

Thermal Decomposition Kinetics of Rigid Polyurethane Foam and Ignition Risk by a Hot Particle

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ABSTRACT: Rigid polyurethane foam, one kind of building insulation material used in China, is prone to being ignited by hot particles from fireworks or welding processes and has been the fuel for some catastrophic fire accidents. Thermal decomposition has long been recognized to play an important role in the ignition and fire-spreading processes of materials, and thus, it is important to understand the behavior and kinetics of material decomposition. In this study, the characteristics of the thermal decomposition of polyurethane foam were investigated in an air atmosphere with nonisothermal thermogravimetry and differential scanning calorimetry (DSC). Model-free (isoconversional) methods and model-fitting methods were used to study the decomposition kinetics. The results reveal that the decomposition process of polyurethane foam in air presented three main stages: the loss of low-stability organic compounds (bond fission of the weakest link in the chain), oxidative degradation of organic components, and oxidative degradation of residue material. A scheme containing three consecutive reactions was proposed to describe the decomposition process, and good agreement was found between the experimental and simulated curves. The heat during decomposition was calculated from DSC measurement. On the basis of the kinetics and heat of decomposition, the critical conditions for a hot particle to ignite polyurethane foam was evaluated, and this was helpful for the understanding the ignition risk of polyurethane foam. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39359.

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INTRODUCTION

Because of their low cost and superior adiabatic performance, organic insulation materials, such as rigid polyurethane foam, are widely used for energy savings in buildings in China. However, organic insulation materials are flammable and have been found to be the main combustibles in some catastrophic fires, including the China Center Television fire in 2009 and the high-rise residential building fire in Shanghai's Jing'an district in 2010. The investigation of the China Center Television fire reported that some hot metal particles produced by a fireworks display contacted and ignited the organic insulation materials and subsequently caused violent burning, which resulted in a great economic cost and loss of life. In the residential building fire in Shanghai, it was reported that the organic insulation materials were ignited by hot welding beads and formed a big fire surrounding the whole building, which eventually caused 58 casualties. These fires indicated that these organic insulation materials could be easily ignited by hot particles and could burn quickly.

During the processes of ignition and combustion, solid polymers are thermally decomposed into volatiles first. The occurrence and spread of the fire, in a sense, are determined by the volatile fuels provided by the decomposition process of polymers. The decomposition kinetics also govern the chemical reaction structure of the combustion front, determine the global heat-release rate, and are ultimately responsible for what conditions the material ignites. The proper computation of the reaction rates is particularly essential for ignition, so it is necessary to establish and quantify the kinetic mechanism of thermal decomposition of the organic insulation materials.

Polyurethane foam is one kind of organic insulation material and has a high fire risk. There have been some studies on the characterization and kinetics of polyurethane polymer decomposition, mostly in an inert atmosphere. Ohtani et al.¹ characterized several polyurethanes by pyrolysis (at 600°C) coupled with capillary gas chromatography and mass spectrometry and proposed that polyurethanes were thermally degraded through the dissociation of urethane linkages followed by cleavage at

ester linkages at elevated temperatures. Ravey and Pearce² presented a brief review of the literature concerning the decomposition mechanisms and clearly showed that the products of flexible polyurethane foam depend on the conditions of pyrolysis. Garcia et al.³ proposed a kinetic model for the combustion of varnish wastes originating from the furniture industry by performing testing under different heating rates and different oxidizing atmospheres. Font et al.⁴ proposed a kinetic model of the global weight loss of a polyurethane-based adhesive under an inert atmosphere and used two different fractions that decomposed independently by two parallel reactions. Thermogravimetry (TG) analysis coupled with Fourier transform infrared spectroscopy was used to investigate the thermal decomposition of polyurethane foams under nitrogen conditions.⁵ However, the well-established and quantified kinetic mechanism of thermal decomposition for the ignition of polymers is not sufficient in the literature, especially for rigid polyurethane foam. Research on the decomposition kinetics of typical organic insulation materials will be of great significance to the study of ignition and combustion, which requires the kinetic parameters of thermal decomposition.

The objectives of this study were to

1. Determine the rate and kinetics of the thermal decomposition of polyurethane foam under an air atmosphere, which was closer to the degradation process of spotting ignition of polyurethane foam by hot particles. Emphasis was given to thermal and oxidative degradation of the material because these were the most important processes involved in ignition.
2. Propose a three-step consecutive reaction scheme to simulate the thermal decomposition of polyurethane foam under an air atmosphere.
3. Investigate the heat-release characteristics of the degradation and oxidation process.
4. Use the decomposition kinetics and hot-spot ignition theory to evaluate the ignition risk of polyurethane foam by hot particles.

