Central European Journal of Energetic Materials
ISSN 1733-7178; e-ISSN 2353-1843

Cent. Eur. J. Energ. Mater. 2018, *15*(1): 131-149; DOI: 10.22211/cejem/81176

Influence of Bismuth Complex Catalysts on the Cure Reaction of Hydroxyl-terminated Polyether-based Polymer Bonded Explosives

Yapeng Ou, Qingjie Jiao,* Shi Yan, Yanli Zhu

State Key Laboratory of Explosion Science and Technology,
Beijing Institute of Technology, Beijing 100081, PR China
**E-mail: jiaoqingjie@126.com*

Abstract: The kinetics of catalyzed urethane-forming reactions of hydroxyl-terminated polyether (HTPE) with toluene di-isocyanate (TDI) in the presence of bismuth complex catalysts was investigated by non-isothermal differential scanning calorimetry (DSC). Fourier transform infrared spectroscopy (FTIR) was employed to monitor the chemical interactions of relevant groups. The kinetic parameters, including the apparent activation energy (E_a) and reaction rate constants (k) at typical temperatures calculated by the Kissinger and Crane methods, were used to evaluate the catalytic activities of triphenylbismuth (TPB) and tris(3-ethoxyphenyl)bismuthine (TEPB). The variations of E_a were studied to obtain an insight into the consistency of catalytic mechanism for the bismuth complex catalysts. The viscosity build-up of HTPE-based polymer bonded explosive (PBX) slurry was then measured to verify the catalytic activity and the pot-life during an actual manufacturing process, which fitted with the kinetics of the catalyzed cure reaction. The cure process was evaluated by the hardness of the PBX grains maintained at a temperature below typical manufacturing conditions. The results showed that TEPB is an effective catalyst, reducing the E_a of the cure reaction and the manufacturing temperature and time with an acceptable pot-life. The mechanical, thermal characteristics and compatibility of the HTPE-based PBXs were also investigated. The results suggest that TEPB is compatible with HTPE-based PBXs and contributes to improving the mechanical properties and thermal safety.

Keywords: HTPE, bismuth complex catalyst, pot-life, manufacture time reduction, mechanical and thermal characteristics

1 Introduction

Polyurethanes based on hydroxyl-terminated polybutadiene (HTPB) and glycidyl azide polymer (GAP) are extensively applied as prepolymer binders in composite solid propellant and polymer bonded explosives (PBXs) [1]. Hydroxyl-terminated polyether (HTPE) is a block copolymer of ethylene oxide (EO) and tetrahydrofuran (THF) (Figure 1) which differs from the random copolymer of EO and THF, referred to as P(E-*co*-T) [2-4]. Within recent years, composite propellant and PBX formulations based on HTPE have been developed as insensitive replacements for HTPB composites since they have similar mechanical properties and processability [5, 6]. According to current research, HTPE-based propellants react less violently when exposed to a thermal stimulus, which give a less severe response in the slow cook-off test for insensitive munitions (IM) compliance [7-9]. The prepolymer binder imparts dimensional stability and structural integrity to the filler particles [10]. However, the low reaction rate of the urethane forming reaction necessitates a high cure temperature, which reduces the safety of the propellant and PBX during manufacture. The typical cure temperature of a PBX is about 55 °C [11]. At this temperature, the energetic material grain acquires a tacky surface and residual internal stress, which reduces the mechanical properties of the PBX and propellant, such as tensile strength and breaking elongation, after being cooled to ambient temperature [12, 13]. Furthermore, migration of plasticizers occurs at high temperature due to the non-ideal miscibility of HTPE and plasticizers [14, 15]. Considering the manufacturing hazards, the unsatisfactory mechanical properties and homogeneity, catalysts such as triphenylbismuth (TPB) and tris(3-ethoxyphenyl)bismuthine (TEPB) have been used in HTPB-based polyurethanes, which effectively reduce the cure temperature below 35 °C [16]. Their catalytic activity and mechanism have been investigated using various techniques [17, 18]. Previous researchers proved that these catalysts accelerate the crosslinking process of HTPB and the curing agent by forming complexes with the reactive groups and decreasing the activation energy of the reaction [19, 20]. Understanding the explicit influence mechanism of these catalysts on the cure reaction is a prerequisite for the application in HTPE-based PBXs.

