

Investigation of Thermal Decomposition Kinetic of Polyethylene 100 Compounds with Kissinger Model

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Abstract. The thermal stability and non-isothermal degradation kinetics of the polyethylene 100(PE100) compounds were studied by thermogravimetric(TG) and derivative thermogravimetric(DTG) analyses using multiple heating rates (2, 5, 10, 20 °C/min) under nitrogen gas atmosphere. The thermal features of PE100 compounds was examined and the average activation energy(Ea) thus obtained with Kissinger method is 333.79 kJ/mol.

1. Introduction

With the development of modern energy, the use of natural gas to replace coal-fired fuel in production and life is becoming more and more widespread, and the scale and number of gas pipeline networks are also rapidly increasing[1-2]. As an important part of the distribution system, the performance of the natural transmission pipeline is related to the safety of the entire system. Among the medium and low-pressure gas transmission and distribution pipelines in cities and towns, polyethylene (PE) has become a preferred material as gas pipe because of its good welding performance, chemical resistance, toughness and weather resistance, and good resistance to rapid crack propagation[3-4]. The development and application of polyethylene pipes have undergone four stages. In the 1940s, in order to replace the traditional metal pipe, people produced the first generation polyethylene pipe material PE63 with corrosion resistance, but its environmental stress crack resistance was poor. In the 1960s, as the relative molecular mass and the content of comonomer were increased, the second-generation polyethylene pipe PE80 with long-term service life was developed with slow crack resistance. However, it has been found that the relative molecular mass is too high to reduce the processing performance of the material, while the increase in the comonomer content leads to a decrease in the rigidity of the material. In order to take into account both processing and use properties, the PE100, a third generation PE pipe material, was developed. The important performance of gas-fired polyethylene pipes is long-term service life. In the past decade or more, one of the developments in PE pipe materials has been to lock in with slow crack growth or stress cracking resistance in search of new applications. Based on the third-generation PE100, the fourth-generation PE pipe material, PE100RC, was further developed through molecular structure design to improve the resistance to slow cracking. The representative product is a bimodal molecular weight distribution of hexene copolymerized PE100-RC.

Polyethylene pipeline contains a flammable special medium such as natural gas, and several gas fire accidents have occurred in life [5-6]. Once a fire breaks, polyethylene will burn and decompose at high temperatures, and the remaining pipes will also become garbage. How to understand the thermal decomposition mechanism of polyethylene pipe materials is of great significance to the safety protection of pipes and the reuse of waste polyethylene. Its efficient reutilization has a growing importance these years due to the increased demand for resource recycling and environmental protection. In general, plastic waste has been mainly disposed of by landfill or incineration, but these processes are not fully acceptable under current international policy, which focuses on efficient recovery of raw material and energy. Pyrolysis and gasification processes are promising routes for optimal upgrading from waste. Moreover, pyrolysis of plastic, based on the decomposition of polymers at different temperatures, allows the treatment of polymers with simultaneous decomposition and separation [7-8].

Thermal degradation of polymers has great interest as an alternative source of energy or chemical raw materials, as well as it contributes to the solution of environmental problems [9]. The determination of the parameters of the thermal decomposition process by means of TG techniques allows the development of the recycling process of these materials in an industrial scale. Thermal behavior of plastics can be improved by knowing thermal degradation kinetic [10-11]. Pyrolysis of plastic can transform it into valuable chemicals [12], and it becomes a popular way to dispose waste plastics. Meanwhile, thermal degradation is usually occurring during the polymer processing. Designing and implementation of the pyrolysis or process for polymers depends primarily on kinetic analysis [13]. Precised kinetics heavily relies on the reliable kinetic triplets, activation energy (E_a), preexponential factor (A) and reaction model ($f(\alpha)$) [14]. A thermogravimetric analysis technique is an excellent way for studying the kinetics of thermal degradation. TG provides the pathway to determine the macroscopic kinetics of these processes such as the information on activation energy and kinetic model [15].

In this work, the thermogravimetric study of polyethylene compounds was realized using non-isothermal method in order to determine the apparent activation energy with Kissinger model.

2. Measurement and method

2.1. Measurement

The PE100 compound (Borstar® HE 3490LS) was purchase from Borouge company. PE100 samples (~10 mg) were subjected to TG analysis in an inert atmosphere of nitrogen. NETZSCH 209 F1 TG analyzer was used to measure and record the sample mass change with temperature over the course of the decomposition reaction. TG curves were obtained at four different heating rates (2, 5, 10, 20 °C/min) from room temperature 700 °C.

2.2. Kinetic analysis method

Kinetic analysis of a thermal decomposition process is usually expected to produce a satisfactory kinetic description in terms of the reaction model and the Arrhenius parameters. Typically, the generalized form of kinetic equation can be expressed as Eq.1

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Where α is the degree of conversion and it ranges from 0 to 1. Where $k(T)$ and $f(\alpha)$ are temperature dependent rate constant and mass dependent reaction model. The rate constant $k(T)$ is assumed to follow the Arrhenius law such as $k(T)=A\exp(-E_a/RT)$, where the temperature and time coordinates are related as $T= T_0+\beta t$. Eq.1 can be written as following

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (2)$$

Where A is the pre-exponential factor (1/min) and E_a is the apparent activation energy (kJ/mol), respectively, R is the gas constant (8.314 J/mol/K). The differential isoconversional method suggested by Kissinger [16] is based on Eq. 2 given by the following relation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) + \ln[n((1 - \alpha_p))^{n-1}] - \frac{E_a}{RT_p} \quad (3)$$

Where T_p is the peak temperature at the maximum reaction rate. Plot of $\ln\left(\frac{\beta}{T_p^2}\right)$ versus $1/T_p$ should give straight lines, and E_a is calculated from the slope of the fitted straight line.

