Polyurethane curing kinetics for polymer bonded explosives: HTPB/IPDI binder

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Abstract−The kinetics of polyurethane reaction and the effect of catalysts on the curing behavior were studied. The mixtures of hydroxyl terminated polybutadiene and isophorone diisocyanate with different reaction catalysts were dynamically cured in a differential scanning calorimeter. The activation energies were evaluated by the Kissinger and the Ozawa methods. The Chang plot was also used to determine reaction order and rate constant. The results showed that the activation energies were influenced remarkably by the choice of catalysts. The degree of cure and the cure time at given temperatures were calculated by direct integration of modified auto-catalytic kinetic model. It would give valuable information like pot-life estimation during manufacturing polymer-bonded explosives.

Keywords: Polyurethane, HTPB, IPDI, Kinetics, PBX

INTRODUCTION

Polyurethane materials have many applications as coatings, adhesives, foams, sealants, and especially polymer-bonded explosives (PBX) and solid rocket propellants [1-3]. The resin is cured conventionally by a urethane reaction between dihydroxyl terminated prepolymers and diisocyanates [4]. As a curative toluene diisocyanate is widely used for producing general purpose polyurethane, but due to its high reactivity it is not applicable for some special uses which require long processing time. For these purposes, lesser reactive isophorone diisocyanate (IPDI) is favorable and preferred for PBX manufacturing which needs long pot-life [5,6]. As a prepolymer hydroxyl terminated polybutadiene (HTPB) has been used in urethane reaction for PBX and solid composite propellants [7-9]. To form a cured polyurethane elastomer, triphenyl bismuth (TPB), ferric tris-acetyl acetonate (FeAA), and dibutyl tin dilaurate (DBTDL) are generally used. The choice of reaction catalysts and the knowledge of their effects on the reaction rate are also of utmost importance in estimating pot-life and thus processability of PBX paste [10-13].

Generally, a binder has a role of dimensional stability and structural integrity to explosive particles. The hydroxyl groups at both ends of an HTPB chain undergo urethane reaction with isocyanates to form the polyurethane elastomer, resulting in a product with good mechanical properties. The mechanical properties are largely determined by the degree of polyurethane reaction [14,15], and thus the knowledge of the cure kinetics is very important in estimating the pot-life and thus the processability of PBX paste. The kinetic researches for polyurethane formation have been carried out mainly using FT-IR and NMR [16-19]. The differential scan-

ning calorimeter (DSC) has been also extensively employed to study the exothermic cure reactions in polymers [20,21]. For the cure reaction of HTPB, only a few studies with different curatives have been reported using various techniques [22-25].

This study is the second work on the curing of polyurethane as a binder for polymer bonded explosives. The previous work focused on the pot-life, i.e. processability, and chemorheology of polyurethane by plate-plate rheometer [13]. On the other hand, this work did on the curing time and kinetics for final products by DSC. First, the Kissinger plot and the Ozawa plot were used to study the influence of various catalysts on the activation energy. Next, to enhance the accuracy, a modified auto-catalytic kinetic model and the Chang method were combined with some constraints, together. Then, the analytically calculated degree of cure was predicted as a function of time and temperature.

