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Short communication

Non-isothermal thermal decomposition reaction kinetics of dimethylhexane-1,6-dicarbamate (HDC)

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ABSTRACT

The thermal decomposition behavior and reaction kinetics of dimethylhexane-1,6-dicarbamate (HDC) were investigated by TG–DTG, DSC and IR techniques. It is shown that the decomposition process can be divided into 3 main stages and the first stage is the thermal decomposition reaction for HDC to dimethylhexane-1,6-diisocyanate (HDI). The main gaseous products of the decomposition are CO_2 and CH_3OH. The kinetic parameters of the reaction for HDC to HDI are Ea = 119.51 kJ mol^{-1}, lg(A/s^{-1}) = 14.82, respectively. The kinetic equation is $d(\alpha)/d(t) = 10^{15.12}(1-\alpha)^{3/2}\, e^{-1.4375\times10^4/T}$.

1. Introduction

Isocyanates have been widely used in the manufacture of polyurethanes and herbicides [1,2]. They are mainly synthesized by the reaction of amines with phosgene or its derivatives. Many problems may occur during the process, such as the use of extremely toxic reagent phosgene and the seriously corrosive byproduct HCl. Many phosgene-free synthesis routes have been reported, while the thermal decomposition of carbamate is the most promising method. This method contains two steps: the synthesis of carbamate and thermal decomposition of carbamate [3]. Between them decomposition of carbamate to isocyanate is the key process [4–6].

As the decomposition of carbamate is strongly endothermic, great amounts of heat is consumed during the reaction. The reaction should be preceded at high temperature. However, isocyanate is highly active and unstable in high temperature. So, appropriate reactor which could minimize the side-reaction is necessary. Few researches on the study of the decomposition reaction reactor have been reported. Lewandowski and Milchert reported the decomposition of methylene-4,4-diethylphenyl-carbamate (MDC) could be conducted with a conversion of 98% in a reactor filled with aluminum rods [7]. Franz Merger reported the cleavage of HDC in a two-phase mixture by a reactor with baffles [8]. These researches were mainly about the optimization of the reaction condition. However, the thermal decomposition reaction kinetics of carbamate, which is the key to develop high-efficiency reactor, have not been reported.

It is very difficult to get the isothermal kinetics accurately of thermal decomposition reaction of carbamate for the instability of isocyanate. So in this paper, TG–DTG, DSC and FT-IR techniques, which are effective methods to get the non-isothermal kinetics of the thermal decomposition process [9–11], is used to confirm thermal decomposition mechanism and non-isothermal kinetics parameters of dimethylhexane-1,6-dicarbamate (HDC).

2. Experimental

2.1. Material

HDC was synthesized by dimethylhexane-1,6-diisocyanate (HDI) and methanol in our laboratory. The reaction condition was: n(HDI):n(methanol) = 1:10, T = 50 °C, t = 6 h. The compound was purified by crystallization in toluene, with a final purity of >99%. The structure of HDC was characterized by GC–MS, elemental analysis, IR spectrometry and H-NMS. The sample was kept in vacuum desiccators before use.

2.2. Equipment and conditions

TG–DTG and DSC curves under the condition of nitrogen flow were studied on a TGA/DSC-1 thermal analyzer (Mettler Toledo, Switzerland). The conditions of TG–DTG and DSC were as follows:

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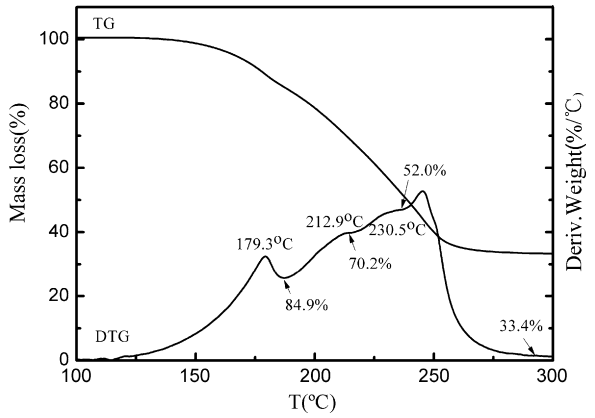

Fig. 1. TG/DTG curve for HDC at a heating rate of 5 °C min^{-1}.

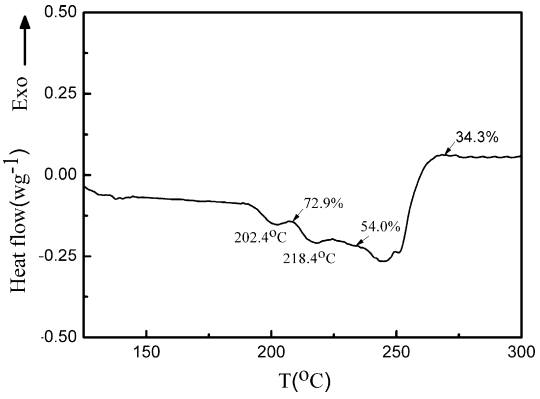

Fig. 2. DSC curve for HDC at a heating rate of 5 °C min^{-1}.

sample weight, about 8 mg; heating rates, 4, 5, 7 and 8 °C min^{-1}; flow rate of N_2, 60 ml min^{-1}; reference sample, α-Al_2O_3.