EXPERIMENTAL

Sample Preparation

The polyurethane sample used in this study was commercial building insulation material from Yantai Wanhua Polyurethanes Co., Ltd., produced by the reaction of polyisocyanates with polyols in the presence of a catalyst. The complete formulations of these rigid polyurethanes were proprietary and were therefore unknown. To obtain more information about materials, elemental analysis was conducted. The raw material was ground into particles, which were subjected to dynamic thermal decomposition experiments. This elemental analysis, determined by a Vario EL cube apparatus with the adoption of diverse combustion analyzers, is shown in Table I.

Thermal Analysis Experiments

The TG curves of polyurethane foam were recorded by a Shimadzu DTG-60H thermogravimetric analyzer. The analyzer was calibrated, and the baselines for different experimental condi-

Table I. Elemental Composition of the Polyurethane Foam

Element	wt %
N	6.14
C	61.89
H	6.24
O	20.10

tions were obtained before the experimental measurements. In each experimental run, the furnace temperature was increased from room temperature to 1073 K until the sample mass was nearly constant at heating rates of 5, 10, 20, 30, 40, or 50 K/min. Sweeping air was continuously passed into the furnace at a flow rate of 50 mL/min (at normal temperature and atmospheric pressure). The initial amounts of the sample were all kept at 5 mg or so. To investigate the heat of polyurethane foam decomposition process, a TA Instruments SDT-Q600 simultaneous analyzer was also used to record the TG/differential scanning calorimetry (DSC) curves of the polyurethane decomposition at a heating rate of 10 K/min under both air and nitrogen atmospheres. Two runs were performed with the same experimental conditions, and the reproducibility was verified.

RESULTS AND DISCUSSION

Characteristics of Polyurethane Decomposition

The TG/derivative thermogravimetry (DTG) curves of the polyurethane foam at various heating rates under an air atmosphere are presented in Figure 1. As the heating rate increased, the TG/DTG curves shifted to higher temperatures. There were four mass loss peaks in the DTG curves at various heating rates. The first peak occurred from room temperature to 373 K, and the mass loss was about 1% of the initial sample mass (1.2, 0.8, 1.2, 1, 1.7, and 1.5%, respectively, for the curves at heating rates of 5, 10, 20, 30, 40, and 50 K/min). This mass loss step seemed to be due to the evaporation of moisture absorbed in the porous polyurethane foam, and it has not been reported in the literature.^{4,6} Because this step was not an intrinsic reaction of the polyurethane decomposition, it is not considered further in the following sections. As shown in Table II, the second peak in the DTG curves occurred from 346.7 to 524.7 K, the third occurred in the temperature range 479.4–737.9 K, and the fourth occurred in the range 654.2–1051.5 K. We discuss the reactions occurring in these three peaks by taking the curves at a heating rate of 10 K/min as the example.

Figure 2 presents the TG/DTG and DSC curves of the polyurethane foam decomposition at a heating rate of 10 K/min under nitrogen and air atmospheres. The moisture evaporation stage is not presented in this figure. It is obvious that the DTG curve in air presented three mass loss peaks (one minor peak and two major peaks), whereas the DTG curve in nitrogen presented two mass loss peaks (one minor peak and one major peak with two shoulders). The two DTG curves almost coincided in the first distinct mass loss peak from 343 to 490 K; this indicated that the mechanism controlling the mass loss process in this temperature range was independent of oxygen presence and was due to the

