

Kinetics study of hard and soft polyurethane

Xiang Li^{1,3}, Eun Jung Im², Sung Hyun Kim^{3,*}

¹School of Energy Science and Eng., Harbin Institute of Technology, China

²Dept. of Environ. System Eng., Korea University

³Dept. of Chemical and Biological Eng., Korea University
(kimsh@korea.ac.kr*)

Introduction

Polyurethane (PU) are used in a wide range of industrial applications, such as car paints, flexible foams for bedding, rigid foams for insulation, adhesives and other commercial goods [1]. During treating polyurethane, removal of toxic and dangerous refuses has become a serious environmental problem troubling many cities. Pyrolysis and combustion of these wastes are two possible ways of solving the problem. And the pyrolysis is a first step in the combustion process. Therefore the knowledge of the decomposition process of polyurethane and its control, as well as the contaminants produced is important [2]. The mechanisms of polyurethane thermal decomposition in an inert atmosphere have been studied by several authors. M.M.Esperanza et al. [2] identified 31 organic compounds by GC and GC/MS. The main compounds obtained were CO, CO₂, ethylene, naphthalene and acetylene. And showed a correlation model applied to simulation the process. R.Bilbao et al. [3] compared the kinetics of the thermal decomposition of polyurethane foams in different atmospheres.

In this paper, thermogravimetric analyses to characterize the materials behavior was performed and comparable curves for the two kinds of polyurethane: hard polyurethane, is abbreviated as PUh, is used for adiabatic material; soft polyurethane, is abbreviated as PUs, is used for automobile parts. A kinetic model which could be considered agreeing well with experimental results was proposed. And the main components of polyurethane were detected via GC/MS experiment. Their differences of average active energy and components were compared.

Kinetics study

The polyurethane pyrolysis included many reactions and produced kinds of product, so that it was hard to study every reaction of them. This paper studied on the macroscopical kinetic of polyurethane and ignored every product reaction mechanism in the pyrolysis process. It was supposed that polyurethane makes up of finite kinds of component (for an instant two kinds of components were proposed here), and each component reacts independently in the pyrolysis process. A consecutive kinetic model for polyurethane pyrolysis was proposed based on the hypothesis that each stage of weight loss, which showed as a peak in DTA curve shape, corresponded with an independent reaction of sample. And the kinetic parameters of each reaction keeping constant over the whole temperature range of the

experiment were considered. In this paper the evaporation of water was ruled out and the conversion rate was adopted to indicate the reacting degree [4].

The kinetics model of each independent pyrolysis reaction is following as:

$$\frac{d\alpha_i}{dt} = k_i(1-\alpha_i)^{n_i} = A_i \exp\left(-\frac{E_i}{R_iT}\right)(1-\alpha_i)^{n_i} \quad i=1,2 \quad (1)$$

Considering α_i is the degree of conversion of the reaction i .

$$\alpha_i = \frac{w_{i0} - w_i}{w_{i0} - w_{i\infty}} \quad (2)$$

w_i as the weight of reaction i is detected by the thermogravimetric analysis that includes solid residue generated as well as unreacted solid w_{i0} is the initial weight of reaction i at time t $w_{i\infty}$ is the residual weight of reaction i at last. E_i (KJ/mol) is activation energy of reaction i A_i (min^{-1}) is the frequency factor of reaction i n_i is the reaction order of reaction i .

In the pyrolysis process, heating rate β is considered as constant.

$$\beta = \frac{dT}{dt} \quad (3)$$

Each independent reaction was analytically integrated considering small intervals [5].

$$\int_{\alpha_r}^{\alpha_{T+\Delta T}} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_T^{T+\Delta T} \exp\left(-\frac{E}{RT}\right) dT \quad (n \neq 1) \quad (4)$$

The each independent part after differentiated can be showed as follows:

$$\frac{d\alpha}{dT} = \sum_{i=1}^k x_i \frac{d\alpha_i}{dT} \quad (5)$$

α as the general conversion rate of the sample at time t is seen as 1 here. k is the number of independent reaction. x_i is the fraction of the weight of part i to the global loss weight of the sample.

In calculation objective functions (O.F.) was applied in order to fit DTA curve shapes.

$$\text{OF} = \sum \left(\left(\frac{d\alpha}{dT} \right)_{\text{exp}} - \left(\frac{d\alpha}{dT} \right)_{\text{cal}} \right)^2 \quad (6)$$

Experimental

Elemental analysis of the major components was carried out in TCD (Column: CHNS-Porapak PQS). Table 1 shows the characteristics of two kinds of polyurethane. The experiment was performed in a 2960 SDT. Nitrogen with a gas flow rate of 100ml/min was used. To PUh the initial weight is 1-2mg, and the initial weight of PUs is always about 10mg. Different experiment conditions were performed, using four different heating rates (5, 10, 15 and 20°C/min). A LECO Pegasus III type spectrometer linked with a Agilent 6890N gas chromatograph equipped with a DB-5 column, 10m length and 0.18 μm internal diameter, was used. Ion detection was done by an 1800eV electronic impact (EI) mode. Mass were

recorded in the 30-500amu (atomic mass unit) range. Injector temperature was 280°C (to PUh) and 250°C (to PUs) respectively.

