting of Indian azalea showed no significant difference in effectiveness compared to the use of conventional nitrogen, phosphorus, and potassium fertilizers, and no significant toxic effects were found. Almeser *et al.* [18] investigated the effect of waste latex paint on concrete. The results showed that waste latex paint can improve the workability and durability of concrete, while obtaining sufficient compressive strength. Liu *et al.* [19] studied the thermal degradation behavior and evolution products of polyester paint and waste enamelled wire during the pyrolysis process. They found that the pyrolysis of polyester paint and waste polyester enamelled wire can be divided into three stages, and the pyrolysis products mainly contain long-chain HC, long-chain olefins, alcohols, phenols, ketones, aldehydes, aromatics, *etc.*

Heat treatment is a highly promising waste disposal technology due to its ability to minimize waste reduction and harmless treatment, as well as recover energy. Therefore, assessing the pyrolysis characteristics of paint slags is of great significance. Qian and Wu [9] studied the pyrolysis characteristics of paint slag in the paint spraying workshop of a manufacturing plant and found that the volatile content and calorific value of the paint slag were high. After industrial analysis, the received base low calorific value was 18.84 MJ/kg, mak-

ing it a good thermal energy resource. In the pyrolysis products, gas accounts for about 40% of the mass of paint slag, with a calorific value of about 30 MJ/m³, solids account for about 20%, with a calorific value of about 18 MJ/kg, and also produce some tar. Yu and Li [20] studied the pyrolysis characteristics and pyrolysis process of paint waste slag, and found that the mass of pyrolysis gas accounts for 38~42% of the mass of paint slag. The pyrolysis slag accounts for 18.2~21.4%, with a calorific value of 16.53~19.09 MJ/kg, which is similar to the calorific value of some bituminous coal and can be used as fuel. It also produces tar with a calorific value of 35.5~43.2 MJ/kg. Tao *et al.* [21] investigated the pyrolysis characteristics of waste mixtures composed of paint slag (40%), tar slag (35%), $CaCO_3$ (10%), CaO (5%), and paper (10%), and discussed the effect of heating rates (20 K per minute, 50 K per minute, and 80 K per minute) on pyrolysis kinetics. The results showed that as the heating rate increased, the initial weight loss temperature decreased, while the initial pyrolysis temperature, maximum pyrolysis rate temperature, and final temperature all increased.

At present, the research of paint waste disposal mainly focuses on oily paint waste, and the research of waterborne paint waste is less. Up to now, there are fewer studies on the product generation type and release characteristics during the thermal disposal of paint waste residue. Therefore in this study, specifically in order to assessed the pyrolysis characteristics of waterborne polyurethane paint slag and oily polyurethane paint slag were chosen using thermogravimetric analysis (TGA). In addition the influence of different heating rates (10 °C per minute, 20 °C per minute, and 30 °C per minute) on their weight loss characteristics were assessed analysed. The composition of the gas released from pyrolysis was analysed by combining thermogravimetric Fourier transform infrared spectroscopy gas chromatography mass spectrometry (TG-FTIR-GC/MS) technology. The research results can provide reference for studying the pyrolysis characteristics of paint waste and selecting the best heat treatment process in the process of thermal treatment of paint waste. In addition, the analysis of pyrolysis product types can be of guiding significance for the prevention and control of pollutants in the thermal disposal process of paint slag.

Material and experimental methods

Proximate and ultimate analysis

Mitar brand waterborne polyurethane paint and oily polyurethane paint were selected as samples. They were baked in a 105 °C constant temperature oven for 24 hours. After the quality is constant, the two types of polyurethane paint blocks obtained were crushed, ground. Furthermore screened the samples in an air atmosphere using a crusher to obtain powder with a particle size less than 0.3 mm, which is sealed and stored.

The proximate and ultimate analysis are given on dried basis and the results are shown in tab. 1. In addition, fixed carbon, FC, and O_2 were calculated by difference. It can be seen from the proximate analysis results that the volatile content of both types of paint slags is relatively high. The volatile content of waterborne polyurethane paint slag is as high as 97.81%. Figure 1 shows the appearance of two types of polyurethane paint slag samples before and after grinding, as well as before and after proximate analysis of ash content. The waterborne polyurethane paint slag is in a burnt yellow block shape, with strong viscosity and a faint irritating odour. Oily polyurethane paint slag is a black block of rubber texture with a strong irritating odour. There is almost no slag in the crucible in fig. 1(d), which also indicates the high volatile content of waterborne polyurethane paint slag.