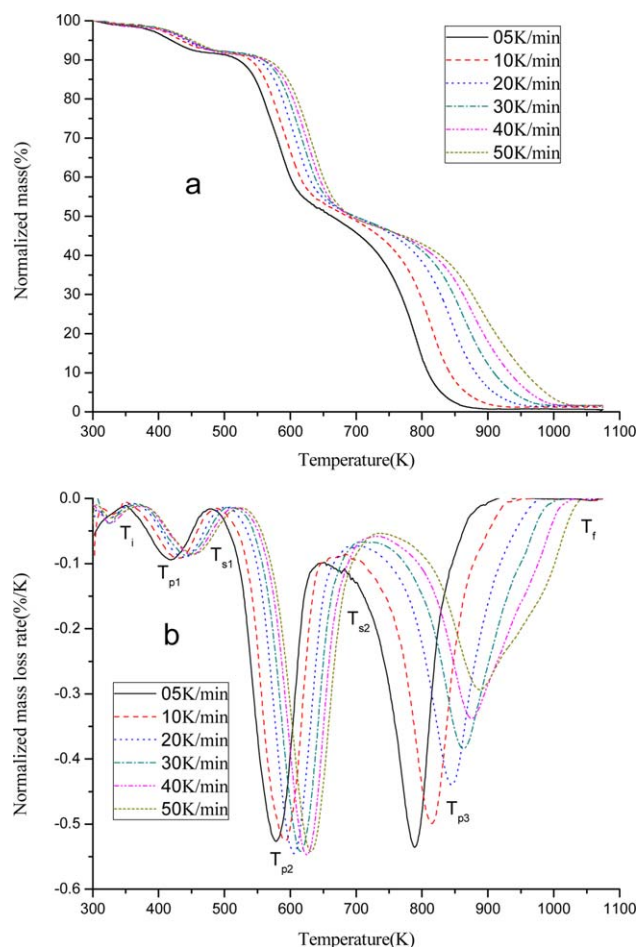


Figure 1. (a) thermogravimetry (TG) and (b) derivative thermogravimetry (DTG) curves of the polyurethane foam decomposition at different heating rates under air. (The temperatures labeled in part b are listed in Table II). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degradation of the polymer structure. The mass loss of this stage was approximately 8% of the initial mass and may have been due to the bond fission of the weakest link in the chain. It was reported that biuret and allophanate were the thermally weakest links in the matrix of flexible polyurethane foams, and the dissociation of both types generally takes place at about 110°C (383 K) and is completed by about 170°C (443 K).²

Compared with that of the DTG curve in air, the second peak of the DTG curve in nitrogen occurred at a higher and wider temperature range. In this stage, the organic components of the polyurethane foam decomposed to the volatiles and solid residues, in which the residues contained char and also polyether or polyester (soft segment). The dissociation of the urethane ground is one of the first reactions when polyurethanes are heated above 473 K.² Up to 473 K, random bond scission occurs at the urethane links, whereas unzipping of the polyether chain occurs in the range 523 to 593 K. It is agreed that the urethane linkage in polyurethanes decomposes by one or more of three mechanisms: depolymerization; dissociation to a pri-

mary amine, an olefin, and CO₂; and the extrusion of CO₂, which leads to the replacement of the urethane link by a secondary amine group.^{2,7} The complexities of the reactions were reflected by the two shoulders in the second peak of the DTG curve in nitrogen. This peak spanned from 490 to 873 K with a long tail. However, the second peak of the DTG curve in air only spanned from 490 to 690 K, and then, the third peak at 690–973 K followed; this indicated that the presence of oxygen changed the decomposition reactions. Backus et al.⁸ pointed that foam decomposes into volatile products in two main stages. The first stage occurs at 225–400°C (498–673 K), and the second stage occurs at 400–600°C (673–873 K).⁸ The temperature ranges of these two stages were close to but slightly smaller than the ranges of the corresponding stages shown in Figure 2 because the flowing rate of the purge gas in ref. 8 (0.35 standard cubic foot per hour (SCFH) air flow, equal to 165 mL/min) was higher than that in our experiments (50 mL/min). The oxidative process was obvious from the DSC measurements. The DSC curve in air presented a distinct exothermic process, whereas that in nitrogen showed a very small endothermic peak. The DSC curve in air also presented a distinct exothermic peak in the temperature range corresponding to the third mass loss peak of the DTG curve in air. This stage could be attributed to the oxidative degradation of the residue material; this was in accordance with Duquesne et al.⁹ We also found that the final residue of from the TG curve in nitrogen was 17% of the initial mass, whereas the residue in air was nearly zero.

Thermal decomposition has long been recognized to play an important role in the ignition process of solid materials. It not only provides necessary volatile fuels for ignition processes but also determines the quantity of heat available for inducing the ignition process. For this reason, understanding the behavior and kinetics of thermal decomposition is of key importance to studying the ignition processes. The second mass loss peak of the DTG curve in air was the most important decomposition process during the ignition of the polyurethane foam by hot particles. So it is important to study the kinetics and the reaction heat of the polyurethane decomposition, especially for the second decomposition stage.

Model-Free Analysis of Polyurethane Decomposition

Model-free or isoconversional methods can calculate the activation energy (E_a) without prior knowledge of the reaction mechanism.^{10,11} The classical isoconversional methods, Friedman method, and Ozawa–Flynn–Wall method were used here to calculate the distribution of E_a values along with the conversion.

According to nonisothermal kinetic theory, the thermal decomposition kinetic equation of solid-state material follows:

$$\frac{d\alpha}{dT} = kf(\alpha) = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (1)$$

where β is the constant heating rate (K/min), E_a is the activation energy (kJ/mol), A is the pre-exponential factor (s⁻¹), T is the absolute temperature (K), R is the universal gas constant (8.314 J·mol⁻¹·K⁻¹), and $f(\alpha)$ is a reaction model function,

Table II. Characteristic Parameters of the TG/DTG Curves of the Polyurethane Foam Decomposition under Air

	β (K/min)	Initial temperature (K)	Peak temperature (K)	Final temperature (K)	Ratio of the mass loss to the total mass loss (%)
First stage	05	346.7	413.9	479.4	7.1
	10	354	433.8	490.9	7.0
	20	358.5	439	498.9	6.8
	30	358	444	504.5	7.1
	40	373.6	448.8	518.2	7.1
	50	381.8	450.9	524.7	7.3
Second stage	05	479.4	583.2	654.2	41.2
	10	490.9	586.9	690.6	42.9
	20	498.9	604.7	698.9	42.8
	30	504.5	618.4	706.1	43.3
	40	518.2	626.4	733.8	44.8
	50	524.7	631.5	737.9	45.1
Third stage	05	654.2	789.7	940.4	50.4
	10	690.6	814.2	971.9	49.3
	20	698.9	844.8	982.8	49.1
	30	706.1	863.1	1009.6	48.6
	40	733.8	875.9	1035.1	46.4
	50	737.9	887.9	1051.5	46.1

which has various forms depending on the physical mechanism. α is calculated from the TG curve:

$$\alpha = (m_0 - m) / (m_0 - m_\infty) \quad (2)$$

where m_0 , m , and m_∞ are the initial, instantaneous, and final sample masses, respectively.