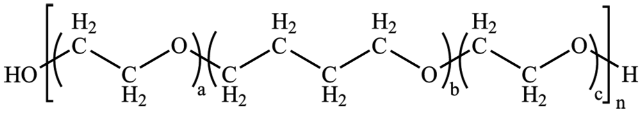


Figure 1. Molecular structure of the hydroxyl-terminated polyether prepolymer

Differential Scanning Calorimetry (DSC) is one of the effective techniques for investigating the cure kinetics of polyurethanes. In this study, the kinetic parameters of the catalyzed urethane reaction were calculated from the DSC characteristic temperatures at different heating rates. The kinetic equations of the cure reaction were established and the reaction rate constants at typical temperatures were calculated in order to evaluate the influence of the catalysts on PBX and propellant manufacture. Fourier Transform Infrared Spectroscopy (FTIR) was employed to analyze the changes in relevant groups before and after DSC measurement. Two bismuth complex catalysts were added to a typical polymer bonded explosive formulation PBXN-109, and the prepolymer binder, HTPB, used in this formulation was replaced by HTPE. The viscosity of the PBX slurry mixed from the binder and fillers at specified temperatures was measured to verify the catalytic activity and to determine the pot-life. The hardness of the PBX grains during the isothermal cure process was also tested to estimate the cure time of the PBX with these catalysts in an actual manufacturing process. Mechanical and thermal characteristics and compatibility of the substituted PBXN-109 were also investigated in order to observe the influence of the catalysts.

2 Experimental

2.1 Materials and preparation of the polyurethane samples

The HTPE used was synthesized by the School of Materials Science and Engineering, Beijing Institute of Technology. The THF/EO mole ratio was 1, average molecular weight (VPO) of the HTPE was 3600 g/mol and hydroxyl value was 0.5536 mmol/g. The density was 1.05 g/cm^3 and the viscosity was 1579 cP (25 °C). The triphenylbismuth (TPB) and tris(3-ethoxyphenyl) bismuthine (TEPB) used as catalysts were synthesized by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, the purity was >99.5%. The molecular structure of TPB and TEPB are shown in Figure 2. 2,4-Toluene diisocyanate (TDI), the curing agent, was purchased from Sinopharm Chemical Reagent Co., Ltd.

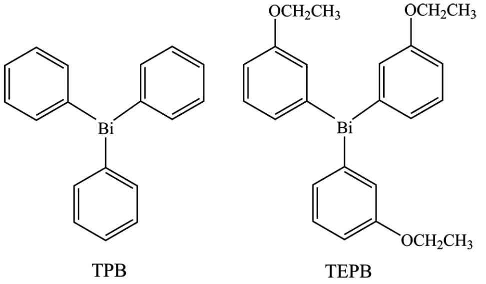


Figure 2. Molecular formulae of two organic bismuth complex catalysts

In this study, the stoichiometric ratio of the isocyanate groups in TDI and hydroxyl groups in HTPE was 1. The concentration of the catalysts in the blended samples was 0.2% [21]. The blends, including HTPE, TDI and catalysts, were stirred for 15 min to ensure proper dispersion and degassed for 10 min.

2.2 Differential scanning calorimetry

DSC measurements were performed using a Netzsch STA449C calorimeter. Non-isothermal heating experiments were conducted in an argon flow of 50 mL/min. The heating was from room temperature to 300 °C at heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min in order to study the kinetics of the cure reaction. Samples of 10 mg were used for these measurements. The cure reaction was assumed to be complete when the non-isothermal curve of the blend levelled off to the baseline.

2.3 Fourier transform infrared spectroscopy

Freshly prepared blends were taken for FTIR before DSC analysis. Afterwards, the samples cured after DSC measurement were subjected to analysis of the characteristic absorptions in the range 4000-800 cm^{-1} using a Nicolet 6700 FTIR spectrometer. The spectra were obtained as percentage transmittance against wavenumber.