Table 1. Proximate and ultimate analysis of polyurethane paint slags

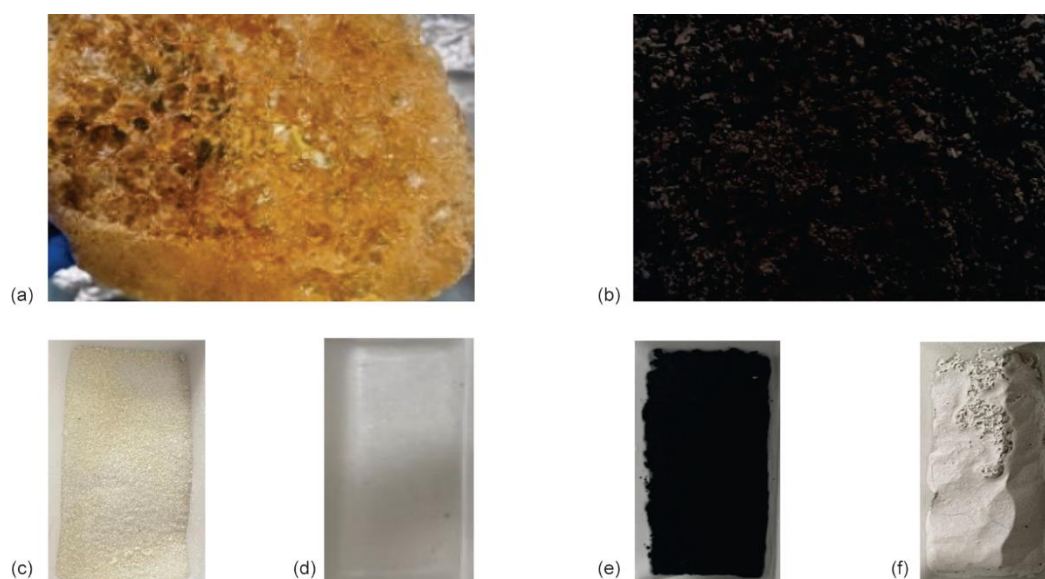| Sample	Proximate analysis, ω [%]				Ultimate analysis, ω [%]				
	M_{ar}	A_d	V_d	FC_d	C_d	H_d	O_d	N_d	S_d
Waterborne	1.14	0.72	97.81	1.47	70.88	9.26	15.68	2.83	0.63
Oily	0.41	38.33	60.24	1.43	27.61	3.42	28.83	1.67	0.15

Figure 1. Physical image of polyurethane paint slags; (a) waterborne polyurethane paint slag, (b) oily polyurethane paint slag, (c) before ash content measurement, (d) after ash content measurement, (e) before ash content measurement, and (f) after ash content measurement

Experimental purpose and method

In this experiment, a German NETZSCH synchronous thermal analyser model STA-449-F5 was used to study the effect of heating rate on the pyrolysis weight loss characteristics and characteristic temperature of waterborne polyurethane paint slag and oily polyurethane paint slag. The TG-FTIR-MS analyser with model STA8000-Spectrum 3-Clarus690 SQ8C was used to dynamically analyse the bond interruption, functional group changes, and product generation characteristics during the pyrolysis process of paint slag. All experiments should be repeated at least twice to ensure reproducibility and minimize random errors.

Among them, the initial mass of the experimental sample is 10 ±0.5 mg. The heating rates for the thermogravimetric experiment were set at 10 °C per minute, 20 °C per minute, and 30 °C per minute, with an initial temperature of 30 °C and an end temperature of 900 °C. The N_2 was selected as the protective gas, and the flow rate is constant at 100 mL per minute. The experimental parameters of TG-FTIR-GC/MS are nitrogen flow rate of 50.0 mL per minute, heated from 30 °C to 900 °C at a rate of 30 °C per minute. The start temperature T_i, final temperature T_f, and T_{max} corresponding to the maximum weight loss rate during the pyrolysis process of two types of polyurethane paint slags were selected as the characteristic temperatures.

Results and discussion

Effect of heating rate on pyrolysis characteristics of oil polyurethane paint slag

By comparing and analysing the thermogravimetry (TG) and differential thermogravimetry (DTG) curves of two types of polyurethane paint slags at different heating rates, the entire pyrolysis processes of waterborne and oily polyurethane paint slags were analysed. Furthermore, the pyrolysis characteristics of two types of paint slags were obtained at different heating rates.