Friedman's Method (Differential Method)¹². The logarithm of eq. (1) gives

$$\ln \left(\frac{\beta d\alpha}{dT} \right) = \ln [Af(\alpha)] - \frac{E_a}{RT} \quad (3)$$

The apparent E_a is obtained by plotting $\ln \left(\frac{\beta d\alpha}{dT} \right)$ versus $1/T$ at a given α .

Ozawa–Flynn–Wall Method (Integral Method)^{13,14}. Setting

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp(-E_a/RT) dT = \frac{AE_a}{\beta R} P \left(\frac{E_a}{RT} \right) \quad (4)$$

Here $G(\alpha)$ is integral function of reaction mechanism, P is the temperature integral, T_0 is the room temperature. When we consider the Doyle approximation on the function,¹⁵ we get

$$P \left(\frac{E_a}{RT} \right) = 0.00484 e^{-1.0516 \frac{E_a}{RT}} \quad (5)$$

The Ozawa equation can be obtained by the combination of eq. (4) with eq. (5):

$$\log \beta = \log \left(\frac{AE_a}{RG(\alpha)} \right) - 2.315 - 0.4567 \frac{E_a}{RT} \quad (6)$$

E_a is obtained by the plotting of $\log \beta$ versus $1/T$ at a given α .

Figure 3 shows the E_a distribution calculated by the Friedman and Ozawa–Flynn–Wall methods. Despite some differences, the two curves of E_a showed similar variation tendencies and could be divided into three segments. The division points of these segments were $\alpha = 0.1$ and 0.5 . This feature was clearly in accordance with the three significant mass loss peaks of the DTG curves. A three-step reaction was applied in the model-fitting analysis of polyurethane decomposition, whereas the E_a values in Figure 3 were used as the initial values for the optimization computation of model-fitting analysis.

Model-Fitting Analysis of the Polyurethane Decomposition

From the analysis of the previous two sections, the thermal decomposition of the polyurethane foam in air presented three main stages: the loss of low-stability organic compounds (bond fission of the weakest link in the chain), the oxidative degradation of the main organic components, and the oxidative degradation of the residue material. It could be modeled by three-step consecutive reactions, as Scheme 1 shows. In Scheme 1, S represents the polyurethane foam, S_0 represents the original mass of polyurethane foam, V_i represents the volatiles, and R_i represents the solid residues of each reaction. While k_i ($i = 1, 2, 3$) represents the rate of i -th reaction.

For the mass loss process of each fraction, it is necessary to solve eqs. (7–9) for each fraction to describe the polyurethane foam decomposition:

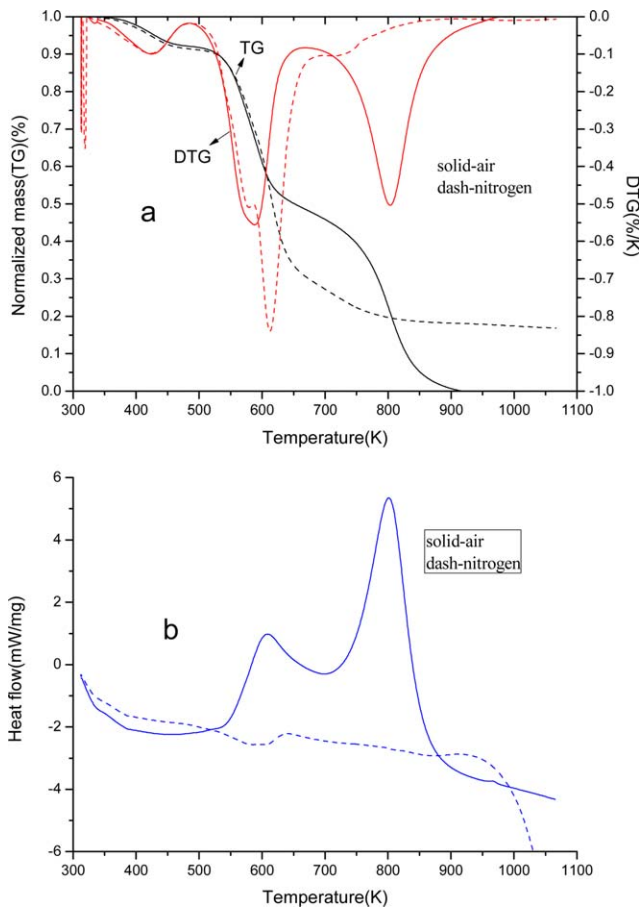


Figure 2. (a) TG/DTG and (b) DSC curves of the polyurethane foam decomposition at a heating rate of 10 K/min under air and nitrogen atmospheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\frac{d(S/S_0)}{dt} = -k_1(S/S_0)^{n_1} \quad (7)$$

$$\frac{d[R_1/(a_1S_0)]}{dt} = k_1(S/S_0)^{n_1} - k_2[R_1/(a_1S_0)]^{n_2} \quad (8)$$