2.4 Viscosity and hardness measurements

HTPE was used to replace the HTPB in the widely applied polymer bonded explosive formulation designated as PBXN-109 [22]. The original and substituted formulations are listed in Table 1; and some functional additives such as antioxidant were omitted in the substituted formulation to exclude their influence. The PBX slurries were prepared according to conventional practice, the binder precursors including HTPE, plasticizer and catalysts were thoroughly mixed and degassed for 30 min before adding the solid ingredients, aluminum powder and then RDX. The last step of the mixing operation was the addition of TDI, which was mixed for a period of about 10 min prior to casting the PBX into a mould. A 5-L planetary action mixer was used for preparing the PBX slurries. A vacuum casting box was used and vibration was applied to the entire assembly to facilitate degassing. The whole mixing procedure was conducted at a temperature of 60 °C for 2 h to ensure homogeneity of the PBX slurry. A Brookfield RST plus controlled stress rheometer was used to measure the viscosity build-up of the slurry after mixing all of the ingredients. The temperature of the slurry was maintained at 60 °C by a Brookfield TC-550AP temperature controller. The slurries were cast into the moulds and kept under isothermal condition to complete the cure process. PBX slurries without catalyst were placed in an oven at 40 °C and 60 °C respectively, and the slurries with catalyst were placed in an oven at 40 °C. These PBX slurries were then cured for 5 days in order to prepare the PBX grains. The hardness of the PBX during the cure process was measured using a Bareiss Digi Test II Shore A type durometer as stipulated by ASTM D 2240 [23].

Table 1. Original and substituted PBXN-109 formulation

Original formulation of PBXN-109		Substituted formulation	
Ingredient	Nominal [wt.%]	Ingredient	Nominal [wt.%]
Hydroxyl-terminated polybutadiene (HTPB)	7.346	Hydroxyl-terminated polyether (HTPE)	7.515
Dioctyl adipate (DOA)	7.346	Dioctyl adipate (DOA)	7.515
Cyclotrimethylene-trinitramine (RDX)	64	Cyclotrimethylene-trinitramine (RDX)	64
Aluminum	20	Aluminum	20
Isophorone diisocyanate (IPDI)	0.95	2,4-Toluene diisocyanate (TDI)	0.95
Catalysts (TPB)	0.02	Catalysts (TPB or TEPB)	0.02
Antioxidant 2246 (AO)	0.10		
Dantocol DHE	0.26		

2.5 Mechanical and thermal properties test

The tensile test was processed after the hardness reached 30 HA. A Shimadzu AGS-J 5KN/1KN electronic mechanical universal testing machine was used at a crosshead speed of 10 mm/min according to ASTM D 882-12 [24]. The dimensions of the specimens were width 5 mm, length 70 mm and thickness

0.5 mm. The operational processes were performed at 25 °C and a relative humidity of 50% after the samples had been treated at 23 ±2 °C and relative humidity 50 ±10% for 5 days.

The thermal stability and compatibility were investigated by DSC-TGA using a Netzsch STA449C calorimeter. Samples of 5 mg were used for these measurements. The heating was from room temperature to 400 °C at 10 °C/min under an argon flow of 10 mL/min.

3 Results and Discussion

3.1 Cure reaction investigation

The DSC curves of different cure systems at 10 °C/min are shown in Figure 3. The heat generated during the cure reaction of an uncatalyzed HTPE/TDI system was far below that of the catalyzed cure reactions. In this scenario, the uncatalyzed cure reaction was assumed to be incomplete since the HTPE cure process requires several days under isothermal conditions during PBX manufacture [25].

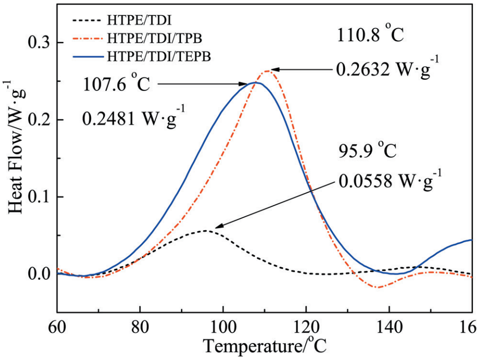


Figure 3. DSC curves of different curing systems at 10 °C/min

FTIR analysis was performed to study the significant chemical interactions of the characteristic groups involved before and after DSC measurement. The spectra of HTPE and TDI blends are shown in Figure 4 with significant bands being marked. The broad weak stretching vibration band of hydroxyl in the region of 3400-3500 cm^{-1} resulted from the low hydroxyl value of HTPE. Thus, absorption peaks near 1200 cm^{-1} in the spectrum should be noted due to the stretching vibrations of C−O bonds between hydroxyl and carbon atoms. The main peaks observed before DSC measurement occurred at 1218 cm^{-1} and 2272 cm^{-1} were due to the hydroxyl and isocyanate groups respectively.

