Characterization of volatile fire effluent from thermoplastic polyurethane under variable oxygen concentration using TG-FTIR

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1 Abstract and keywords

In this paper, experiments are conducted to measure the thermal degradation and volatile fire effluents of a thermoplastic polyurethane under atmospheres with varying oxygen concentrations at a certain heating rate. The thermoplastic polyurethane is investigated by thermogravimetric analysis/infrared spectrometry. The results show that the thermoplastic polyurethane has low thermal stability at high temperatures in an oxygen-enriched atmosphere. The thermogravimetric analysis/infrared spectrometry data show that high concentrations of fire effluents of the thermoplastic polyurethane appeared in the reduced oxygen atmosphere. Decomposition is affected by the oxygen concentration. As the oxygen concentration increases, the combustion of the thermoplastic becomes the dominant factor that affects decomposition over a 30% oxygen concentration. The release of CO and HCN increased with the increase of the oxygen concentration.

Keywords: Thermogravimetric analysis/infrared spectrometry, thermoplastic polyurethane, variable oxygen concentration, fire effluent

2 Introduction

The thermoplastic polyurethane (TPU) is one of the most versatile engineering thermoplastics. TPU is widely used in wires, cables, conveyor belts and protective coatings because of its excellent abrasion resistance, good processing ability, high chemical stability and mechanical performance1. However, The TPU is provided with high combustible potential due to its high calorific value. The thermal decomposition and combustion of polymer produce toxic gas, such as CO, HCN, and NOX [1, 2].

The oxygen concentration is important for predicting the performance of polymer materials in real fire scenarios. It is expected that under different oxygen contents of the surrounding atmosphere, the model and rate of degradation for the evolved gases and char samples will be affected. Thus, the fire effluent of the samples will be further affected, and therefore, the atmospheric oxygen concentration needs to be considered to assess the fire safety of polymer materials. However, previous works have focused on the decomposition of cellulose and biomass, including the rate of the temperature increase, release of pyrolysis gas and rate of mass loss. Further, most studies used experimental conditions that

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include limited oxygen as reduced oxygen concentrations simulate real fires and oxygen-enriched concentrations achieve high-efficiency decomposition. In this work, we studied the TG-FTIR characterization of the thermoplastic polyurethane under variable oxygen concentrations at a certain heating rate (20℃/min); the oxygen concentration range was expanded and continuous (0%, 5%, 10%, 15%, 21%, 30%, 50%, 70%), and the volatile fire effluents (HCN and CO) from the thermoplastic polyurethane were analyzed.

3 Methodology

3.1 Materials

The thermoplastic polyurethane was obtained from Dongguan Xinsu yuan plastic technology Co., Ltd. (Dongguan, China). Materials were used without further purification. The weight of each sample was approximately 10.0 mg. The density was 1.17 g/cm3, and the softening temperature was 73 ℃. Thermogravimetric analysis/infrared spectrometry (TG-IR) of TPU was performed using a TGA Q5000 IR thermogravimetric analyzer (TA, USA) that was interfaced with a Nicolet 6700 FTIR (Thermofisher, USA) spectrophotometer. Approximately 10.0 mg of the samples were placed in an alumina crucible and heated from 30 to 700℃ at a constant heating rate (20/min). The atmospheres tested had oxygen concentrations of 0%, 5%, 10%, 15%, 21%, 30%, 50%, and 70% (flow rate of 45 ml/min). The stainless steel transfer pipe and gas cell were maintained at 180 ℃ to avoid the condensation of volatile compounds.

4 Findings

4.1 Thermogravimetric analysis

4.1.1 Thermal stability and char formation

TGA data for TPU in an N2 flow (TPU-0%) are presented in Fig. 1 as an illustration to interpret how to obtain the initial decomposition temperature T-5wt% (the temperature at which the loss is 5 wt%), T1 (the temperature of the first peak decomposition rate) and T2 (the temperature of the second peak decomposition rate). A summary of the thermal data for TPU under all variable oxygen concentrations is provided in Table 1. As shown, all samples have two main decomposition stages, and T1 and T2 are slightly affected by the oxygen concentration with the same trend. T1 decreased from 367℃ to 353℃ when the oxygen concentration increased from 0 to 70%, and the change regulation of T2 was similar.