The TG/DTG analysis of waterborne polyurethane paint slag

Figure 2 shows the TG and DTG curves of waterborne polyurethane paint slag under pyrolysis conditions. Table 2 presents the pyrolysis characteristic parameters of waterborne polyurethane paint slag. The β Indicates the heating rate. It can be observed that there are two stages in the pyrolysis reaction of waterborne polyurethane paint slag. The first stage is at 200~325 °C, which is the release stage of a small amount of volatile matter in the paint slag. The DTG curve begins to show a weak weight
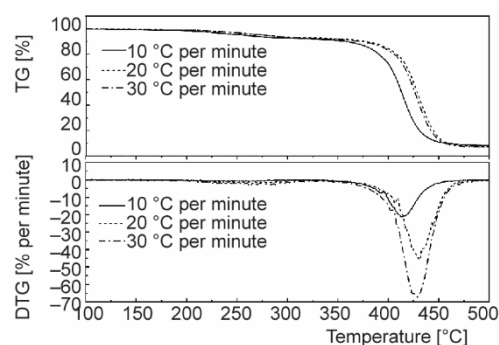

Figure 2. The TG and DTG curves of pyrolysis reaction of waterborne polyurethane paint slag at different heating rates

Table 2. Characteristic temperature of pyrolysis reactions of waterborne polyurethane paint slag under different heating rates

β [°C per minute]	T_i [°C]	T_f [°C]	T_{max}
10	372.8	445.2	418.6
20	395.6	452.0	438.9
30	368.5	456.3	436.9

loss peak. In the second stage, at 330~500 °C, the weight loss process is more intense, mainly due to the decomposition of a large amount of organic matter in the paint slag and the cracking reaction of large molecules, thereby releasing gaseous small molecules. As the heating rate increases, the weight loss curve shifts towards the high temperature zone, while the weight loss rate of the reaction remains almost unchanged. This phenomenon is similar to the research results of Liu *et al.* [19]. The TG curves of waterborne paint slag pyrolysis at different heating rates are similar. Indicating that the law of weight loss during paint slag pyrolysis is not significantly affected by changes in heating rate. When the heating rate increases from 10 °C per minute to 20 °C per minute, the maximum weight loss rate, T_i and T_{max} all significantly increase. The heating rate affects the heat transfer difference and temperature gradient between the measurement point and the sample, and between the outer sample and the inner sample, which will lead to the aggravation of the thermal hysteresis phenomenon and cause the curve to move to the high temperature side. When the heating rate increases from 20 °C per minute to 30 °C per minute, there is no significant change in the weight loss curve. As can

be seen from tab. 2, the temperature range of the reaction is maximum at 30 °C per minute, so there is enough time to promote complete pyrolysis. Increasing the heating rate can promote the pyrolysis reaction of waterborne polyurethane paint slag.

The TG/DTG analysis of oily polyurethane paint slag

The TG and DTG curves under the pyrolysis conditions of oily polyurethane paint slag are shown in fig. 3. It can be seen that there are four stages of pyrolysis of oily polyurethane paint slag. Table 3 shows the characteristic parameters of the pyrolysis reaction of oily polyurethane paint slag, with peak temperatures recorded as T_{max1}, T_{max2}, T_{max3}, and T_{max4}, respectively. The in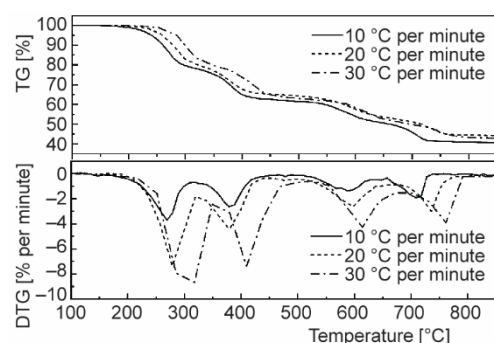crease in pyrolysis temperature can promote the generation of combustible gases, which is related to the cracking reaction of light HC [22]. When the heating rate is 10 °C per minute, the first stage of pyrolysis reaction is between 200~300 °C, and the second stage is between 300~435 °C. The weight loss process in the first two stages is the strongest, mainly due to the decomposition of a large amount of organic matter in the paint slag and the cracking reaction of large molecules, thereby releasing gaseous small molecules. The third stage is at 435~640 °C, which is the release stage of a small amount of volatile matter in the paint slag, and a weak weight loss peak appears on the DTG curve. The fourth stage is at 640~790 °C. According to the research on the pyrolysis of polyurethane paint in reference [23], it is found that this stage is a fixed carbon pyrolysis stage. When the heating rate was increased to 20 °C per minute and 30 °C per minute, the start temperature T_i slowly increased, and the final temperature T_f significantly increased. The T_{max} of each stage increased, and the weight loss rate of the reaction decreased by 4.43% and 2.80%, respectively. This is because the pyrolysis process of oily polyurethane paint slag is an endothermic chemical reaction. At the same ambient temperature, the higher the heating rate, the shorter the endothermic time of polyurethane paint slag. Therefore, the interior of the paint slag has not been heated to the required temperature for the pyrolysis reaction, resulting in a *thermal delay* phenomenon during pyrolysis [24, 25]. By increasing the heating rate, the weight loss curve of oily polyurethane paint slag shifts towards the high temperature zone, the maximum weight loss rate increases, and the pyrolysis strength increases.