The characteristic peak of the amide II band was also observed near 1536 cm^{-1} because of urethane formation before the DSC measurement. The appearance of a narrow band at 1732 cm^{-1} in the sample after DSC measurement was due to the presence of C=O bonds in the urethane generated during the non-isothermal heating. However, peaks at 1218 cm^{-1} and 2272 cm^{-1} present after heating implies that the quantitative consumption of reactant was incomplete and hence the cure reaction was incomplete.

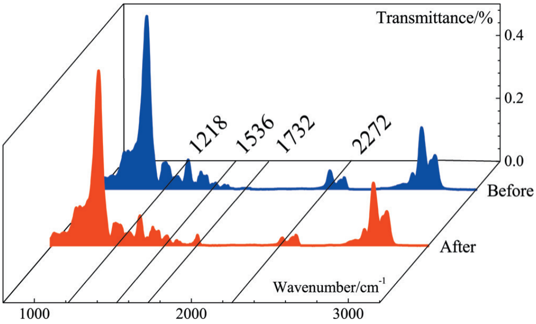


Figure 4. FTIR spectra of uncatalyzed sample, before and after DSC measurement

3.2 Cure kinetic analysis

The DSC characteristic exotherm temperatures of an uncatalyzed HTPE/TDI cure reaction including initial (T_i), peak (T_p) and final (T_f) temperatures were also measured. Although an incomplete cure reaction was confirmed by FTIR, the kinetic parameters of the cure reaction without catalyst are meaningful for comparison with the catalyzed cure reactions.

The characteristic temperatures of the catalyzed cure reactions are listed in Table 2. TEPB shifted the characteristic temperatures downwards compared with the TPB catalyzed cure reaction, however, the temperature intervals (T_f - T_i) of the TPB catalyzed cure reaction were smaller. This indicates that the catalytic activity of TEPB is higher than that of TPB as the cure temperature of the TEPB catalyzed reaction is lower. According to earlier research, charge distribution in the isocyanate group is the electronic resonance structure, therefore the isocyanate nitrogen is hydrogen bonded to the hydroxyl hydrogen, while the nucleophilic hydroxyl oxygen is associated with the electrophilic isocyanate carbon, resulting in an incremental electron density on the carbon of the associated isocyanate. Hence the catalytic mechanism of TPB involves association of TPB with a hydroxyl hydrogen, increasing the nucleophilicity of the adjacent oxygen in the hydroxyl due to the electron withdrawing effect of the benzene ring in

TPB [26]. The ethoxyl group in TEPB increases the electronegativity of the ethoxyphenyl group and the increased nucleophilicity of the catalyst-hydroxyl hydrogen association is thought to be the reason why the catalytic activity of TEPB is enhanced.

Table 2. DSC exotherm temperatures of the catalyzed cure reactions

Catalyst	β [°C/min]	T_i [°C]	T_p [°C]	T_f [°C]	$T_f - T_i$ [°C]
TPB	5	85.1	98.4	108.5	23.4
	10	91.6	110.8	126.6	35.0
	15	97.2	117.6	138.1	40.9
	20	106.2	125.9	157.7	51.5
TEPB	5	77.3	94.2	105.6	28.3
	10	82.0	107.4	126.1	44.1
	15	91.4	115.7	134.7	43.3
	20	102.1	121.9	155.0	52.9

The original Kissinger equation [27] and Crane method [28] were used to calculate the kinetic parameters, *viz.*, apparent activation energy (E_a), pre-exponential factor (A) and reaction order (n).

Kissinger equation:

$$-E_a/R = d[\ln(\beta/(T_p^2)]/d(T_p^{-1}) \tag{1}$$

Crane equation:

$$-(E_a/nR + 2T_p) = d(\ln\beta)/d(T_p^{-1}) \tag{2}$$

Since $E_a/nR >> 2T_p$, the Crane equation can be simplified to:

$$-E_a/nR = d(\ln\beta)/d(T_p^{-1}) \tag{3}$$

where β is the heating rate (°C/min); E_a is the apparent activation energy (kJ/mol); n is the reaction order and R is the gas constant (8.314 J/mol/K).