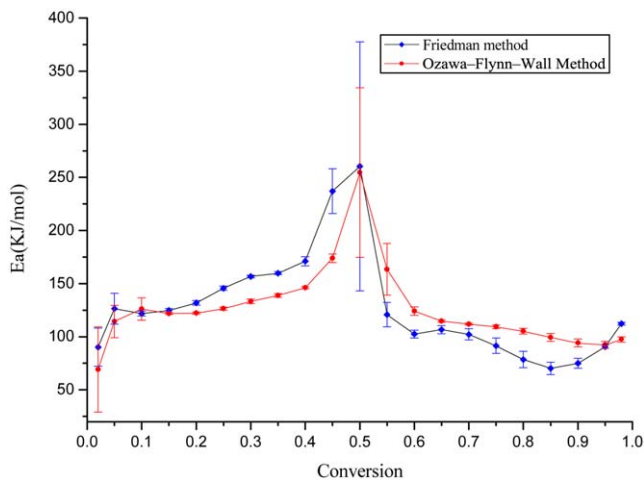
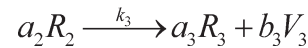
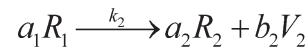
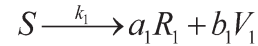


Figure 3. Relationship between E_a and α under air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1. A scheme of three consecutive reactions to simulate the polyurethane foam decomposition kinetics.

$$\frac{d[R_2/(a_2S_0)]}{dt} = k_2(R_1/(a_1S_0))^{n_2} - k_3[R_2/(a_2S_0)]^{n_3} \quad (9)$$

where the variable $a = (m_0 - m)/(m_0 - m_\infty) = V/V_\infty$ is the degree of transformation and $a_i = V_i/V_\infty$ corresponds to the degree of transformation of the i th fraction ($i = 1, 2, \text{ or } 3$). b_i ($i = 1, 2, 3$) is the mass fraction of volatile generated by the i -th reaction.

According to the mass conservation theorem, eqs. (10–12) can be obtained:^{3,16}

$$\frac{S}{S_0} = 1 - \frac{V_1}{b_1} = 1 - \frac{V_1}{V_{1\infty}} \quad (10)$$

$$\frac{R_1}{S_0} = a_1 \frac{V_1}{b_1} - a_1 \frac{V_2}{b_2} = a_1 \left(\frac{V_1}{V_{1\infty}} - \frac{V_2}{V_{2\infty}} \right) \quad (11)$$

$$\frac{R_2}{S_0} = a_2 \frac{V_2}{b_2} - a_2 \frac{V_3}{b_3} = a_2 \left(\frac{V_2}{V_{2\infty}} - \frac{V_3}{V_{3\infty}} \right) \quad (12)$$

Here V_i infinite is the maximum mass of volatiles of i th reaction. When eqs. (7–12) are combined, the conversion rate of the three reactions can be described as follows:

$$\frac{d\alpha_1}{dT} = \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right) (1 - \alpha_1)^{n_1} \quad (13)$$

$$\frac{d\alpha_2}{dT} = \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}\right) (\alpha_1 - \alpha_2)^{n_2} \quad (14)$$

$$\frac{d\alpha_3}{dT} = \frac{A_3}{\beta} \exp\left(-\frac{E_3}{RT}\right) (\alpha_2 - \alpha_3)^{n_3} \quad (15)$$

Here n_i corresponds to the order of i th reaction. The overall rate of conversion is given by

$$\frac{d\alpha}{dT} = r_1 \frac{d\alpha_1}{dT} + r_2 \frac{d\alpha_2}{dT} + (1 - r_1 - r_2) \frac{d\alpha_2}{dT} \quad (16)$$

where $r_i = (m_{i0} - m_{i\infty})/(m_0 - m_\infty)$ and r_i is the yield coefficient of fraction i with $r_i < 1$ and $\sum_{i=1}^n r_i = 0$, where $i = 1$ or 2 . The parameter r_i reflects the ratio of the mass loss of i to the total mass loss during the decomposition process.