Figure 3. The TG and DTG curves of pyrolysis reaction of oily polyurethane paint slag at different heating rates

Table 3. Characteristic temperature of pyrolysis reactions of oily polyurethane paint slag under different heating rates

β [°C per minute]	T_i [°C]	T_f [°C]	T_{1max} [°C]	T_{2max} [°C]	T_{3max} [°C]	T_{4max} [°C]
10	236.5	727.7	269.2	378.4	587.3	712.8
20	247.2	773.6	278.0	379.6	596.7	735.5
30	245.7	809.8	315.4	409.3	614.3	761.8

The FTIR analysis of pyrolysis gas products

The 3-D FTIR is used to analyse and measure the formation profile of gaseous compounds in real-time, and to analyse the changes in non-condensable gas functional groups during the pyrolysis process of waterborne polyurethane paint slag and oily polyurethane paint slag. Selecting certain characteristic functional groups to represent specific gas products can obtain the release patterns of specific gas products.
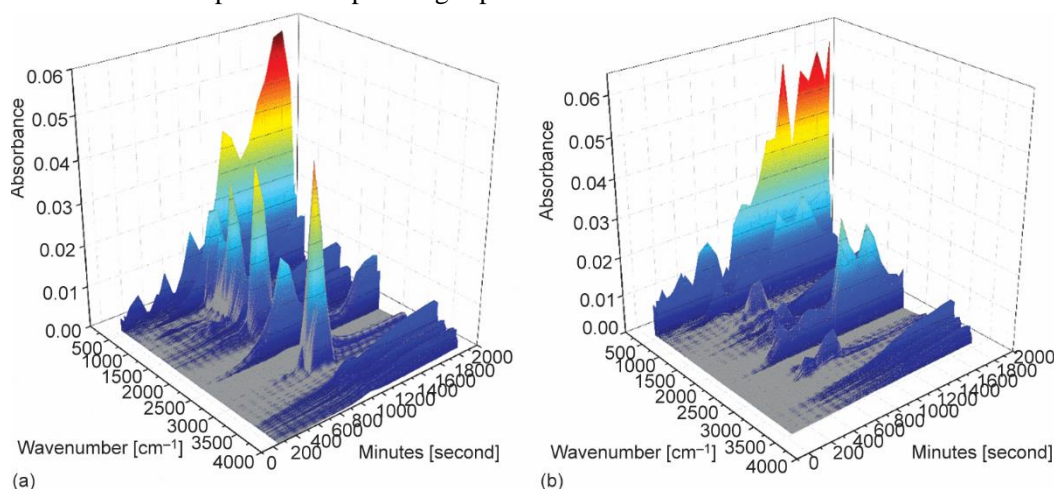

Figure 4. The 3-D TG-FTIR of the evolved gases from the pyrolysis of polyurethane paint slags; (a) waterborne polyurethane paint slag and (b) oily polyurethane paint slag

Figure 4 shows 3-D TG-FTIR of the evolved gases from the pyrolysis of polyurethane paint slags at a heating rate of 30 °C per minute. The wavenumber range is from 500-4000 cm^{-1}, and the *X*-, *Y*-, and *Z*-axes represent the wavenumber [cm^{-1}], minutes [s], and absorbance [%], respectively. A lot of information can be obtained from the 3-D graph. The plane formed by *YZ*-axis can be used to analyse the escape of functional groups at a specific temperature. The *XZ*-axis plane can be used to analyse the wavenumber of the absorption peak corresponding to the functional groups and bonds vibration form of the gas, so as to determine the type of volatilization. The *XY*-axis plane gives an intuitive view of the wavenumber and temperature corresponding to the escaping gas at the peak absorbance. By selecting the absorbance diagram corresponding to the wavenumber at the corresponding temperature, the gas components that escape during the pyrolysis of the two paint waste residues can be judged, as shown in fig. 5. There are numerous absorption peaks in the spectra, reflecting the complexity of the products. The characteristic peaks corresponding to CH_4, CO_2, CO, H_2O, as well as alkanes, olefins, and aromatic compounds can be clearly observed at the locations where the weight loss rates of the two types of polyurethane paint slags are the highest. The wavenumbers of infrared spectral bands/peaks corresponding to several characteristic functional groups are shown in tab. 4 [26]. Based on fig. 5. and tab. 4, the identification of characteristic absorption peaks in the FTIR spectrum is as follows. The characteristic peaks in the 3400~3650 cm^{-1} wavenumber range correspond to the symmetric and antisymmetric stretching vibrations of the O-H bond, indicating that this wavenumber range generates the product H_2O. The characteristic absorption peaks appearing in the wave number range of 3100~2850 cm^{-1} are attributed to the symmetric and antisymmetric stretching vibrations of
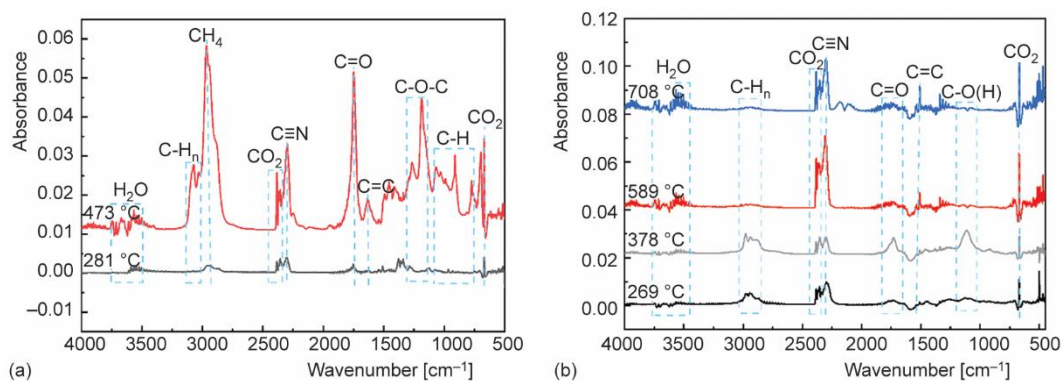
Figure 5. The FTIR spectra at various temperatures of the evolved gases from the pyrolysis of polyurethane paint slags; (a) waterborne polyurethane paint slag and (b) oily polyurethane paint slag