Results and discussion

Fig 1 shows the evolution of solid conversion, in terms of weight fraction and da/dT with temperature in a nitrogen atmosphere. The weight fraction was defined as the ratio between the solid weight loss at a given time and the initial solid weight. For decomposing adequately, the relatively low heating rate was given in experiments. Dynamic experiments with a heating rate of 5°C/min and different material densities (PUh and PUs) were carried out.

To PUh curves two temperature ranges for significant solid conversion variation occurs can be appreciated. The first range corresponds to a conversion of about 0.90, starting at about 200°C and extending to 410°C. These were seen clearly from DTA curve shape. The maximum conversion variation appears at about 319°C. But the PUs curves show another posture. The main decomposition process takes place between 280°C and 430°C. Especially in a narrow range (from 350°C to 420°C) the decomposing rate enhance evidently. Further there are many small peaks in PUs's DTA curve shape which were considered that there are more reactions in the pyrolysis process and the component of PUs is complicated. The distinct differences in the solid conversion must be caused mainly by the influence of the chemical composition.

The type of signals was obtained on two kinds of polyurethane using PyGC/MS. Eleven kinds main compounds of PUh are detected, and the number is more than that of PUs. These explained expressly that the PUh's pyrolysis analysis curves are smoother than the PUs's and the PUs's DTA curve has more peaks. More components corresponded more reaction in pyrolysis process.

PUh's DTA curve shapes between 200°C and 410°C the range was counted major weight loss, and the rest of range was regard as the other weight loss. Then the above kinetic method was adopted for studying kinetic parameters of PUh. Table 2 shows the optimized kinetic parameters of hard polyurethane, which are obtained using O.F. Fig 2 reveals experimental and calculated TG and DTA curves of PUh and PUs with the kinetic method above mentioned. It can be seen that the calculated curves agreed with the experimental trend basically. This means that the kinetic model used is viable. The activation energy of soft polyurethane at different heating rate and average activation energy were obtained in table 3. Comparing with Table 2 and Table 3, the difference of two kinds of polyurethane' active energy is clear. PUs's average active energy is almost 1.67 times more than PUh's.

During compounds and pyrolysis kinetics study, the differences between hard polyurethane and soft polyurethane on composition and kinetics aspects were seen obviously. The compounds of soft polyurethane are more complex than that of hard polyurethane. The main decomposition process of the former takes place between 200°C and 410°C, and the latter appears between 280°C and 430°C. Using a consecutive kinetic model for pyrolysis of

polyurethane the calculated curves fitted with experimental curves. And the kinetic parameters such as active energy, frequency factor and reaction order were determined.

References

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Table 1
Elemental analysis of PUh and PUs

Sample Name	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Oxygen (%)
PUh	10.3	79.3	6.4	3.4
PUs	9.6	81.0	3.8	3.5

Table 2
Kinetic parameters of hard polyurethane heating energy

Operating condition	5°C/min		10°C/min		15°C/min		20°C/min	
	fraction1	fraction2	fraction1	fraction2	fraction1	fraction2	fraction1	fraction2
	1.5855mg		1.9555mg		1.2177mg		1.4716mg	
E(kJ/mol)	139.18	76.73	137.29	44.65	130.89	45.45	126.60	34.46
E _{average}	125.12KJ/mol							

Table 3
Activation energy of PUs at different rate and average activation

Operating condition	5°C/min	10°C/min	15°C/min	20°C/min
	10.0965mg	9.5932mg	9.5188mg	10.8611mg
E(KJ/mol)	209.90	203.34	217.43	206.54
E _{average}	209.30 KJ/mol			

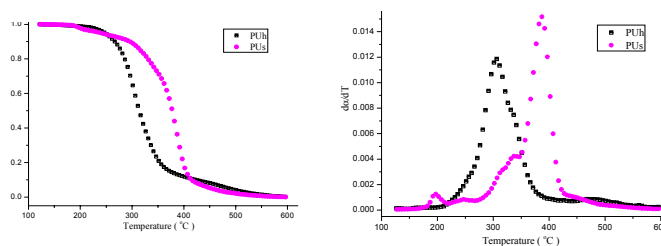


Fig. 1 Experimental TG and DTA comparison of PUh and PUs (5°C/min)

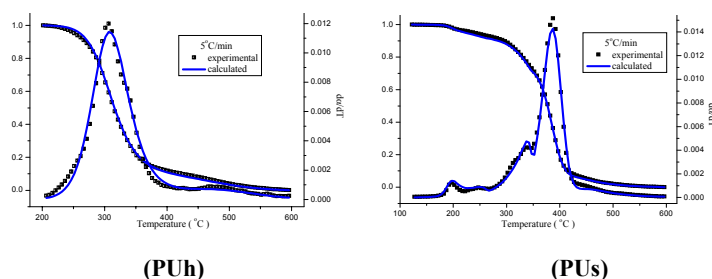


Fig. 2 Experimental and calculated TG and DTA curves of PUh and PUs at 5°C/min