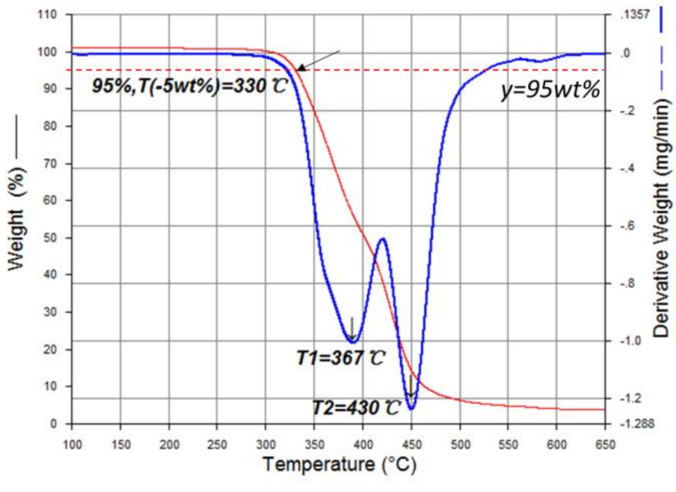

Figure 1: Temperature profiles of TPU under nitrogen atmosphere.

4.1.2 Kinetic analysis

Flynn-Wall-Ozawa dynamic analysis is an integral method that can neglect the choice of the reaction mechanism and directly determine the thermal decomposition activity energy, Ea. Compared with other methods, Flynn-Wall-Ozawa dynamic analysis avoids possible errors due to the different assumptions of the reaction mechanism. Its expression is:

$$\lg\beta = \lg\frac{AE_a}{R\beta} - 2.315 - 0.4567\frac{E_a}{Rt}$$

where t corresponds to the temperature when the weight loss rate is∂, $\beta$is the heating rate, A is the frequency factor, and R is the ideal gas constant. A straight line can be obtained by plotting $lg\,\beta$ vs. $1/t$. The thermal decomposition activation energy can be calculated from the slope of the straight line, $-0.4567\frac{E_a}{R\beta}$.

As shown in Fig. 2, the value of Ea is from 142 kJ/mol to 588 kJ/mol, and the highest value is 1001 kJ/mol under a 15% oxygen concentration. The activation energy increases with the addition of oxygen and reaches the highest value at an oxygen concentration of 15%. When the oxygen concentration is over 15%, the combustion is more efficient as a result of having sufficient oxygen, and the value of Ea decreases.

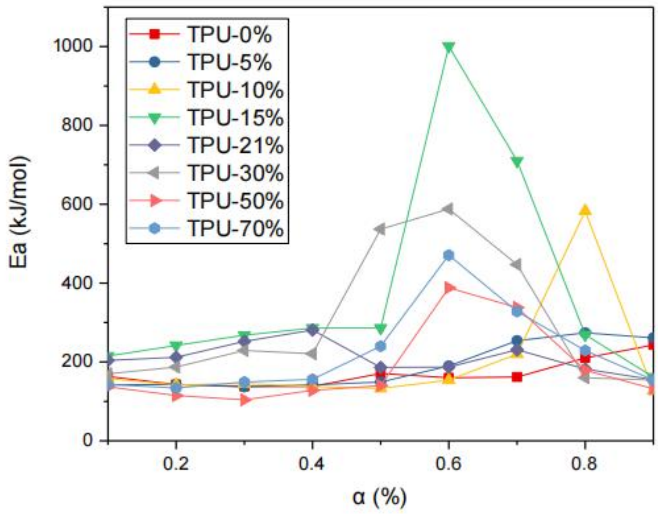

Figure 2: The activation energy of thermal decomposition in different weight loss rate of TPU at different heating rates

4.2 Volatile gases analysis

4.2.1 Total decomposition products

TG-IR is selected to analyze the gaseous products of the TPU under variable oxygen concentrations. To compare the results of thermal decomposition under different conditions, the total decomposition gaseous products of TPU are shown in Fig. 3. It is evident that the decomposition peak is affected by the oxygen concentration. From an oxygen concentration of 0% to 30%, the peak intensity value of the total decomposition products of TPU increased. As the oxygen concentration continued to increase, the peak value decreases because of the incomplete combustion of TPU in the oxygen-controlled stage and the formation of incomplete combustion products (including CO and polyol fragment) caused the higher absorbance peak. When the oxygen concentration increased to 70%, complete combustion and less product formation occurred in the fuel-controlled stage.