Table 4. A summary of FTIR bonds selected for analysis of functional groups

Wavenumber [cm^{-1}]	Functional group	Possible species
3650~3400	O-H stretching	H_2O
3100~2850	C-H stretching	Alkanes, alkenes
2388~2262, 680~660	C=O stretching	CO_2
2260~2215	C≡N stretching	Nitrile compound
1800~1600	C=O stretching C=C stretching	Aldehydes, ketones alkenes
1280~1020	C-O-C stretching	Esters
3100~2800, 1680~1600	C-H, C=C stretching	Aromatic compounds

C-H bonds, corresponding to the generation of some small molecule alkyl functional groups such as -CH$_3$, -CH$_2$, -CH [27]. The absorption peaks of saturated and unsaturated HC groups around 3000 cm^{-1} indicate the presence of various saturated and unsaturated HC in the product. Within this wavenumber range, CH$_4$ and other types of small molecule HC gases such as C$_2$H$_6$ and C$_2$H$_4$ are generated [28]. As shown in fig. 5(a), the absorption peak of CH$_4$ in the pyrolysis product of waterborne polyurethane paint slag is more obvious, with the highest content. The characteristic peaks of infrared characteristic absorption wavenumbers at 2262~2388 cm^{-1} and 660~680 cm^{-1} characterize the generation of pyrolysis product CO$_2$, attributed to the antisymmetric stretching of CO$_2$ molecules and the bending vibration of CO$_2$ molecules, respectively [29-31]. The absorption peak near 2298 cm^{-1} is the stretching vibration of the C≡N bond, indicating the presence of nitrile compounds in the pyrolysis products. From fig. 5(b), it can be seen that in the pyrolysis products of oily polyurethane paint slag, the characteristic peak corresponding to nitrile compounds is the most obvious, and the absorption peak of CO$_2$ in the pyrolysis products is the most obvious, with the highest content. A continuous low absorption peak appeared in the wavenumber range of 1800~1620 cm^{-1} and 1500~1250 cm^{-1}, which corresponds to the presence of CO in volatile matter [28]. There are characteristic peaks of carbonyl (C=O) double bond stretching vibration in the range of 1650~1900 cm^{-1}, indicating that the pyrolysis products contain aldehydes, ketones, carboxylic

acids, esters and lactones, anhydrides, and amides [32]. At 1642 cm^{-1}, the characteristic peaks of C=C stretching vibration of olefins, C=C skeleton stretching vibration of aromatic HC, and C-H bending vibration indicate the presence of alkynes, olefins, and aromatic HC. The absorption peaks near 3100~2800 cm^{-1}, 1680~1600 cm^{-1} also indicate the possible presence of benzene series and benzene ring substituents in the product [33]. The 1448~1571 cm^{-1} corresponds to the skeleton vibration of aromatic and fused aromatic rings. The characteristic peaks of waterborne polyurethane paint slag in the wave number range of 1020~1280 cm^{-1} are attributed to the symmetric and antisymmetric stretching vibrations of C-O-C bonds, corresponding to the generation of ester substances. The peak at 770~1000 cm^{-1} is attributed to the out of plane bending vibration of C-H, corresponding to the generation of olefins and aromatic substances [34]. The C-C stretching at 615~761 cm^{-1} corresponds to the presence of various carboxylic acids, HC, aldehydes, ketones, and other substances [35].