Plots of $\ln\beta$ and $\ln(\beta/T_p^2)$ *vs.* $1/T_p$ (where T_p is the peak temperature in K) both gave straight lines. The linear relation and the adjusted coefficients of determination of the fittings were well maintained, especially for the TEPB catalyzed cure reaction. The kinetic parameters calculated according to the fitting lines of the above cure reactions are listed in Table 3. The E_a values were expected to be lower for reactions with higher reaction rates and were used to evaluate the reactivity of the cure reactions and catalytic activity of the catalysts. The E_a value of the uncatalyzed cure reaction was significantly reduced from 66.41 kJ/mol to 56.96 kJ/mol and 54.06 kJ/mol by TPB and TEPB, respectively. However, the consistent reaction order of these cure reactions indicated that the bismuth complex catalysts applied in this study did not change the basic reaction of the HTPE/TDI urethane reaction. The urethane forming reaction follows *n* order reaction model according to research on the curing kinetic model.

$$d\alpha/dt = k(1 - \alpha)^n \tag{4}$$

where α, *t* and *k* follow the Arrhenius equation:

$$k = A\ \exp(-E_a/RT) \tag{5}$$

where *k* is the reaction rate constant (s^{-1}); α is the degree of curing; *A* is the pre-exponential factor (s^{-1}) and *t* is the reaction time.

Table 3. Kinetic parameters of the cure reactions

Catalyst	E_a [kJ/mol]	A [s^{-1}]	n
uncatalyzed	66.41	1.57×10^9	0.91
TPB	56.96	2.61×10^7	0.90
TEPB	54.06	1.19×10^7	0.90

The kinetic equations of the catalyzed cure reactions, calculated by the above kinetic parameters, are listed in Table 4. Since it was found to be incomplete, the kinetic equation of the uncatalyzed cure reaction was not established.

Table 4. Kinetic equations of the cure reactions

Catalyst	Kinetic equations of the curing reaction
TPB	$d\alpha/dt = 2.61\times10^7\ \exp(-6851/T)\ (1-\alpha)^{0.90}$
TEPB	$d\alpha/dt = 1.19\times10^7\ \exp(-6502/T)\ (1-\alpha)^{0.90}$

The Kissinger and Ozawa [29] methods were both used to calculate the E_a of the catalyzed cure reactions at various degrees of curing from 0% to 100% in steps of 10%. The results calculated by two methods were only slightly different in the values as shown in Figure 5. The same variation tendency of E_a at various α values should be attributed to the catalytic mechanism of the bismuth complex catalysts. The increment of E_a in the earlier stage of the cure process is caused by the initial formation of a catalyst-hydroxyl association while the subsequent reaction of the formed association with the isocyanate generating the urethane group leads to a significant reduction of E_a. Finally, the catalyst is regenerated with a slight increment of E_a. The continuous decreasing tendency of E_a in the later stage may be explained by the interaction of the catalysts and the "autocatalysis" effect [30].

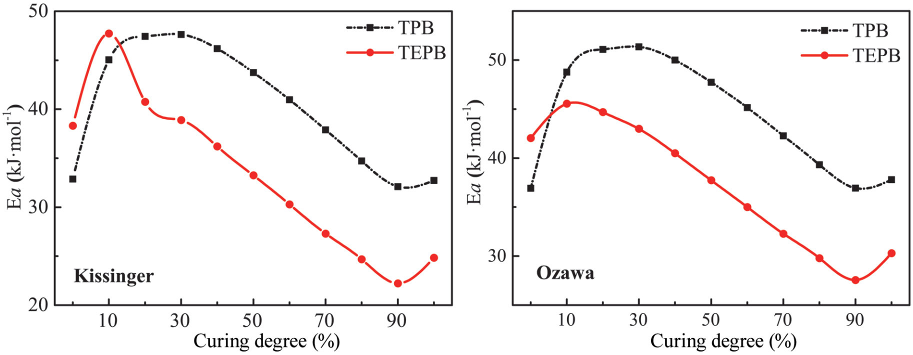


Figure 5. Apparent activation energies of catalyzed curing reaction at various degrees of curing

Figure 6 depicts the spectra of a freshly prepared blend and the raw materials, including HTPE, TDI and TEPB. The absorption peaks near 1541 cm^{-1} and 1732 cm^{-1} were due to the amide II band and urethane groups in the blend sample. Since the catalytic activity of TEPB is high, as mentioned above, the formation of urethane group during sample preparation is predictable. The shifted absorption band of the amide indicated a change in the N−H bond energy, which resulted from the catalyst-hydroxyl group association in the intermediate formed at the earlier stage.