3. Results and discussion

3.1. Thermal features of PE100

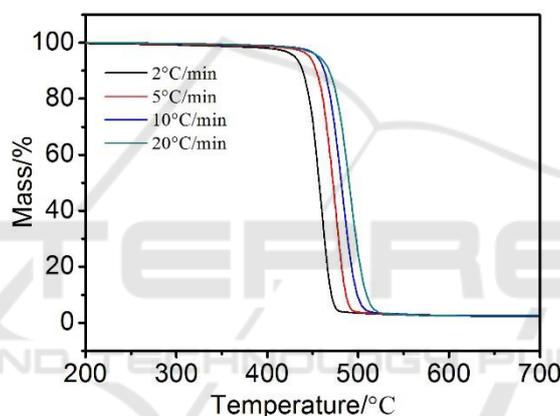


Figure 1. TG profiles of PE100 at four heating rates (2, 5, 10 and 20 °C/min).

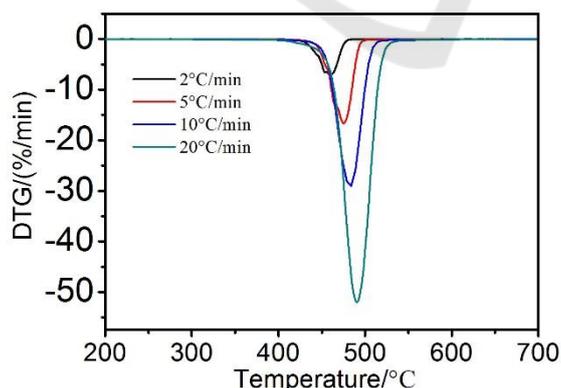


Figure 2. DTG profiles of PE100 at four heating rates (2, 5, 10 and 20 °C/min).

The TG and DTG curves of PE100 at a heating rate of 2, 5, 10 and 20 °C/min in N₂ are shown in Figure 1 and Figure 2 respectively. From TG curves it can be observed that the shape of the weight loss curve does not change with the variation of heating rate. The TG characteristic temperatures of PE100 at the different heating rates are illustrated in Table 1. T_p and the decomposition temperature

at 5% weight loss ($T_{5\%}$) shift to higher temperature with increasing β from 2 to 20 °C/min is mainly due to the time and temperature history subjected to the materials. At higher heating rates, the time required to reach the decomposition temperature becomes shorter, causing the temperature difference between the sample inside and outside turning to be larger as well, and subsequently causes thermal lagging which may delay the sample inside thermal decomposition. It can be seen from Figure 2 that the DTG peak becomes stronger and wider as heating rate increases from 2 to 20 °C/min, and in the meantime T_p is promoted from 460 to 490 °C.

Table 1. Characteristic temperatures of thermal degradation of the PE100 compound (HE 3490LS).

β (°C/ min)	2	5	10	20
$T_{5\%}$	241	290	329	336
T_p	460	476	484	490

$T_{5\%}$: the decomposition temperature at 5% weight loss.

3.2. Kinetic analysis with Kissinger method

This method derives from the correlation between the peak temperature (T_p) and β . Suited for more than four thermal analytical curves of the derivation type, it is an efficient model-free differential method. According to Eq.3, the linear fitted plots between $\ln(\beta/T_p^2)$ versus $1/T_p$ obtained for PE100 are shown in Figure 3. The results show that the activation energy (E_a) is 333.79 kJ/mol. Westerhout has examined the pyrolysis kinetics of low-density polyethylene below 450 °C, and also made a comparison of activation energy (E_a) with literature models and data [17]. The thermal decomposition E_a for low-density polyethylene varied from 201 to 330 kJ/mol, all of which is lower than that of PE100 compound with Kissinger method. The above results may be due to the higher molecular weight. As proper selection of the conversion function is extremely important to formulate a self-consistent global pyrolysis kinetic model that performs uniformly well in a practically realizable range heating rates occurring in polymer combustion [18], Kissinger method gives an average E_a overall the decomposition process.

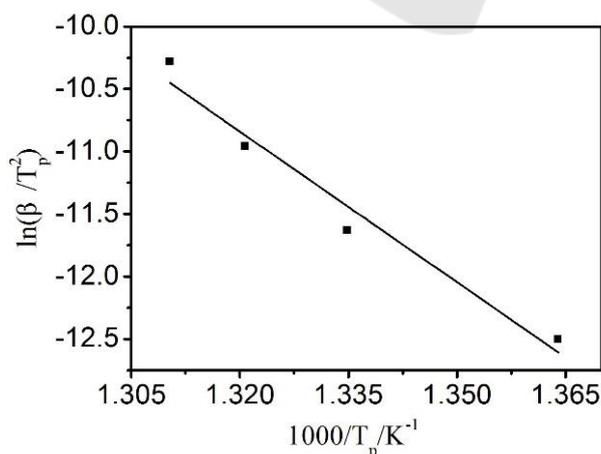


Figure 3. Kissinger method plots of $\ln(\beta/T_p^2)$ versus $1/T_p$.

4. Conclusions

In this work, thermal decomposition kinetics of the PE100 compounds has been investigated, and the measurements were carried out under N₂ atmosphere at different heating rates. TG and DTG results show that the thermal features of PE100 compounds are strongly depend on the heating rates with a single decomposition step. With the Kissinger method, the apparent activation energy (E_a) of PE100 compounds during thermal degradation is 333.79 kJ/mol.

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