

Thermal Degradation Kinetics of Rigid Polyurethane Foams Blown with Water

Xiao-Bin Li,^{1,2} Hong-Bin Cao,¹ Yi Zhang¹

¹Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100080, China

²Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

Received 29 November 2005; accepted 12 February 2006

DOI 10.1002/app.24379

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The thermal decomposition behavior of rigid polyurethane foams blown with water was studied by dynamic thermogravimetric analysis (TGA) in both nitrogen and air atmosphere at several heating rates ranging from room temperature to 800°C. The kinetic parameters, such as activation energy (E), degradation order (n), and pre-exponential factor (A) were calculated by three single heating rate techniques of Friedman, Chang, and Coats-Redfern, respectively. Compared with the decomposition process in nitrogen, the decomposition of foams in air exhibits two distinct weight loss stages. The decomposition in nitrogen has the same mechanism as the first stage weight loss in air, but the second decomposition stage in air appears to be dominated by the thermo-oxidative degradation. The heating rates have insignificant

effect on the kinetic parameters except that the kinetic parameters at 5°C/min have higher values in nitrogen and lower values in air, indicating different degradation kinetics in nitrogen and air. The kinetic parameters of foam samples blown with different water level in formulation decline firstly and then increase when water level increases from 3.0 to 7.0 pph. According to the prediction for lifetime and half-life time of foams, water-blown rigid foams have excellent thermostability, when used as insulation materials below 100°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4149–4156, 2006

Key words: rigid polyurethane foams; thermogravimetric analysis; thermal degradation; degradation kinetics

INTRODUCTION

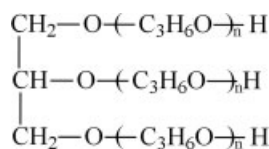
Rigid polyurethane foams (PUFs) have been used for many applications such as pipeline insulation materials, automotive parts, solar water heater, and construction materials,^{1,2} due to their desirable physical properties. Traditional rigid PUF is produced by the reaction of a polyol and polymeric 4,4'-diphenylmethane diisocyanate (PMDI) with chlorofluorocarbons (CFCs), in particular trichlorofluoromethane (CFC-11) and/or HCFC-141b as blowing agents. However, the CFC blowing agents contain halogens, which may deplete the ozone layer and cause environmental issues such as global warming.³ Differing from CFCs, water, a chemical blowing agent, can also be used to make cellular rigid PUF by reaction with PMDI, which generates carbon dioxide to form the bubbles. Since water is a non-ozone depleting, non-toxic, and cheap blowing agent, some researches on

water-blown rigid foams and their applications have been performed.^{4–6}

Unfortunately, the rigid PUFs often have relatively low thermal stability, primarily due to the presence of urethane bonds. Previous work has focused on the pyrolysis characterization of polyurethane materials by using different analytical techniques. Ohtani et al.⁷ and Font et al.⁸ studied several polyurethane by pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS). Hatchett et al.⁹ examined the chemical composition, density, and modulus of PUFs, and analyzed the remaining composition of foam using FT-IR spectroscopy. Branca et al.¹⁰ investigated the reaction kinetics and morphological changes of rigid PUF during combustion. Recently, Tang et al.¹¹ and Pielichowski et al.¹² used thermogravimetric analysis (TGA), Py-GC/MS, and FT-IR to study thermal degradation behavior of rigid PUFs blown with several physical blowing agents, such as HCFC-141b and pentane. However, thermal degradation kinetics of rigid PUFs blown with water was seldom referred to. In this article, the rigid PUFs blown with different water level were prepared, and the kinetics of thermal degradation of foams in nitrogen and air from room temperature to 800°C were discussed in detail by three single heating rate methods under the aid of TGA.

Correspondence to: H.-B. Cao (hbcao@home.ipe.ac.cn).

Contract grant sponsor: Joint Research Foundation of CAS and Hebei Province, China; contract grant number: 2004-015.



Scheme 1

BACKGROUND

According to the reaction theory, kinetic equation for solid decomposition can be usually expressed as:

$$dx/dt = kf(x) \quad (1)$$

where k is the reaction constant (min^{-1}), x is the weight loss of the foam undergoing degradation at time t , and $f(x)$ depends on the particular degradation mechanism.

Usually, $f(x)$ is considered to be proportional to the amount of available material for decomposition. Therefore,

$$f(x) = (1-x)^n \quad (2)$$

where n is the reaction order. According to the Arrhenius equation,

$$k = A \exp(-E/RT) \quad (3)$$

where A is the pre-exponential factor, E is the apparent activation energy, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K).

The combination of eqs. (1)–(3) gives

$$dx/dt = A \exp(-E/RT)(1-x)^n \quad (4)$$

In eq. (4), the heating rate constant $\beta = dT/dt$, then we obtain

$$dx/dT = A/\beta \exp(-E/RT)(1-x)^n \quad (5)$$

Friedman method¹³

Taking logarithms of eq. (4) yields:

$$\ln(dx/dt) = \ln A + n \ln(1-x) - E/RT \quad (6)$$

From this equation, it is easy to determine the activation energy value by plotting $\ln(dx/dt)$ against $1/T$. The slope of line is $-E/R$. Additionally, the $-E/(nR)$ value can be obtained from the slope of a linear plot of $\ln(1-x)$ against $1/T$.