EXPERIMENTAL

1. Materials

As a polyol hydroxyl-terminated polybutadiene (HTPB) was kindly supplied by Hanwha Corporation and as a curative isophorone diisocyanate (IPDI) was purchased from Sigma-Aldrich, respectively. Triphenyl bismuth (TPB), ferric tris-acetyl acetonate (FeAA), and dibutyl tin dilaurate (DBTDL) were used as curing catalysts. All the reagents were used as received without further purification. The properties of HTPB and IPDI are shown in Table 1. The reactivity and the selectivity of NCO groups of IPDI in the solvent media have been reported [10,26]. The reactivity of the secondary NCO group was much higher than that of the primary NCO group. Though the reactivity in the bulk might be somewhat different from that in solution, the expected reaction scheme of HTPB and IPDI could be as shown in Fig. 1. For the preparation of polyurethane reaction, HTPB, IPDI, and a catalyst were thoroughly mixed by mechanical stirrer in a beaker for 2 min at room temperature. The formu-
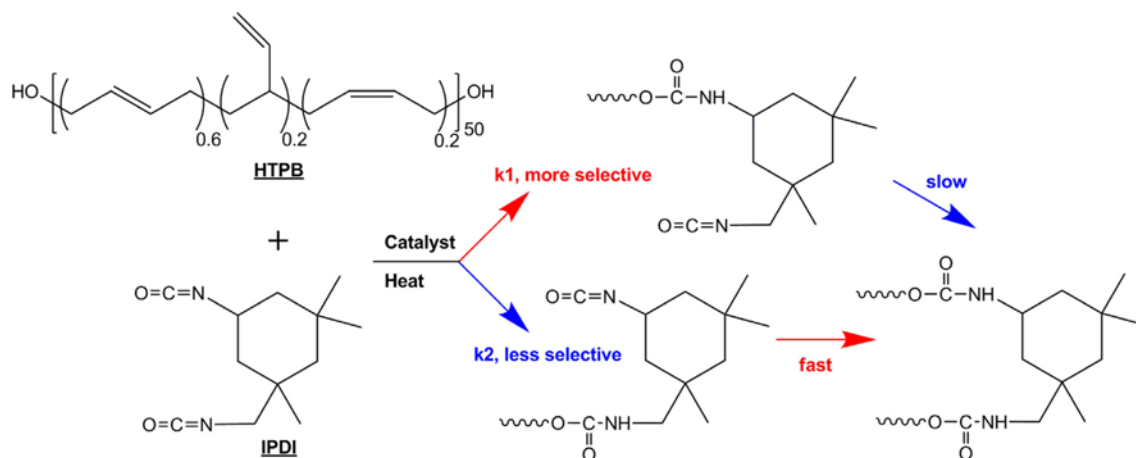
Table 1. Properties of materials used in this study

Trade name	Material	Producer	Density (g/cm^3)	Viscosity (mPa·s)	Remark
Poly bd R-45HTLO	Hydroxyl terminated polybutadiene	Cray valley	0.901	8000@23 °C 5000@30 °C	M_n: 2137 g/mol PDI: 2.5 T_g: −75 °C
Isophorone diisocyanate	Isophorone diisocyanate	Sigma-Aldrich	1.049	-	MW: 222 g/mol T_b: 158-159 °C

Fig. 1. Reaction scheme of HTPB with IPDI.

Table 2. Formulation for HTPB/IPDI cure reaction

Material	Mole ratio	Composition	Remark
HTPB	1.00	90.1757 wt%	
IPDI	1.05	9.8243 wt%	Slightly excess
Catalyst		0.015 wt% (basis: HTPB/IPDI 100)	TPB, FeAA, DBTDL

lation of the mixture is shown in Table 2.

2. Instruments

Differential scanning calorimetry (DSC) was performed on DSC 2910 (TA Instrument) to investigate the curing behavior. Samples of about 3-5 mg were heated from −50 to 350 °C at various heating rates (5, 10, 20, and 40 °C/min) in flowing nitrogen gas. A linear baseline was used for the integration of dynamic heat flux signals.

RESULTS AND DISCUSSION

Dynamic cure of HTPB/IPDI system was studied by determining the heat release rate during heating. Fig. 2 shows the dynamic DSC thermogram at four different heating rates when a different catalyst was incorporated. In cases of TPB and FeAA catalyzed samples at 5 °C/min, several exothermic peaks could be observed, and among them the peak near 180 °C-200 °C was believed attributable to urethane reaction. On the other hand, DBTDL-catalyzed sample showed the main urethane peaks near 100 °C. The position of the peak shifted to the higher temperature as heating rate increased. This temperature shift might be due to a heat transfer effect similar to pyrolysis [27]. Table 3 summarizes the peak temperatures of DSC for HTPB/IPDI system at four different heating rates.

To make sure that the exothermic peak originated from the urethane reaction, the second heating was carried out for quenched TPB catalyzed sample after the first heating. The peak which was observed at 180 °C in the first heating DSC thermogram disappeared in the second heating DSC thermogram as shown in Fig. 3.