The simultaneous determination of the kinetic parameters for each fraction was performed by minimization of the S_{DTG} coefficient of the difference of experimental and calculated derivative thermogravimetric data ($T, d\alpha/dT$):

Table III. Apparent Kinetic Parameters of Each Reaction in Scheme 1 for the Polyurethane Foam Decomposition in Air

	Weakest bond fission	Oxidative degradation of organic components	Oxidative degradation of residue material	Deviation (%)
$\log A$ (s^{-1})	7.56	13.34	6.86	
E (kJ/mol)	78.126	171.22	143.27	
n	2.91	2.98	1.31	2.8
r	0.0809	0.4398	0.4793	

$$S_{DTG} = \sum_j S_j = \sum_j \sum_k \left[(d\alpha/dT)^{Exp} - (d\alpha/dT)^{Calcd} \right]^2 \quad (17)$$

where the superscripts Exp and Calcd indicate the experimental and calculated values, respectively; j is the number of experimental curves, and k is the number of data points of each experimental curve. The minimization of S_{DTG} was carried out with the Levenberg–Marquardt nonlinear fitting algorithm in MATLAB software.¹⁷

One parameter (Dev) is proposed to evaluate the deviation between the experimental and calculated curves as follows:

$$Dev = 100\% \left[\frac{\sum_j \frac{\sqrt{S_j / (Z_j - N_j)}}{\max(-(d\alpha/dT)^{Exp})}}{j} \right] \quad (18)$$

where Z_j is the number of data points and N_j is the number of independent parameters needed to be determined in the simulation. Max is the maximum of the corresponding function, S_j is S_{DTGj} .

The simulated curves were generated by eq. (17) and were compared to the experimental curves. The difference quantity shown as eq. (18) was minimized through optimization iteration computation. Then, the optimum kinetic parameters could be obtained and are shown in Table III. As an example, Figure 4 shows the experimental and calculated curves of the conversion and differential conversion at a 10 K/min heating rate; these were in a good agreement.

For the stage of oxidative degradation of the main organic components, the kinetic parameters were comparable with the literature data. It is acknowledged that in an inert atmosphere, the pyrolysis of polyurethane foam can be modeled by two stages, whose apparent activations were 133.6 and 190.4 kJ/mol, respectively.^{4,18} Obviously, these values were somewhat higher than the calculated results in this study, and this may have been due to the reactivity difference under the effect of air. Branca et al.¹⁹ studied the reaction kinetics of rigid polyurethane foam during combustion and obtained the kinetic parameters for the three reaction steps: (I) $A_1 = 2.6 \times 10^{12} s^{-1}$, $E_1 = 133.6$ kJ/mol, (II) $A_2 = 3.3 \times 10^4 s^{-1}$, $E_2 = 81$ kJ/mol, (III) $A_3 = 8.7 \times 10^8 s^{-1}$, and $E_3 = 180$ kJ/mol (Here A_1 , A_2 , A_3 and E_1 , E_2 , E_3 respectively represented frequency factor and activation energy of each reaction step). The difference of these results from the data in this article may be attributed to the discrepancy of gas flow and the precision of the thermogravimetric data. Pattnaik et al.²⁰ studied the decomposition of several polymers, including polyurethane, and considered two processes and different mechanisms. Some of the apparent E_a values were in the same magnitude as those found in this article.

Reaction Heat

The heat flow rate data obtained from the DSC measurements were the sum of two components: the energy necessary to heat up the sample and the heat emission from the reaction.²¹ This can be expressed as follows:

$$\frac{dQ/dt}{m_0} = \frac{mc_{p,s}(dT/dt) + (dm/dt)H_p}{m_0} \quad (19)$$

where Q is the caloric requirement of the decomposition of polyurethane foam (J), $c_{p,s}$ is the specific heat capacity of the