Considering that the absorption rate of infrared light is directly proportional to the concentration of gas products, in order to analyse the release trend of gas products more clearly, the relationship between absorption rate and time is transformed into the relationship between absorption rate and temperature. The apparent generation process of the main gas products CH_4, CO_2, CO, and H_2O in the pyrolysis of waterborne and oily polyurethane paint slags is compared. Figure 6. shows the relationship between the reaction temperature and the absorbance of the main pyrolysis gas products of two types of polyurethane paint slags at a specific wavenumber at a heating rate of 30 °C per minute. The increase in pyrolysis temperature can promote the generation of combustible gases, which is related to the cracking reaction of light HC [22]. In the pyrolysis products of waterborne polyurethane paint slag, the peaks of CH_4 and H_2O correspond to the highest and lowest absorbance, respectively. The emission concentrations of the main gas products are ranked: $CH_4 > CO_2 > CO > H_2O$. In the pyrolysis products of oily polyurethane paint slag, the peaks of CO_2 and CH_4 correspond to the highest and lowest absorbance, respectively. The emission concentrations of the main gas products are ranked as follows: $CO_2 > CO > H_2O > CH_4$.
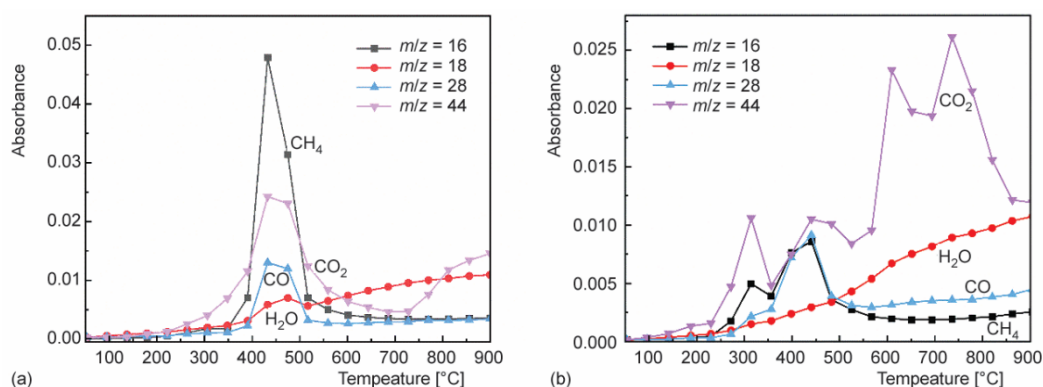
Figure 6. The mass spectra of the main pyrolysis gas products at a specific wave number at the heating rate of 30 °C per minute; (a) waterborne polyurethane paint slag and (b) oily polyurethane paint slag

The GC/MS analysis of pyrolysis products

The GC/MS analysis was conducted on the pyrolysis products of waterborne polyurethane paint slag at a temperature of 437 °C corresponding to the maximum weight loss rate.

The composition and relative content of the pyrolysis products are shown in tab. 5 and fig. 7. These pyrolysis products can be divided into HC, O-compounds, *etc.* According to the statistical results, the highest content of HC (57.75%) is found in the pyrolysis products of waterborne polyurethane paint slag, followed by O-compounds (42.25%). The main HC are alkenes and benzenes, with relative contents of 52.68% and 5.06%, respectively. According to reports, hydroxy acrylic resin is the main chemical component in waterborne polyurethane paint [36]. The formation of HC may be related to the cracking, cyclization, and aromatization of this substance [37]. The O-components mainly include five categories: alcohols, esters, anhydrides, alkanes, and aldehydes. The relative content order of these substances in the pyrolysis products of waterborne polyurethane paint slag is: alcohols (35.09%) > esters (6.70%) > anhydrides (0.18%) > alkanes (0.16%) > aldehydes (0.13%).

Table 5. The typical pyrolytic products of waterborne polyurethane paint slag at 437 °C