Among the methods for calculating activation energy, the Kissinger plot is one of the simplest methods that does not need precise knowledge of the reaction mechanism.

$$\ln\frac{\beta}{T_p^2} = \ln\frac{k_0 R}{E_a} + \ln[n(1-\alpha_p)^{n-1}] - \frac{E_a}{RT_p} \tag{1}$$

where T_p and α_p are the temperature and the degree of cure at peak, respectively. By the plot of $\ln(\beta/T_p^2)$ against $1/T_p$ the activation energy can be determined from the slope [28,29]. Similarly, in the Ozawa plot, it is assumed that the degree of cure has a constant value independent of the heating rate when a DSC curve reaches its peak, and is represented by following equation:

$$\log\beta = \text{const} - \frac{0.457E_a}{RT_p} \tag{2}$$

The activation energy can be obtained from a plot of $\log\beta$ against $1/T$ for given degree of cure [30-32]. The Chang method for n-th
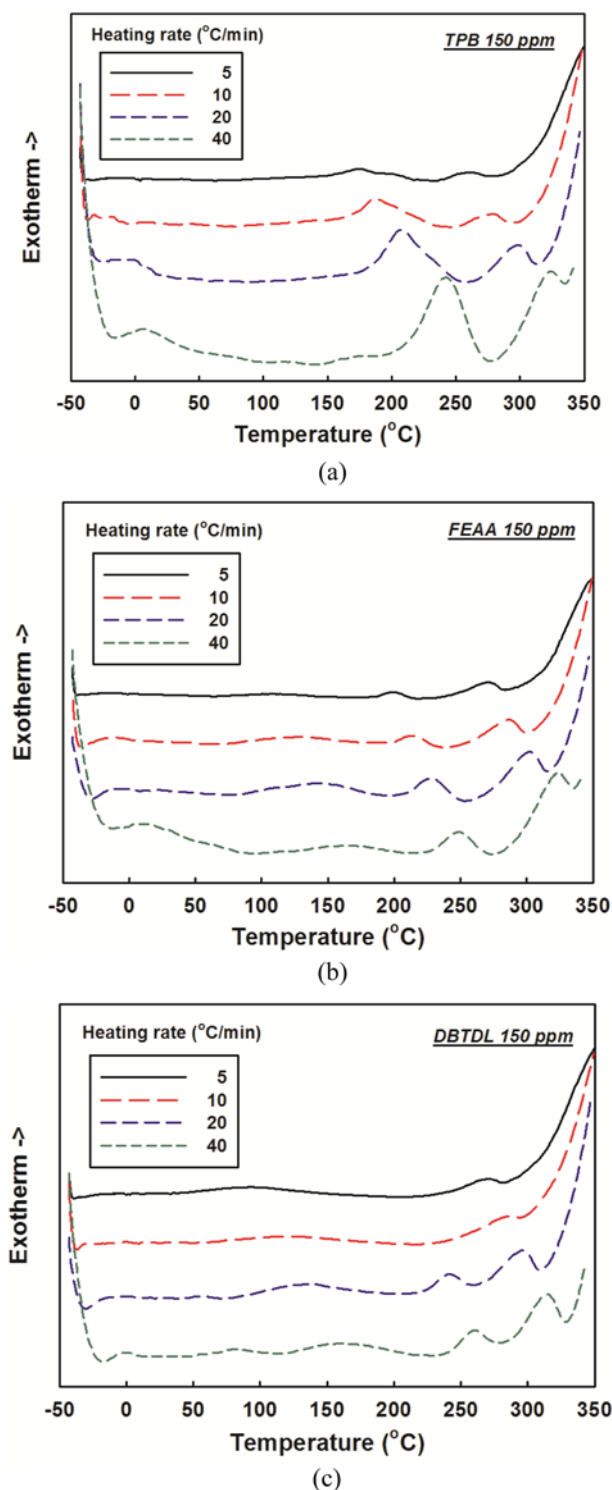
Fig. 2. Dynamic DSC curves for HTPB/IPDI mixtures with cata-
lysts (a) TPB, (b) FeAA, and (c) DBTDL, respectively, at dif-
ferent heating rates.

order reaction employs the following equation:

$$\ln\frac{\beta(d\alpha/dT)}{(1-\alpha)^n}=\ln k_0-\frac{E_a}{RT} \qquad (3)$$

A plot of $\ln[\beta(d\alpha/dT)/(1-\alpha)^n]$ against $1/T$ can yield a straight line