Chang method¹⁴

By rearranging eq. (6), the following equation can be obtained:

$$\ln[(dx/dt)/(1-x)^n] = \ln A - E/RT \quad (7)$$

In eq. (7), reaction order n is chosen in advance. The linear regression of $\ln[(dx/dt)/(1-x)^n]$ against $1/T$ will give the apparent activation energy E and pre-exponential A , if the correlation coefficient of regression is close to unity. The suitable value of reaction order is also obtained.

Coats-Redfern method^{15,16}

By integrating eq. (5), the following equation is obtained:

$$\int_0^x dx/(1-x)^n = (A/\beta) \int_0^T \exp(-E/RT) dT \quad (8)$$

In eq. (8), the right hand side can not be integrated directly, but is written as,

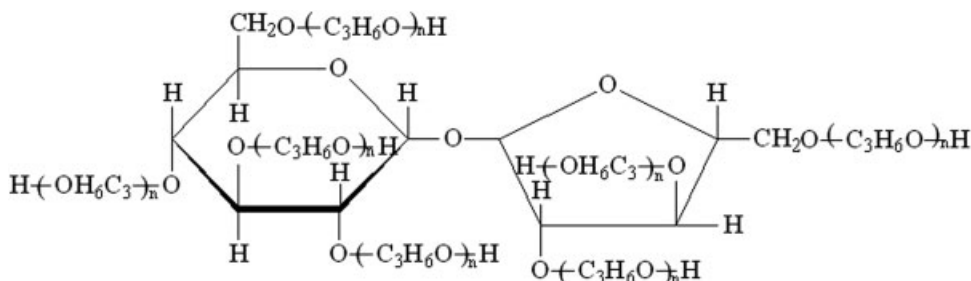
$$\int_0^x dx/(1-x)^n = (AE/\beta R) \int_0^\infty \exp(-\mu)\mu^{-2} d\mu \quad (9)$$

where, $\mu = E/RT$, and the approximate integration of $\int_0^\infty \exp(-\mu)\mu^{-2} d\mu = \mu^{-1} \exp(-\mu)[1/\mu - 2/\mu^2]$. So, eq. (9) can be easily integrated as the following expression:

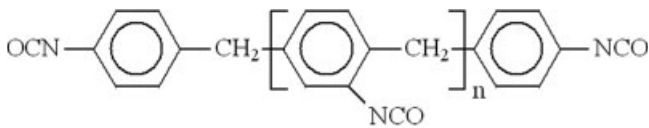
$$\begin{aligned} \text{For } n = 1, \\ -\ln(1-x) = (ART^2/\beta E)(1 - 2RT/E) \exp(-E/RT) \end{aligned} \quad (10)$$

Taking logarithms of eq. (10) yields:

$$\ln \left[\frac{-\ln(1-x)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} (1 - 2RT/E) \right] - E/RT \quad (11)$$



Scheme 2



Scheme 3

Similarly, for $n \neq 1$,

$$\ln \left[\frac{1 - (1-x)^{1-n}}{T^2(1-n)} \right] = \ln \left[\frac{AR}{\beta E} (1 - 2RT/E) \right] - E/RT \quad (12)$$

Usually, $\ln \left[\frac{AR}{\beta E} (1 - 2RT/E) \right]$ is considered as a constant in test temperature. Thus, a plot of $\ln \left[\frac{-\ln(1-x)}{T^2} \right]$ ($n = 1$) or $\ln \left[\frac{1 - (1-x)^{1-n}}{T^2(1-n)} \right]$ ($n \neq 1$) against $1/T$ should be a straight line with a slope of $-E/R$, if the decomposition order n is correctly selected.

Determination of half-life time $t_{1/2}$ ¹⁷

According to eq. (4), the half-life time $t_{1/2}$ can be obtained from following equation:

$$t_{1/2} = (1 - 0.5^{1-n})/[k(1-n)] \quad (n \neq 1) \quad (13)$$

$$t_{1/2} = \ln 2/k = 0.693/k \quad (n = 1) \quad (14)$$

Determination of lifetime t_f ¹⁷

The lifetime t_f of foam is generally defined as the time that weight loss of foam reaches 5%. Therefore,

$$t_f = (1 - 0.95^{1-n})/[k(1-n)] \quad (n \neq 1) \quad (15)$$

$$t_f = 0.0513/k \quad (n = 1) \quad (16)$$

EXPERIMENTAL

Materials

Glycerin/sugar-based polyether polyol with a hydroxyl value 365 ± 15 mg KOH/g synthesized in our laboratory (structural formula shown in Schemes

TABLE I
Formulation Data of the Rigid PUFs

Component	3-W	5-W	7-W
Polyether polyol (pph) ^a	100	100	100
Triethylene diamine (pph)	0.2	0.2	0.2
B8462 (pph)	2.0	2.0	2.0
Glycerin (pph)	1.0	1.0	1.0
Water (pph)	3.0	5.0	7.0
Dibutyltin dilaurate, pph	0.1	0.1	0.1
Isocyanate index (—OH/—NCO)	1.05	1.05	1.05

^a pph, based on 100 parts polyether polyol by weight.