Retention time [seconds]	Compounds	Formula	Area [%]
2.93	1-Butanol	$C_4H_{10}O$	34.96
3.41	1,4-Dioxane	$C_4H_8O_2$	0.16
4.14	Toluene	C_7H_8	3.93
4.76	Acetic acid, butyl ester	$C_6H_{12}O_2$	0.90
5.42	Ethylbenzene	C_8H_{10}	0.55
5.83	1,3,5,7-Cyclooctate traene	C_8H_8	49.93
6.00	Propanoic acid, butyl ester	$C_7H_{14}O_2$	0.63
6.52	Benzene, 2-propeny1-	C_9H_{10}	0.27
6.62	propy1-Benzene	C_9H_{12}	0.12
6.89	n-Butyl methacrylate	$C_8H_{14}O_2$	0.59
6.96	α-methyl styrene	C_9H_{10}	1.96
7.52	Benzene, 2-propeny1-	C_9H_{10}	0.10
7.70	Benzene, 3-butenyl-	$C_{10}H_{12}$	0.09
7.85	Benzene, (1-methylenepropyl)-	$C_{10}H_{12}$	0.08
7.90	n-Butyl tiglate	$C_9H_{16}O_2$	0.07
9.26	1-Tetradecene	$C_{12}H_{24}$	0.46
10.57	Phthalic anhydride	$C_8H_4O_3$	0.18
11.23	1-Tetradecene	$C_{14}H_{28}$	0.26
11.44	Dodecanal	$C_{12}H_{24}O$	0.13
11.84	Dimethyl phthalate	$C_{10}H_{10}O_4$	1.83
12.07	1-Dodecanol	$C_{12}H_{26}O$	0.13
14.03	Butyric acid, 4-phenyl-, butyl ester	$C_{14}H_{20}O_2$	2.69

The GC/MS analysis was conducted on the pyrolysis products of oily polyurethane paint slag at the four peak temperatures corresponding to the maximum weight loss rate. The composition and relative content of the pyrolysis products are shown in tabs. 6-9 and fig. 8.
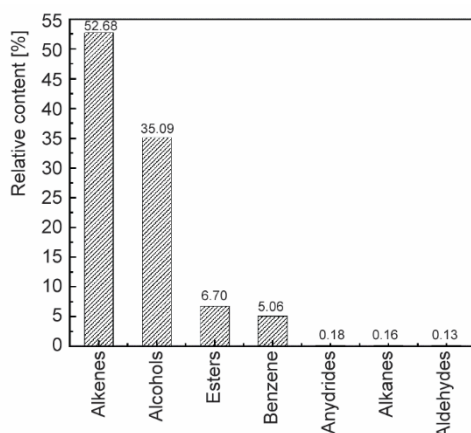
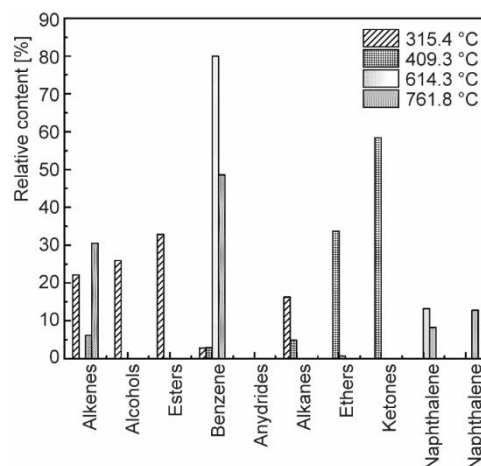**Figure 7. Distribution of pyrolysis products at 437 °C**

Figure 8. Distribution of pyrolysis products of oily polyurethane paint slag

These chemicals can also be divided into HC, O-compounds, N-compounds, *etc.* Obviously, the relative content of different components in the pyrolysis products of oily polyurethane paint slag differs greatly from that of waterborne polyurethane paint slag. Salihoglu *et al.* [38] found that oily paints mainly contain mixtures of aromatic HC, fatty HC, and other HC, while waterborne paints mainly contain ketones, esters, and alcohols. Under low temperature pyrolysis conditions (315.4 °C and 409.3 °C), the pyrolysis products are mainly O-compounds and N-compounds, with a total proportion of 58.82% and 100%, respectively. When the pyrolysis temperature is 315.4 °C, the main pyrolysis products are esters (32.87%), alcohols (25.95%), alkenes (22.15%), and alkanes (16.26%). When the pyrolysis temperature is 409.3 °C, the main pyrolysis products are ketones (58.42%) and ethers (33.72%). Under high temperature pyrolysis conditions (614.3 °C and 761.8 °C), all pyrolysis products are HC, mainly aromatic HC, accounting for 79.95% and 48.56% respectively, accompanied by the generation of naphthalene.