**Table 3. Exothermal peak temperature for HTPB/IPDI curing with
various catalysts**

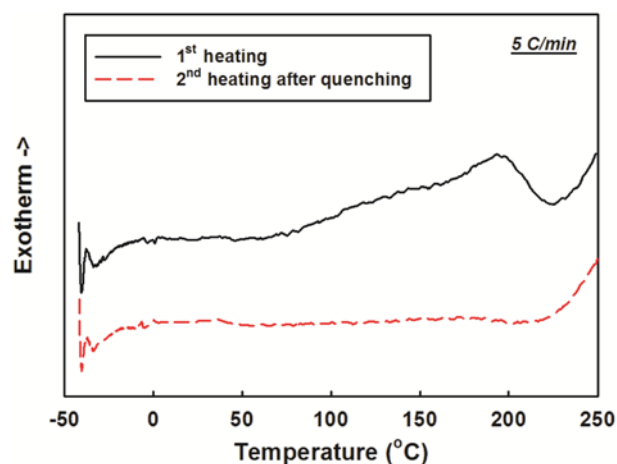| Heating rate (°C/min)	Peak temperature (°C)		
	TPB	FEAA	DBTDL
5	175	200	93
10	188	213	126
20	208	235	137
40	243	258	172

Fig. 3. 1st and 2nd dynamic DSC thermogram of HTPB/IPDI (with
TPB) mixtures at 5 °C/min.

only if the reaction order n is correctly selected. The slope and the
intercept are $-E_a/R$ and $\ln k_0$, respectively [33].

The Kissinger and the Ozawa plots were employed to calculate
the activation energies from DSC data of HTPB/IPDI system, which
are shown in Fig. 4. They are generally reasonable for describing
n-th order epoxy curing reactions [34]. Using the Kissinger plot in
Fig. 4(a), the values of activation energy were obtained from the
slope of $\ln(\beta/T_p^2)$ against $1,000/T_p$ plot. The activation energy could
also be determined from the Ozawa plot of $\ln\beta$ against $1,000/T_p$,
shown in Fig. 4(b). The activation energies obtained from the above
two methods are summarized in Table 4. The activation energy
values obtained from the Ozawa plot were somewhat higher than
those from the Kissinger plot.

To obtain the rate of cure and the degree of cure, the heat release
rates and their running integrals were divided by the total heat of
reaction and are shown in Fig. 5. As heating rate increased, the de-
gree of cure increased slowly in the early stage of curing and then
increased sharply and finally approached to 1. For elastomeric mate-
rials that cure above their glass transition temperatures, the model
accurately predicts the total process [35]. This condition gives suf-
ficient free volume between the molecules to allow for freedom of
movement during the molecular curing process, and therefore dif-
fusion does not play a large role [36,37]. The initiation of curing
and the slope of curve became earlier and stiffer as heating rate
increased, respectively.

To describe the curing behavior of HTPB/IPDI system more ac-
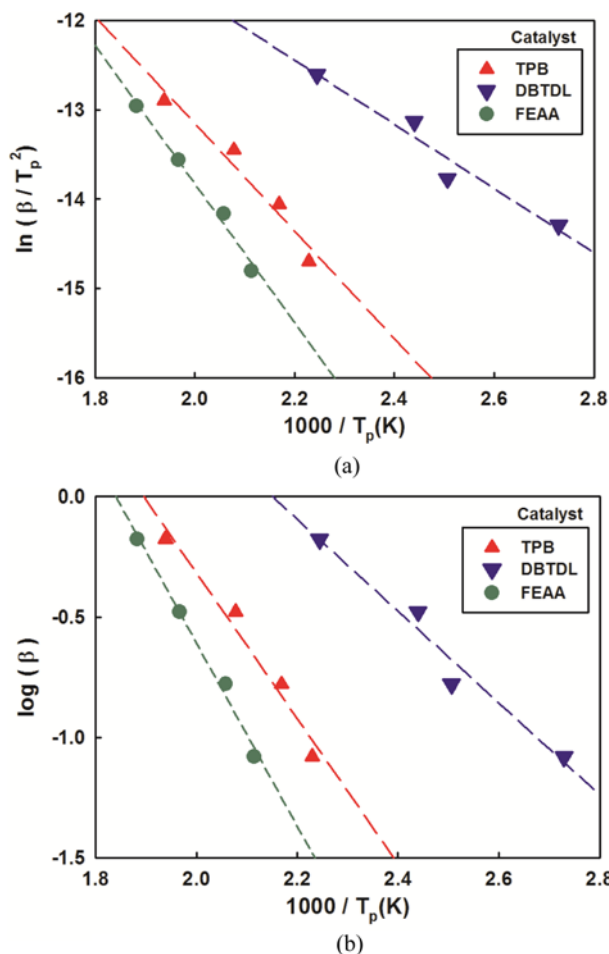curately, an autocatalytic reaction kinetic model with two reaction