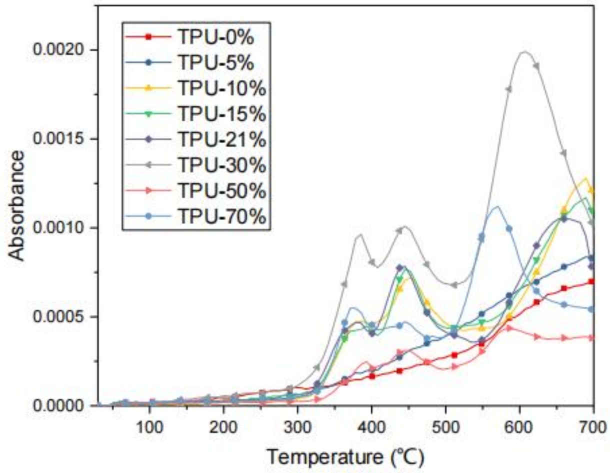

Figure 3: Intensity of total decomposition products for TPU versus temperature

4.2.2 Volatile gases product analysis

The FTIR spectra of decomposition products at the maximum decomposition rate at 20℃/min under an atmosphere with oxygen concentrations of 0%, 10%, 30%, and 70% are presented in Fig. 4. The evolved gaseous products are the same in each sample and include the characteristic bands of water (3575 cm-1), -CH3 and -CH2- groups (2980 cm-1), CO2 (2360 cm-1), -C=O (1750 cm-1), -NHC=O (1528 cm-1), esters (1750 cm-1, 1150 cm-1, 913 cm-1) and HCN (722 cm-1). The absorption intensity of CO2 (2360 cm-1) increased with the increased oxygen concentration, while the other products did not significantly change.

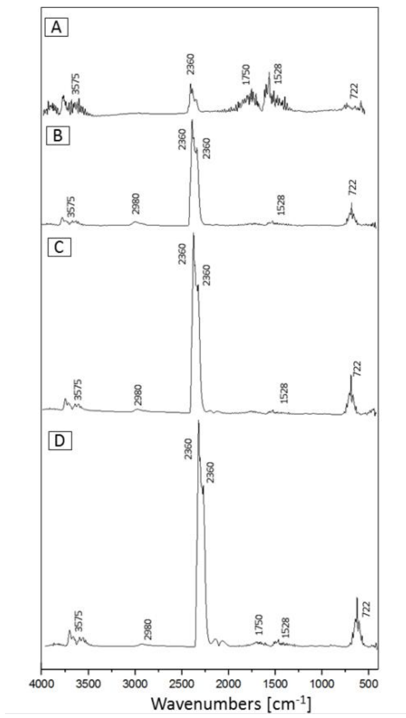

Figure 4: TG-IR spectra of the decomposition products from the TPU at T1. (a) TPU-0%, (b) TPU-10%, (c) TPU-30%, (d) TPU-70%

4.2.3 HCN analysis

HCN is considered to be one of the principal fire effluents from the combustion of TPU. The decomposition of the infrared absorption intensity of HCN for TPU is portrayed in Fig. 5. The release of HCN is sustained during the combustion of TPU, even reaching the temperature of the maximum decomposition rate. There is only one peak of HCN under the N2 atmosphere, and two or three peaks appear after oxygen is added because the more oxygen in the atmosphere, the more fiercely the samples burn and the more complete the decomposition is during combustion. It is also obvious that the HCN intensity is increased under and atmosphere with a higher oxygen concentration because of higher temperatures, which are caused by complete decomposition. This phenomenon has also been reported by Singh an Jain and Woolley et al. [3]. A higher evolution rate is observed at higher temperatures, and the amount of HCN is increased when the temperature increases. Blasi et al.[4] reported that the viscous force of the molten layer could be reduced in an oxygen-enriched atmosphere, and therefore, volatiles became easier to release.

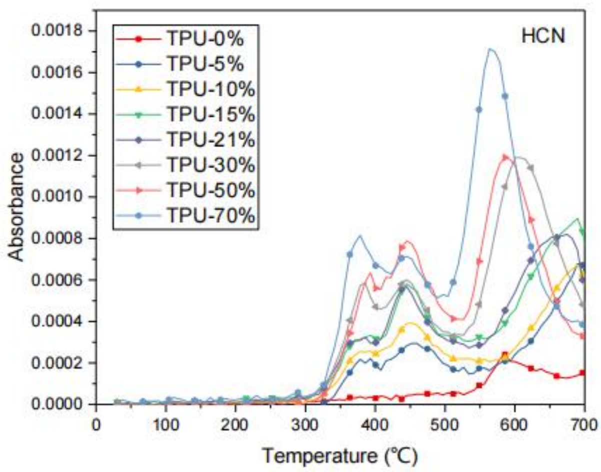

Figure 5: Intensity of HCN for TPU versus temperature.

5 Conclusion

A series of TPU samples are tested by TG-IR under an N2 to 70% oxygen concentration atmosphere at 20℃/min. The oxygen concentration has a weak effect on the decomposition and combustion of TPU.

For the TG results, the temperatures at the maximum decomposition rates are significantly affected. An increase in the oxygen concentration causes T1 and T2 to decrease. As the oxygen concentration increases, combustion and char formation fiercely compete with each other, and combustion becomes dominant over a 30% oxygen concentration. The value of Ea is increased with the addition of oxygen, reaches the highest value at a 15% oxygen concentration, and decreases with the continued addition of oxygen.

The FTIR data show that the highest total product intensity of TPU appears underflows of a low oxygen concentration because of incomplete combustion. The oxygen concentration has an effect on both decomposition stages. Combined with the absorption curves of two principal fire effluents, CO and HCN increase with the addition of oxygen.

References

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