Table 6. The typical pyrolytic products of oily polyurethane paint slag at 315.4 °C

Retention time [seconds]	Compounds	Formula	Area [%]
4.17	Toluene	C_7H_8	2.77
4.44	Heptane, 3-methylene-	C_8H_{16}	10.73
4.57	4-Octene, (4E)-	C_8H_{16}	11.42
7.34	Heptane, 3-(chloromethyl)-	$C_8H_{17}Cl$	16.26
7.52	1-Hexanol, 2-ethyl-	C_8H18O	25.95
10.9	Benzene, 1, 3-diisocyanato-2-methyl-	$C_9H_6N_2O_2$	16.26
10.95	Benzene, 2,4-diisocyanato-1-methyl-	$C_9H_6N_2O_2$	16.61

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Table 7. The typical pyrolytic products of oily polyurethane paint slag at 409.3 °C

Retention time [seconds]	Compounds	Formula	Area [%]
2.87	Propane, 1-(1-methylethoxy)-	$C_6H_{14}O$	3.03
3.12	1-Propene,2-(1-methylethoxy)	$C_6H_{12}O$	3.61
3.61	1,3-Dioxolane,2,2,4-trimethyl-	$C_6H_{12}O_2$	4.87
3.81	2,3-Hexanedione	$C_6H_{12}O_2$	45.19
4.54	Di isopropyl ether	$C_6H_{14}O$	21.67
4.82	2-Propanone,1-(1-methylethoxy)-	$C_6H_{12}O_2$	13.24
5.39	Di isopropyl ether	$C_6H_{14}O$	5.41
10.89	Benzene, 1,3-diisocyanato-2-methyl-	$C_9H_6N_2O_2$	1.26
10.94	Benzene, 2,4-diisocyanato-1-methyl-	$C_9H_6N_2O_2$	1.74

Table 8. The typical pyrolytic products of oily polyurethane paint slag at 614.3 °C

Retention time [seconds]	Compounds	Formula	Area [%]
2.73	1,3-Cyclohexadiene	C_6H_8	1.04
2.93	Benzene	C_6H_6	34.76
4.17	Toluene	C_7H_8	29.32
7.17	Benzene, 1-ethenyl-2-methyl-	C_9H_{10}	5.10
7.78	Indene	C_9H_8	8.11
8.6	Benzene, 1-methyl-4-(2-propenyl)-	$C_{10}H_{12}$	0.70
8.94	2-Methylindene	$C_{10}H_{10}$	4.06
9.14	Cycloprop[38]indene,1,1a,6,6a-tetrahydro-	$C_{10}H_{10}$	3.71
9.37	Naphthalene	$C_{10}H_8$	8.00
10.49	1-Methylnaphthalene	$C_{11}H_{10}$	1.74
10.65	2-Methylnaphthalene	$C_{11}H_{10}$	3.48

Table 9. The typical pyrolytic products of oily polyurethane paint slag at 761.8 °C

Retention time [seconds]	Compounds	Formula	Area [%]
2.94	Benzene	C_6H_6	29.26
4.18	Toluene	C_7H_8	15.32
5.45	Ethylbenzene	C_8H_{10}	3.99
5.85	Styrene	C_8H_8	28.46
6.99	α-methyl styrene	C_9H_{10}	2.02
7.78	1-Phenyl-1-propyne	C_9H_8	12.77
9.14	1,2-dihydronaphthalene	$C_{10}H_{10}$	2.02
9.37	Naphthalene	$C_{10}H_8$	6.17

Conclusion

In this study, TG-FTIR-GC/MS was used to investigate the pyrolysis behavior and products of waterborne and oily polyurethane paint slags. The thermal pyrolysis of waterborne polyurethane slag weight loss included two stages, while the pyrolysis reaction of oily polyurethane slag weight loss included four stages. As the heating rate increased, the weight loss curves of both types of polyurethane paint slags shifted towards the high temperature zone, and the pyrolysis strength also increased. The FTIR results showed that both types of polyurethane paint slags emitted a large number of gases such as CH_4, CO_2, CO, H_2O, as well as alkanes, olefins, aromatic compounds, *etc.* during pyrolysis. The emission concentration of the main gas products from waterborne polyurethane paint slag was arranged in an order as $CH_4 > CO_2 > CO > H_2O$, while that of oily polyurethane paint residue was in an order as $CO_2 > CO > H_2O > CH_4$. The GC/MS results showed that the pyrolysis products of waterborne polyurethane paint slag were mainly HC and O-containing compounds. The relative content order of the pyrolysis products was alkenes (52.68%), alcohols (35.09%), esters (6.70%), benzene (5.06%), anhydrides (0.18%), alkanes (0.16%) and aldehydes (0.13%). The relative content of pyrolysis products of oily polyurethane slag was quite different from the waterborne polyurethane slag. Under low temperature pyrolysis conditions, the pyrolysis products were mainly O-compounds and N-compounds, with a total proportion of 58.82% and 100%, respectively. Under high temperature pyrolysis conditions, all pyrolysis products were HC, mainly aromatic HC, accounting for 79.95% and 48.56% respectively, accompanied by the generation of naphthalene. Overall, the findings of this research can yield insights into the pyrolysis characteristics, mechanisms and product emissions of paint residue, as well as the condition optimization associated with the pyrolysis of paint residue. Besides, the results can provide a reference for thermal treatment of paint waste residue.

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