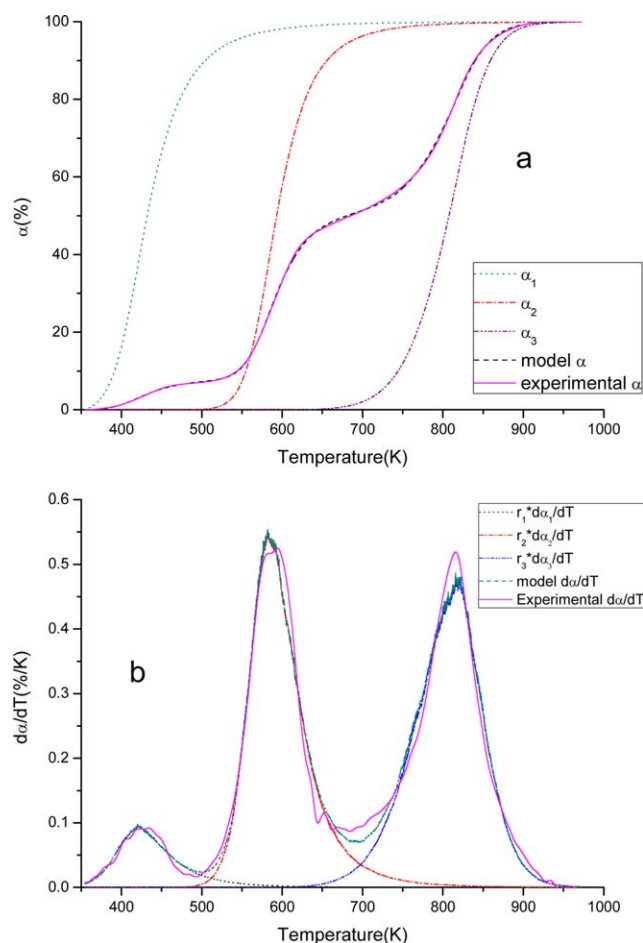


Figure 4. Experimental and simulated (a) conversion and (b) differential conversion curves of the polyurethane foam decomposition at 10 K/min under an air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

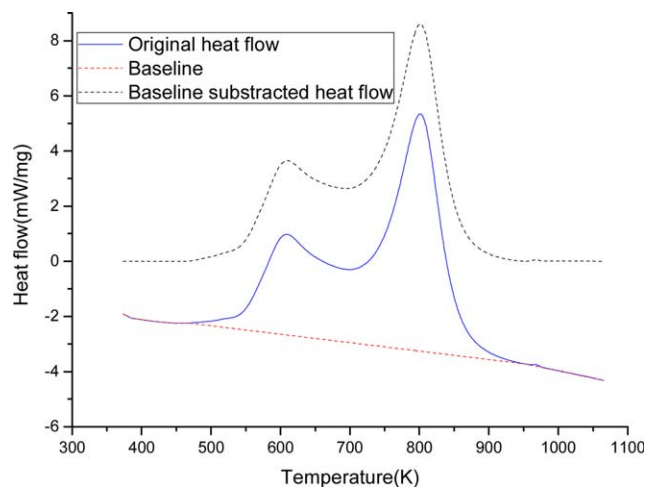


Figure 5. Calibration of the DSC curve by subtraction of the baseline. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sample ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$), and H_p is the reaction heat of the decomposition of the polyurethane foam ($\text{J}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$). As shown in Figure 2, it is obvious that the energy necessary to heat up the sample was much lower than the exothermic effect of the oxidative degradation stages of the main organic components or the residue material; this was in accordance with the results of He et al.²² Thus, $mc_{p,s}dT/dt$ in eq. (19) can be ignored, and the reaction heat can be calculated by the following equation:

$$H_p = \frac{(dQ/dt)/m_0}{(dm/dt)/m_0} \quad (20)$$

The average reaction heat (\bar{H}_p) of each stage of polyurethane thermal decomposition can be calculated from DSC curves in the corresponding temperature range of the stage,²³ that is

$$\bar{H}_p = \frac{\int (dQ/dt)/m_0}{\int (dm/dt)/m_0} = \frac{\int (dQ/dt)/m_0}{\Delta m/m_0} = \frac{\int (\beta dQ/dT)/m_0}{\Delta m/m_0} \quad (21)$$

The numerator in the right-hand side of eq. (21) can be obtained by the integral of the calibrated DSC curve (the experimental DSC curve in air subtracted the baseline, as shown in Figure 5) in the range of each stage. The denominator (Δm) is the corresponding mass loss of TG data in the same temperature range.

The initial and final temperature ranges of the two stages are listed in Table IV, which also shows the corresponding mass loss ratio. The reaction heat of the first peak of DSC curve was 5443.09 kJ/kg; this represents the exothermic heat of oxidative degradation of the main organic components. The reaction heat

of the second peak of the DSC curve was 10,518.51 kJ/kg, which was the reaction heat of the oxidative degradation of the residue material.

Ignition Criterion of Polyurethane by a Hot Particle

There is a thermal requirement for a hot particle to ignite polyurethane foam; that is, the heat reserve of the particle should exceed a critical value. For a given initial temperature of a hot particle (T_p), the minimum particle size (r_{crit}) for ignition of polyurethane foam could be obtained by the Frank–Kamenetskii parameter (δ_{cr}):

$$r_{\text{crit}} = \delta_{\text{cr}} \sqrt{\frac{\lambda_0}{\rho_0 A \bar{H}_p} \frac{RT_p^2}{E} \exp\left(\frac{E}{RT_p^2}\right)} \quad (22)$$

where λ is the thermal conductivity and ρ is the density. The subscript p corresponds to the particle, and the subscript 0 corresponds to the polyurethane foam. The critical Frank–Kamenetskii parameter (δ_{cr}) for the ignition of solid combustibles by a hot particle was proposed by Goldshleger et al.:²⁴