Fig. 4. (a) Kissinger plot and (b) Ozawa plot for HTPB/IPDI reaction with various catalysts.

Table 4. Activation energies determined by Kissinger method and Ozawa method

Catalyst	Activation energy, E_a (kJ/mol)	
	Kissinger	Ozawa
TPB	49	55
FeAA	64	69
DBTDL	30	35

orders was adopted:

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \qquad (4)$$

The reaction orders m and n allow the prediction of the position of the maximum rate in an autocatalytic process, i.e., the amount reacted at the maximum rate at a constant temperature. Because reaction orders higher than 2 are extremely rare, reaction orders were assumed as a constant sum of 2. Similarly, Ryan and Dutta successfully applied the Kamal-Sourour model to an epoxy-amine cured system by using reaction orders of a constant sum of 2 [38-40]. Therefore, applying the above constraint, the modified autocatalytic model becomes:
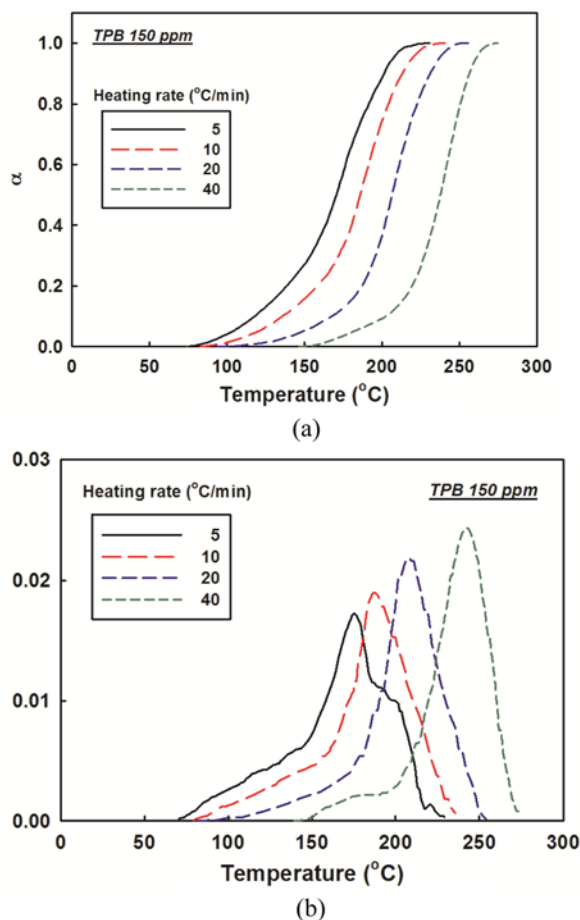
Fig. 5. (a) α and (b) dα/dt curves for HTPB/IPDI (with TPB) at different heating rates.
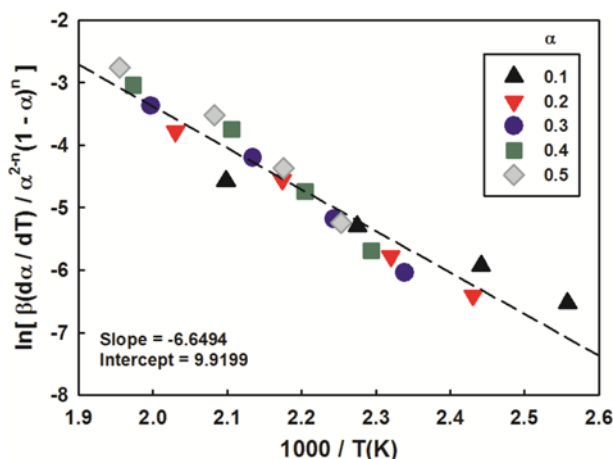