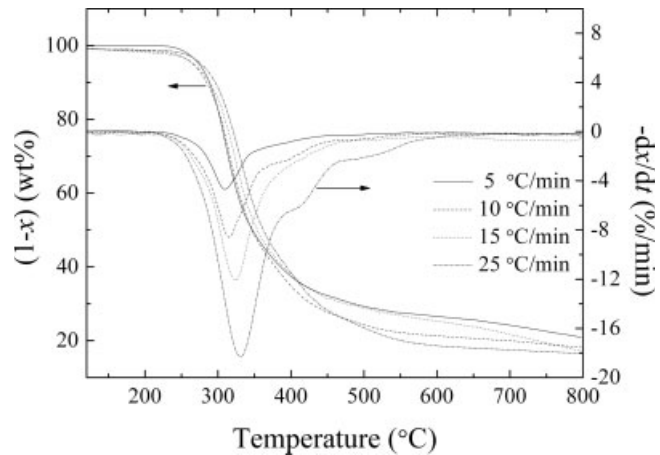


Figure 1 TG and DTG curves of 5-W foam in nitrogen.

1 and 2) was used. Polymeric 4,4'-diphenylmethane diisocyanate (PMDI) was obtained from Huntsman Corp. (Beijing, China; see Scheme 3). Triethylene diamine, an amine catalyst, dissolved in diethylene glycol to 33 wt % was supplied by Air Products Corp. (Beijing, China). B8462, a silicone surfactant, was supplied by Goldschmidt Corp. (Shanghai, China). Dibutyltin dilaurate, a tin catalyst, was supplied by Air Products Corp.

Preparation of rigid foam samples

All of PUF samples were synthesized with a one-shot method. The formulation used for PUFs preparation is presented in Table I. The mixture (consisting of polyether polyol, surfactant, catalyst, and water) was weighed and poured into a paper cup. Then, an appropriate PMDI was added to the mixture and vigorously stirred at 2500 rpm for 30 s. After mixing, the mixture was poured into a 200 mm

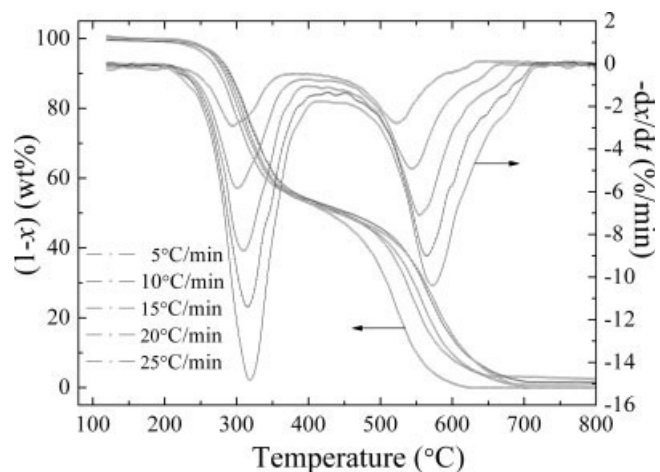


Figure 2 TG and DTG curves of 5-W foam in air.

TABLE II
Thermal Degradation Data of the 5-W Foam Samples at Varying Heating Rates in Nitrogen and Air

Heating rate (°C/min)	Test atmosphere	$T_d/T_{dm1}/T_{dm2}$ (°C)	Char yield at 800°C (wt %)	$(dx/dt)_{m1}$ (%/min)	$(dx/dT)_{m1}$ (%/°C)	$(dx/dt)_{m2}$ (%/min)	$(dx/dT)_{m2}$ (%/°C)
5	N ₂	280.9/309.4/–	22.0	4.7	0.94	–	–
10	N ₂	284.6/315.5/–	18.1	8.61	0.86	–	–
15	N ₂	290.6/325.4/–	17.1	12.29	0.82	–	–
25	N ₂	292.1/331.0/–	16.5	19.32	0.77	–	–
5	Air	263.7/294.6/523.5	0.0	2.92	0.58	2.79	0.56
10	Air	266.9/301.3/544.0	2.48	5.83	0.58	4.93	0.49
15	Air	273.5/309.4/554.5	0.96	8.76	0.58	7.1	0.47
20	Air	275.7/315.3/564.4	1.68	11.4	0.57	9.0	0.45
25	Air	277.8/318.0/572.9	0.0	14.16	0.57	10.11	0.4

× 200 mm × 80 mm mold with a detachable lid to produce free-rise foam. The foam was cured in this mold for 24 h at room temperature before being removed, cut, and tested.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on the NETZSCH-STA 449C thermal analyzer (made in Germany) under nitrogen and air atmosphere flowing at 60 mL/min. Samples (5.5 ± 0.5 mg) were heated from room temperature to 800°C at the heating rates of 5, 10, 15, 20, and 25°C/min, respectively.