FT-IR measurements were conducted with Model 60SXR FT-IR. The temperature range is 40–400 °C. The conditions of FT-IR were as follows:

sample weight, 4.418 mg; heating rate, 10 °C min^{-1}; flow rate of N_2 50 ml min^{-1}. IR spectra in the 800–4000 cm^{-1} were detected at 2 scans s^{-1}.

3. Results and discussion

3.1. The thermal decomposition mechanism of HDC

3.1.1. TG/DTG

Typical TG/DTG curve and TG–DTG data for HDC are shown in Fig. 1 and Table 1, respectively. It is indicated that the decomposition process can be divided into 3 main stages in the DTG curve. The first mass loss stage ranges from 154.8 °C to 215.5 °C with a mass loss of 29.8%, which is in agreement with the mass loss for the thermal decomposition of HDC to HDI (27.6%). The second stage ranges from 215.5 °C to 237.2 °C with a mass loss of 48.0%, which is in agreement with the mass loss for the polymerization of HDI to carbodiimide (19.4%). And the third stage ranges from 237.2 °C to 292.1 °C, with a mass loss of 66.6%.

3.1.2. DSC

The DSC curve of HDC is shown in Fig. 2. There are 3 endothermic peaks in the DSC curve of HDC thermal decomposition. The first peak ranges from 182.1 °C to 208.9 °C with a peak at 202.4 °C. The mass loss of this stage is 27.1%. The second peak ranges from 208.9 °C to 234.3 °C with a mass loss of 46.0%. The third peak ranges from 234.3 °C to 268.9 °C with mass loss of 65.7%.

3.1.3. FT-IR

FT-IR was used to measure the phase products of the thermal decomposition of HDC at a heating rate of 10 °C min^{-1}. The infrared spectra of gas products of HDC decomposition at different temperatures are shown in Fig. 3.

It is shown that the peaks of methanol are merged in 2947 cm^{-1}, 1061 cm^{-1} and 1006 cm^{-1} at 200 °C. The peak of CO_2 IR absorption in 2270 cm^{-1} comes out at 230 °C, which indicate the polymerization process of HDI to carbodiimide. These data help to confirm that the first stage of thermal decomposition process is for HDC to HDI, which release methanol. The second stage should be the polymerization process of HDI to carbodiimide with releasing CO_2. With the temperature rose, no other obvious peak comes out in the IR spectra. The possible reason is that the gas phase produced in this stage is very little, which is submerged in the background of the peak.

3.1.4. The thermal decomposition mechanism of HDC

According to the results above, the thermal decomposition mechanism of HDC is supposed to 3 stages as Scheme 1.

The first stage is the process for the thermal decomposition of HDC to HDI with a mass loss of 27.6%, which would be studied deeply as follows. The second and third stages are about the further reaction of HDI, which is complicated and would not be discussed in this paper any more.

3.2. The thermal decomposition kinetics of HDC to HDI

In order to obtain the kinetic parameters [apparent activation energy (E) and pre-exponential factor (A)] of the first endothermic decomposition reaction for HDC, the Kissinger's method and Ozama's method were employed. These methods are as follows:

Table 1
TG–DTG data of HDC (β = 5 °C min^{-1}).

The first stage of mass loss	T_{p1} (°C)	T_{p2} (°C)	Mass loss (%)
	179.3	212.9	29.8
The second stage of mass loss	T_{p3}		Mass loss (%)
	230.5		18.2
The third stage of mass loss	T_{p4}		Mass loss (%)
	245.3		18.6

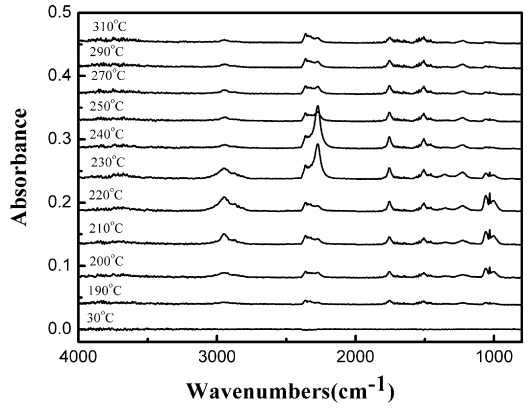

Fig. 3. Infrared spectra of gas products of HDC decomposition at different temperatures.