Fig. 6. Chang plots for modified autocatalytic model at different curing degrees.

$$\frac{d\alpha}{dt} = k\alpha^{2-n}(1-\alpha)^n \qquad (5)$$

All of the kinetic parameters--activation energy, E_a, pre-exponential factor, k_0, and reaction order, n--could be obtained from the plot based on the Chang method. A plot of $\ln[\beta(d\alpha/dT)/\alpha^{2-n}$

Table 5. Estimated parameters of modified autocatalytic model, Eq. (5), obtained by Chang method

Modified autocatalytic model	k_0 (s^{-1})	E_a (kJ/mol)	n
$\dfrac{d\alpha}{dt} = k\alpha^{2-n}(1-\alpha)^n$	2.0331×10^4	55	1.43
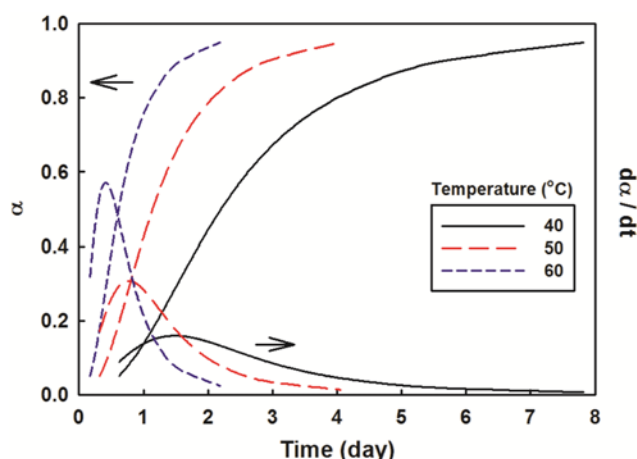
Fig. 7. Simulation of a and da/dt with time for HTPB/IPDI (with TPB) reaction at different temperatures.

$(1-a)^n$] versus 1000/T should be a straight line when adjusting the tentative value for n. The plots are nearly straight lines with almost the same slopes for a given value of n when the correlation coefficient is a maximum value as shown in Fig. 6. The activation energy, E_a, and pre-exponential factor, k_0, were obtained from the slope and intercept of the plot, respectively, as summarized in Table 5. These parameters were used for simulation.

The estimation of the optimum processing temperature and time could provide very useful information for many applications. The curing reaction kinetics equation, Eq. (5), could be integrated analytically and rearranged for degree of cure:

$$\alpha = \frac{1}{[kt(n-1)]^{1/(1-n)}+1} \tag{6}$$

According to Eq. (6), the degree of cure was calculated as a function of time and temperature and presented in Fig. 7. As time went on, the degree of cure of HTPB/IPDI system increased. For instance, the times of cure completion were two days at 60 °C, four days at 50 °C, and eight days at 40 °C, respectively. The rate of cure increased, and its shape became narrower as cure temperature increased. It means that the heat release rate is higher at higher cure temperature. It is believed that this kind of information could be used valuably for the estimation of cure completion time and temperature rise inside the product during cure reaction.

CONCLUSIONS

To investigate the effect of catalysts on the curing phenomena and to estimate the time of cure completion for HTPB/IPDI system, we performed a cure kinetics study by dynamic DSC experiments. The activation energies, which were evaluated from the Kissinger plot and the Ozawa plot with three different reaction catalysts, were influenced remarkably by the choice of catalysts. To enhance the accuracy, a modified auto-catalytic model and the Chang method were also adopted for HTPB/IPDI system with a TPB catalyst. The obtained activation energy (E_a), pre-exponential factor (k_0), and reaction order (n) were 55 kJ/mol, 2.0331×10^4 s^{-1} and 1.43, respectively. From the direct integration of the kinetic model equation, the degree of cure could be calculated analytically as a function of time and temperature. The times of cure completion were two days at 60 °C, four days at 50 °C, and eight days at 40 °C, respectively. It is believed that this kind of information could be valuable for the estimation of cure complete time and temperature rise inside the product during cure reaction.

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