RESULTS AND DISCUSSION

Characteristics of thermal stability

The TG and derivative thermogravimetry (DTG) curves of 5-W foam samples in nitrogen at heating rates of 5, 10, 15, 25°C/min and in air at 5, 10, 15, 20, 25°C/min are shown in Figures 1 and 2, respectively. The DTG curves for the samples decomposition in nitrogen show only single weight loss stage, while the DTG curves in air indicate that two main

weight loss stages occur during degradation, suggesting that degradation mechanism in air is much more complex than that in nitrogen. In nitrogen atmosphere, the samples do not show obvious weight loss until the temperature rises to 250°C, and the rate of weight loss begins to increase gradually to a maximum at about 320°C. Slight weight loss is observed after the samples are heated above 500°C. Attentively, the single DTG peak in nitrogen indicates there is a random sequence distribution in the foam backbone,¹⁸ because no distinct peaks representative of thermal degradation of individual polyether and PMDI are observed during the thermal decomposition of the rigid foam.

In air, the thermal characteristics at first reaction stage appear to be similar to that in nitrogen though the initial decomposition temperature (T_{di}) and temperature at the maximum degradation rate (T_{dm}) are lower in air than in nitrogen. It suggests that the first weight loss stage in air has the same thermal degradation mechanism with decomposition in nitrogen (controlled by pyrolysis mechanism). Different from degradation in nitrogen, however, in air there is also a second weight loss stage which appears between

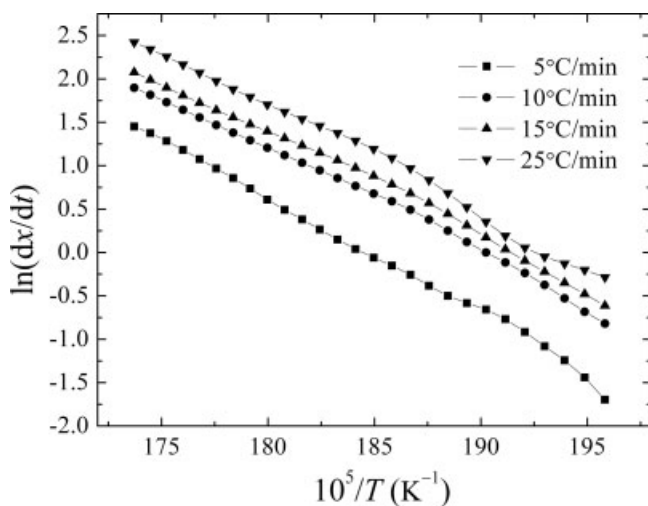


Figure 3 Friedman plots of $\ln(dx/dt)$ versus $1/T$ for the calculation of E at varying heating rates in nitrogen.

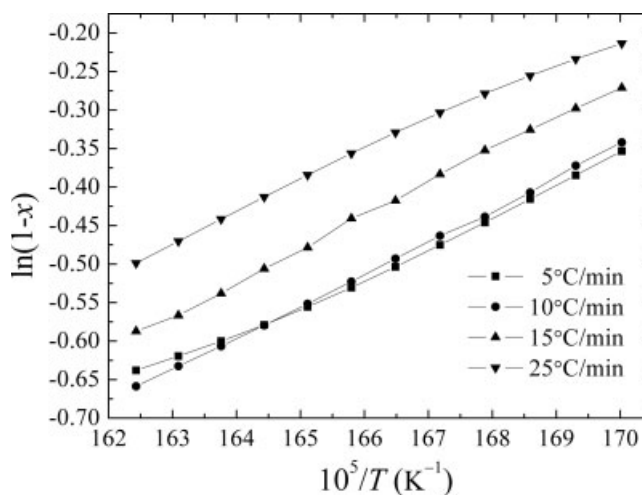


Figure 4 Friedman plots of $\ln(1-x)$ versus $1/T$ for the calculation of order n at varying heating rates in nitrogen.

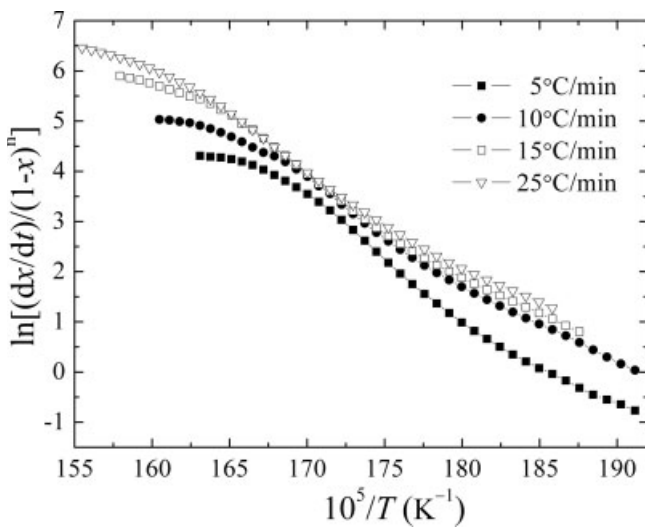


Figure 5 Chang plots of $\ln[(dx/dt)/(1-x)^n]$ versus $1/T$ for the calculation of kinetic parameters at varying heating rates in nitrogen.