$$\delta_{\text{cr}}^* = 0.4 \sqrt{b^2 + 0.25n(n+1)(b+0.1b^3)} \quad (23)$$

$$[\theta_p + 2.25(n-1)]^2 (1 + 0.5\beta\theta_p)$$

$$\delta_{\text{cr}} = \delta_{\text{cr}}^* \left[1 + \frac{(\theta_p - 3)^2 b(n+1)}{30\lambda_r^{2/3}(1+3b^{2/3})} \right] \quad (24)$$

where

$$\theta_p = \frac{E}{RT_p^2} (T_p - T_0) \quad (25)$$

$$b = \frac{\rho_0 c_0}{\rho_p c_p} \quad (26)$$

$$\lambda_r = \frac{\lambda_p}{\lambda_0} \quad (27)$$

$$\beta = \frac{RT_p}{E} \quad (28)$$

where n is a factor whose value depends on the shape of the hot particle ($n = 2$ for a spherical particle). θ_p , b , λ_r , and β are the non-dimensional parameters. The parameters for polyurethane foam and Al_2O_3 particles are listed as follows:

Thermal conductivity: $\lambda_0 = 0.03 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $\lambda_p = 12.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.²⁵

Density: $\rho_0 = 100 \text{ kg/m}^3$, $\rho_p = 3900 \text{ kg/m}^3$.²⁵

Table IV. Exothermic Heat of the Polyurethane Foam Decomposition in Air

	Temperature range (K)	Ratio of mass loss (%)	Reaction heat (kJ/kg)
Oxidative degradation of the organic components	481.2–693.8	45.74	5443.09
Oxidative degradation of residue material	693.8–928.7	46.75	10,518.51

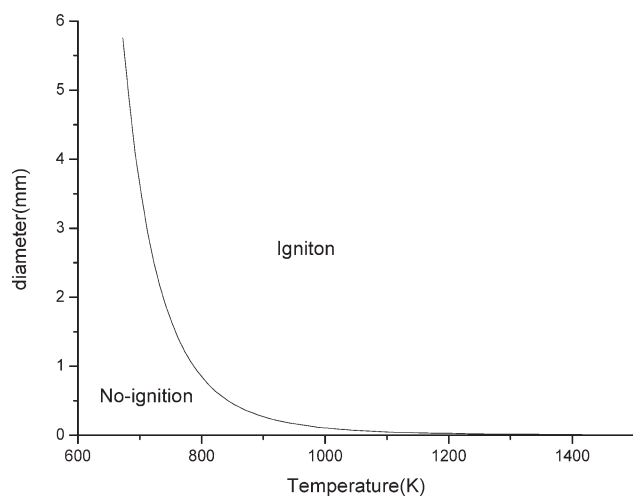


Figure 6. Criterion for a hot aluminum oxide spherical particle to ignite polyurethane foam.

Heat capacity: $c_0 = 1460 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$, $c_p = 765 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$.²⁶

Al_2O_3 particles are products of firework displays. When fireworks explode, the Al powders in the fireworks will burn and form Al_2O_3 particles. The numerical results of the accidental ignition of polyurethane foam by a hot Al_2O_3 particle are shown in Figure 6 via the plotting of r_{crit} versus T on the basis of eq. (22). The diameter of a spherical particle of aluminum oxide at 773 K would need to be about 1.2 mm to ignite the polyurethane foam in which it was embedded.

The critical diameter calculation for the ignition of solid combustibles by a hot particle can be extended and generalized once it is satisfied with the limited parameter ranges put forward by Goldshleger et al.²⁴

CONCLUSIONS

In this study, the thermal decomposition characteristics of polyurethane foam under an air atmosphere were determined with nonisothermal thermal analysis. Kinetic analysis was carried out for polyurethane foam decomposition with the model-free and nonlinear model-fitting methods.

The thermal decomposition of polyurethane foam under air presents three main stages: the loss of low-stability organic compounds (bond fission of the weakest link in the chain), oxidative degradation of the main organic components, and oxidative degradation of the residue material. The model-free isoconversional, Friedman's, and Ozawa–Flynn–Wall methods also proved the three-stage decomposition, and the apparent E_a values for the thermal decomposition of the polyurethane foam varied from 60.17 to 260.39 kJ/mol, depending on the extent of conversion. A scheme containing three consecutive reactions was proposed to simulate the decomposition kinetics. The kinetic parameters for each reaction were calculated by the nonlinear model-fitting method. The good agreement between the experimental and simulated curves proved the validity of the proposed scheme.

The net reaction heat of the polyurethane decomposition in air was calculated from a DSC curve. The reaction heats of the two significant exothermic stages (the oxidative degradation of the main organic components and the oxidative degradation of residue material) were 5443.09 and 10,518.51 kJ/mol, respectively.

The reaction kinetics and heat of oxidative degradation stage of polyurethane in air were used to evaluate the ignition risk of polyurethane foam by a hot particle. The critical diameter of an aluminum oxide spherical particle needed to ignite polyurethane foam was calculated by the hot-spot ignition theory. For a particle at a given temperature, the particle diameter should exceed a critical value to ignite polyurethane foam.

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