480°C and 680°C with a maximum rate of weight loss at about 550°C. The second stage, which has less than 3% residue at 800°C, appears to be thermo-oxidative in nature since it does not exist in nitrogen atmosphere. Table II summarizes the thermal degradation data in nitrogen and air.

From Table II, the T_{di} and T_{dm} in nitrogen and air all increase as the heating rate increases. The char residue at 800°C decreases gradually from 22.0% to 16.5% in nitrogen, but no noticeable change is observed in air with the increase in heating rate probably due to their different degradation mechanism. Additionally, as shown in Table II, the $(dx/dt)_m$ values of DTG peaks maximum in nitrogen and air increase significantly but the $(dx/dT)_m$ values decrease slightly with the increase in heating rate.

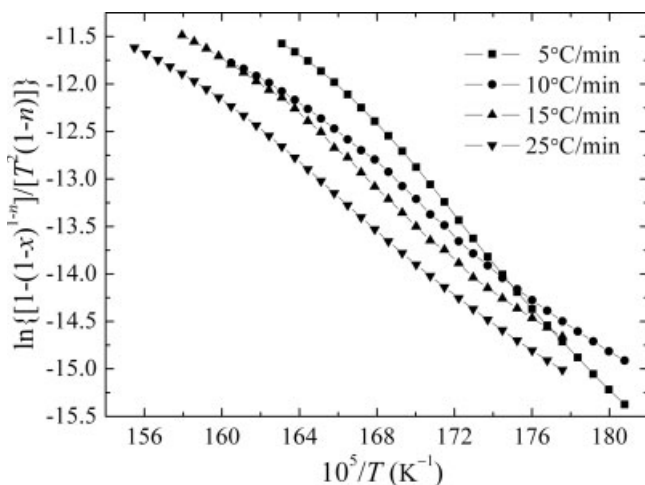


Figure 6 Coats-Redfern plots of $\ln\{[1-(1-x)^{1-n}]/[T^2(1-n)]\}$ versus $1/T$ for the calculation of kinetic parameters at varying heating rates in nitrogen.

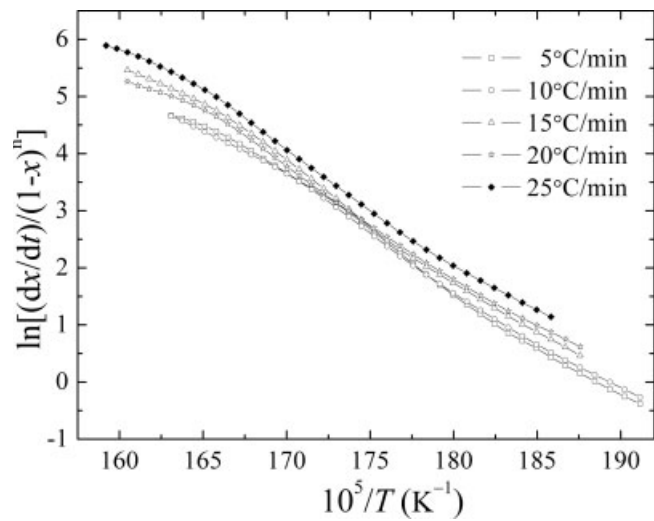


Figure 7 Chang plots of $\ln[(dx/dt)/(1-x)^n]$ versus $1/T$ for the calculation of kinetic parameters of 5-W foam at the first weight loss stage in air.

Kinetics of thermal degradation

Friedman, Chang, and Coats-Redfern methods can be used to determine all of the kinetic parameters for the pyrolysis of 5-W foam samples by using only one heating rate. Figures 3 and 4 show the function relationship of $\ln(dx/dt)$ and $\ln(1-x)$ versus $1/T$ proposed by Friedman technique at the different heating rates. Figures 5 and 6 indicate the relationship given by Chang and Coats-Redfern methods, respectively, where the degradation orders are chosen from 0.1 to 20 having a step 0.1 by a calculation procedure in computer. Attentively, the calculation of kinetic parameters in air should be separated into two parts due to the two weight loss stages. Figures 7 and 8 are the plots obtained by Chang technique at the first and second

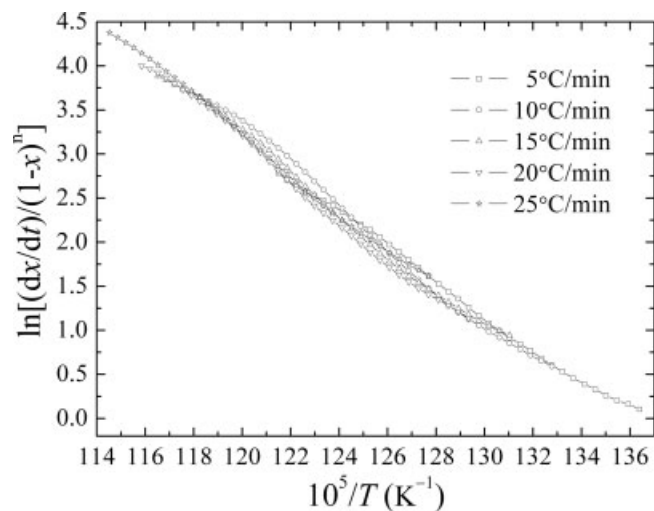


Figure 8 Chang plots of $\ln[(dx/dt)/(1-x)^n]$ versus $1/T$ for the calculation of kinetic parameters of 5-W foam at the second weight loss stage in air.

TABLE III
Kinetic Parameters of Thermal Degradation of 5-W Foam Samples in Nitrogen and Air Calculated by Three Single Heating Rate Methods

Heating rate (°C/min)	Test atmosphere	Friedman ^a		Chang ^a		Coats-Redfern ^a	
		First stage $E/n/\ln A$	Second stage $E/n/\ln A$	First stage $E/n/\ln A$	Second stage $E/n/\ln A$	First stage $E/n/\ln A$	Second stage $E/n/\ln A$
5	N ₂	119.3/3.8/27.2	–	172.2/5.8/38.5	–	188.1/5.6/37.3	–
10	N ₂	99.5/2.9/23.5	–	150.0/5.1/34.3	–	137.0/4.3/26.9	–
15	N ₂	103.0/2.9/24.3	–	159.2/5.7/36.5	–	144.0/4.8/28.6	–
25	N ₂	106.5/3.4/25.3	–	157.5/5.7/36.3	–	135.1/4.5/26.8	–
5	Air	96.4/4.4/22.6	97.1/0.6/17.1	155.9/7.9/36.0	158.1/1.1/25.9	120.4/6.1/23.5	131.6/0.9/17.8
10	Air	98.2/5.0/23.3	98.8/0.9/17.5	149.6/7.7/34.6	189.1/1.8/30.6	157.7/8.0/31.9	185.8/1.7/26.2
15	Air	96.4/4.7/23.1	98.3/0.7/17.2	158.6/8.1/36.8	183.3/1.8/29.7	156.7/7.8/31.8	164.3/1.5/22.8
20	Air	100.0/5.4/24.0	108.6/0.9/18.9	148.4/7.7/34.6	189.6/1.9/30.5	134.9/6.6/26.3	183.2/1.8/25.7
25	Air	92.2/4.9/22.5	104.9/0.8/18.3	154.7/7.6/36.2	183.9/1.8/29.8	123.7/5.9/24.8	183.3/2.0/26.0

^a The units of E and A are kJ mol^{-1} and min^{-1} , respectively.

stages, respectively. From these figures, good linear relationships by different methods at different heating rates are obtained. All of the kinetic parameters calculated by the three techniques are listed in Table III.

From Table III, it can be concluded that in nitrogen although there are some differences in kinetic parameters obtained by different methods, the parameters change insignificantly with the increase in heating rate except that the E , $\ln A$, and n at $5^\circ\text{C}/\text{min}$ have a little higher values. The kinetic parameters of the first weight loss in air exhibit the similar characteristics to that in nitrogen.

Interestingly, for the second stage decomposition in air, the kinetic parameters at $5^\circ\text{C}/\text{min}$ are lower than that obtained at other heating rates, resulting from the changes in the kinetics. A typical change in the degradation of polymeric systems responsible for the variation is shift from diffusion-controlled kinetics to chemical-controlled (degradation-controlled) kinetics or *vice versa*. Under the fast heating rate condition in air, the oxygen diffusion is probably too slow as compared with the heating rate. Thus, the diffusion-controlled kinetics is dominant for the decomposition process in air.¹⁹ In nitrogen, however, the degradation-controlled kinetics is the key factor for decomposition process, which is similar to the first stage degradation in air.

It should be pointed out that there are some differences in the kinetic parameters calculated by differ-

ent methods. From data in Table III it can be seen that in nitrogen the average values of E and n at different heating rates by the three techniques are 107.1, 159.7, 156.4 kJ mol^{-1} and 3.3, 5.6, 5.1, respectively. The Friedman method gives the lowest E and n values of the three methods. However, as shown in Figure 5, only the Chang technique actually forms straight lines in the widest temperature range, which means a smaller error in the calculation of the kinetic parameters by this method. However, the temperature range used for the determination of kinetic parameters by Friedman and Coats-Redfern method is wide enough to obtain reliable results.¹⁷

Additionally, the reaction order n at the second stage in air is much lower than that obtained in nitrogen and at the first reaction stage in air, as listed in Table III. It suggests that PUFs at thermo-oxidative stage have faster rate of degradation and poorer stability than that at the pyrolysis stage.

Effect of blowing agent on kinetic parameters of thermal degradation

Tables IV and V list the kinetic parameters of foam samples blown with different water levels. Interestingly, it is clearly found that T_{div} , T_{dm1} , and T_{dm2} decrease as water level in formulation increases from 3.0 to 5.0 pph, and then increase with water level ranging from 5.0 to 7.0 pph. The probable reason for this is related to cross-

TABLE IV
Thermal Degradation Data of the Various Foam Samples in Nitrogen and Air at a Heating Rate of $10^\circ\text{C}/\text{min}$

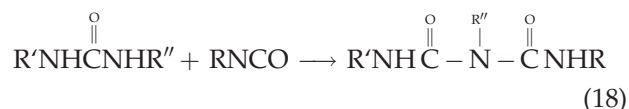
Samples	Test atmosphere	$T_d/T_{\text{dm1}}/T_{\text{dm2}}$ (°C)	Char yield at 800°C (wt %)	$(dx/dt)_{\text{m1}}$ (%/min)	$(dx/dT)_{\text{m1}}$ (%/°C)	$(dx/dt)_{\text{m2}}$ (%/min)	$(dx/dT)_{\text{m2}}$ (%/°C)
3-W	N ₂	293.2/320.9/–	14.3	9.44	0.94	–	–
5-W	N ₂	284.6/315.5/–	18.1	8.61	0.86	–	–
7-W	N ₂	291.4/319.3/–	18.4	8.96	0.9	–	–
3-W	Air	280.6/312.0/546.3	2.06	7.19	0.72	4.87	0.49
5-W	Air	266.9/301.3/544.0	2.48	5.83	0.58	4.93	0.49
7-W	Air	278.7/309.3/543.5	5.7	5.98	0.6	5.3	0.53

TABLE V
Kinetic Parameters of Thermal Degradation of Various Foam Samples in Nitrogen and Air Calculated by Three Single Heating Rate Methods at a Heating Rate of 10°C/min

Samples	Test atmosphere	Friedman ^a		Chang ^a		Coats-Redfern ^a	
		First stage <i>E/n/ln A</i>	Second stage <i>E/n/ln A</i>	First stage <i>E/n/ln A</i>	Second stage <i>E/n/ln A</i>	First stage <i>E/n/ln A</i>	Second stage <i>E/n/ln A</i>
3-W	N ₂	104.7/2.8/24.3	–	161.3/4.6/6.26	–	140.4/3.7/27.2	–
5-W	N ₂	99.5/2.9/23.5	–	150.0/5.1/34.3	–	137.0/4.3/26.9	–
7-W	N ₂	133.2/3.7/30.3	–	176.1/5.3/39.4	–	161.4/4.5/31.6	–
3-W	Air	103.7/4.5/24.1	96.6/0.8/16.8	171.5/7.6/38.6	188.2/1.8/30.5	164.9/6.7/32.8	164.3/1.5/22.9
5-W	Air	98.2/5.0/23.3	98.8/0.9/17.5	149.6/7.7/34.6	189.1/1.8/30.6	157.7/8.0/31.9	185.8/1.7/26.2
7-W	Air	122.0/6.4/27.9	99.1/1.0/17.4	172.0/9.1/38.9	219.1/2.1/35.2	184.2/9.3/36.9	242.3/2.2/34.9

^a The units of *E* and *A* are kJ mol⁻¹ and min⁻¹, respectively.

link density and molecular structure of foams. When water is used as a chemical blowing agent, it reacts with isocyanate to generate polyurea and polybiuret accompanied with release of CO₂:



So, more isocyanate (about 14.0 g of PMDI/1.0 g of water) is needed to react with water with the increase of water level. As we know, polyurea and polybiuret have been considered more "rigid" than polyurethane. All of these rigid structures shift *T*_{dir}, *T*_{dm1}, and *T*_{dm2} to higher temperature. At the same time, however, water is two-functional compound, which decreases the overall crosslink density of foams, causing the decrease of *T*_{dir}, *T*_{dm1}, and *T*_{dm2}. The *E* values of degradation in nitrogen and at the first stage in air exhibit the similar trend though there are some differences for the values calculated by different methods. In Tables IV and V, the *n* values and char yield at 800°C increase with the rising water level in formulation. In general, a decomposition order of zero means the fastest decomposition reaction.

As the activation energy and reaction order increase, the decomposition process becomes slower. Therefore, the highest activation energy and order for the 7-W foam sample reported in Table V indicate that the foam that contained numerous polyurea and polybiuret in molecular structure has a higher thermal stability in nitrogen and air.

Prediction of lifetime *t_f* and half-life time *t*_{1/2}

One of most important applications of decomposition kinetic parameters is to estimate the useable temperature region and the lifetime of PUFs. According to eqs. (13)–(15) and data obtained by Chang technique in Table V, the half-life time *t*_{1/2} and lifetime *t_f* for foam samples at different temperatures in nitrogen and air are calculated. The results are listed in Table VI.

From Table VI, it is apparent that there are insignificant differences in *t_f* and *t*_{1/2} for the decomposition in nitrogen and air due to the similar degradation mechanism, but the lifetime *t_f* decreases dramatically from 10⁴–10⁶ min to ~ 0.01 min as the temperature increases from 100°C to 300°C. The lifetime *t_f* at 200°C is not more than 15 min. It indeed suggests that the rigid foams had very poor thermostability when heated above 200°C in nitrogen and air, which is in agreement with the low decomposition temperature of foams listed in Table II.

TABLE VI
Prediction of Lifetime *t_f* and Half-Life Time *t*_{1/2} for Various Foam Samples at Different Temperatures in Nitrogen and Air

Temperature (°C)	Test atmosphere	3-W		5-W		7-W	
		<i>t</i> _{1/2} (min)	<i>t_f</i> (min)	<i>t</i> _{1/2} (min)	<i>t_f</i> (min)	<i>t</i> _{1/2} (min)	<i>t_f</i> (min)
100	N ₂	2.10 × 10 ⁷	3.83 × 10 ⁵	4.71 × 10 ⁶	6.82 × 10 ⁴	1.55 × 10 ⁸	2.04 × 10 ⁶
150	N ₂	4.51 × 10 ⁴	822.69	1.56 × 10 ⁴	225.7925	1.89 × 10 ⁵	2.49 × 10 ³
200	N ₂	355.05	6.47	172.34	2.5	952.02	12.56
250	N ₂	7.05	0.13	4.51	0.07	13.19	0.17
300	N ₂	0.28	0.01	0.22	< 0.01	0.39	0.01
100	Air	2.53 × 10 ⁸	1.06 × 10 ⁶	1.22 × 10 ⁷	4.86 × 10 ⁴	5.35 × 10 ⁸	1.01 × 10 ⁶
150	Air	3.67 × 10 ⁵	1.54 × 10 ³	4.09 × 10 ⁴	162.83	7.65 × 10 ⁵	1.44 × 10 ³
200	Air	2.13 × 10 ³	8.92	456.93	1.82	4.37 × 10 ³	8.24
250	Air	32.93	0.14	12.06	0.05	67.01	0.13
300	Air	1.06	< 0.01	0.6	< 0.01	2.13	< 0.01

However, when temperature is below 100°C, the rigid foams have excellent thermostability. At 100°C, for example, the $t_{1/2}$ and t_f of 3-W foam in air are 2.53×10^8 min (481 years) and 1.06×10^6 min (2.0 years), respectively. Therefore, water-blown rigid PUFs are usually used as insulation materials in practical application, such as the solar heater, pipeline, and refrigerator where the temperature is often below 100°C.

Moreover, on the basis of the kinetic data reported in this article, it is important and helpful to study and develop a new type of water-blown rigid PUF with more excellent thermostability in air.

CONCLUSIONS

According to the TG and DTG data, thermal decomposition temperature, activation energy (E), decomposition order (n), and pre-exponential factor (A) of rigid PUFs in nitrogen and air were measured and calculated by three single heating rate techniques. The results show that the test atmosphere, heating rate, amount of blowing agent, and calculation method have great effect on the thermal stability and the kinetic parameters of thermal degradation. The Chang method is the most appropriate method to calculate the kinetics. On the basis of the kinetic data, it is predicted that water-blown rigid PUFs exhibit very excellent thermostability when used below 100°C.

References

1. Potts, C. G.; Draaijer, L. M. *J Cell Plast* 1985, 21, 51.
2. Demharter, A. *Cryogenics* 1998, 38, 113.
3. Molina, M. J.; Rowland, F. S. *Nature* 1974, 249, 810.
4. Grunbauer, H. J. M.; Folmer, J. C. W.; Van Lieshout, H. C.; Lidy, W. A.; Thoen, J. A. *Polym Prepr* 1991, 32, 517.
5. Niyogi, D.; Kumar, R.; Gandhi, K. S. *Polym Eng Sci* 1999, 39, 199.
6. Seo, W. J.; Jung, H. C.; Kim, W. N.; Lee, Y.-B.; Choe, K. H.; Kim, S.-B. *J Appl Polym Sci* 2003, 90, 12.
7. Ohtani, H.; Kimura, T.; Okamoto, K.; Tsuge, S.; Nagataki, Y.; Miyata, K. *J Anal Appl Pyrolysis* 1987, 12, 115.
8. Font, R.; Fullana, A.; Caballero, J. A.; Candela, J.; Garcia, A. *J Anal Appl Pyrolysis* 2001, 58, 63.
9. Hatchett, D. W.; Kodippili, G. K.; Kinyanjui, J. M.; Benincasa, F.; Sapochak, L. *Polym Degrad Stab* 2005, 87, 555.
10. Branca, C.; Blasi, C. D.; Casu, A.; Morone, V.; Costa, C. *Thermochim Acta* 2003, 399, 127.
11. Tang, Z.; Maroto-Valer, M. M.; Andrésen, J. M.; Miller, J. W.; Listemann, M. L.; McDaniel, P. L.; Morita, D. K.; Furlan, W. R. *Polymer* 2002, 43, 6471.
12. Pielichowski, K.; Kulesza, K.; Pearce, E. M. *J Appl Polym Sci* 2003, 88, 2319.
13. Friedman, H. L. *J Polym Sci Part C: Polym Symp* 1965, 6, 183.
14. Chang, W. L. *J Appl Polym Sci* 1994, 53, 1759.
15. Coats, A. W.; Redfern, J. P. *Nature* 1964, 201, 68.
16. Coats, A. W.; Redfern, J. P. *J Polym Sci Part B: Polym Lett* 1965, 3, 917.
17. Li, X.-G.; Huang, M.-R.; Guan, G.-H.; Sun, T. *Polym Degrad Stab* 1999, 65, 463.
18. Li, X.-G.; Huang, M.-R.; Guan, G.-H.; Sun, T. *Polym Int* 1998, 46, 289.
19. Day, M.; Cooney, J. D.; Wiles, D. M. *J Appl Polym Sci* 1989, 38, 323.