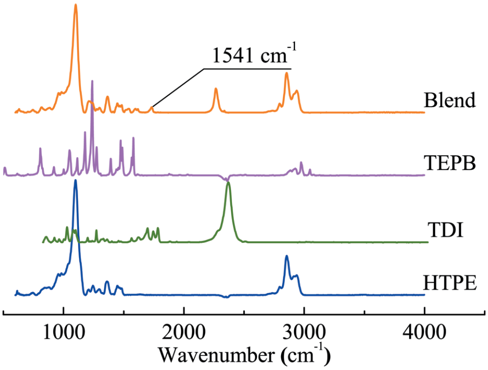
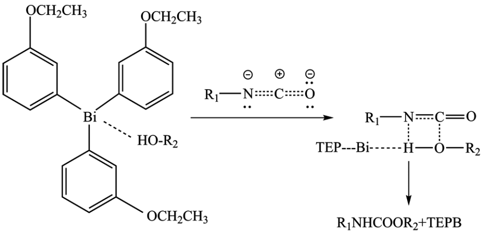


Figure 6. FTIR spectrum of raw materials involved and TEPB catalyzed blend sample

Scheme 1 explains the reaction mechanism of TEPB catalyzed urethane formation. The reaction was supposed to proceed, initially, through an association of TEPB and a hydroxyl group. Then, the reaction between isocyanate and the catalyst-hydroxyl association results in the formation of an intermediate analogous to an amide. The newly generated intermediate then rapidly forms the urethane group under the influence of TEPB. Thus, the cure reaction of HTPE is promoted by the addition of the bismuth complex catalyst to form a polyurethane network.



Scheme 1. Reaction mechanism of TEPB catalyzed urethane formation

The rate constant determines the reaction rate at a specific temperature. The difference in reactivity of reactions catalyzed by different catalysts could be confirmed by the rate constants at different temperatures. The rate constants are listed in Table 5. As a commonly used catalyst, the catalytic activity of TPB is stable at the typical cure temperature. This suggests that the catalytic activity of TEPB is higher since the rate constant of the TEPB catalyzed cure reaction at 40 °C approached the value of the TPB catalyzed cure reaction at 45 °C. TEPB allows a reduction in the HTPE-urethane forming temperature.

Table 5. Rate constants at various temperatures

Catalyst	$k \times 10^{-3}$ [s^{-1}]				
	30 °C	40 °C	45 °C	50 °C	60 °C
TPB	3.95	8.14	11.5	16.0	30.3
TEPB	5.68	11.3	15.6	21.5	39.3

3.3 Viscosity and cure process inspection

The pot life is the process time in which the viscosity of the PBX slurry is suitable for casting. It is a significant technological parameter in the PBX manufacturing process and determines the mixing and casting time [31]. The viscosity of the slurry continues to increase after adding the curing agent due to urethane formation, and high catalytic activity catalysts can greatly accelerate the cure reaction resulting in an unacceptable pot life of the casting PBX. It is found that the pot life of a PBX slurry is the time taken for the corresponding mixture to reach a viscosity of 5000 P, according to the equipment used and previous manufacturing experience. The pot life for the present systems was determined by the viscosity build-up and is shown in Figure 7. In general, the pot life of a slurry is required to be achieved in about 4 h to 5 h, which is satisfactory for the manufacture of conventionally sized grains. The viscosities of the catalyzed slurries at 5.5 h were both below 5000 P and available for casting. This indicates that the catalytic activities of TPB and TEPB satisfy the manufacturing process requirements based on the catalyst concentration of the PBXN-109 formulation. The pot lives of the catalyzed slurries, especially the slurry with TEPB, satisfied the technological requirements.

The high catalytic activity of the bismuth complex catalysts was the reason that the viscosity increases of the catalyzed PBX slurries were much faster than the uncatalyzed one, since the viscosities at the end of mix of the three PBX slurries were almost the same. It was observed that the viscosity increases of the catalyzed slurries proceeded in two stages, a slow first stage succeeded by a fast second stage. Since the catalyst-hydroxyl group association was formed in the first stage according to Luo's research [26] and the variation tendency of E_a at the beginning of the catalyzed cure reaction, the slow viscosity increase stage could be interpreted as the formation process of the association between the catalyst and hydroxyl groups. This stage was supposed to be short in the pure binder system instead of greater than 3 h in the PBX slurries. This seems to be the result of dilution that the other ingredients impede the reaction of HTPE and the catalysts. The viscosity increases of the catalyzed slurries increased analogously in the first stage due to the analogous molecular structures of TPB and TEPB. That the second stage viscosity increase of the TEPB catalyzed slurry was faster than that for the TPB catalyzed slurry, proved that the catalytic activity of TEPB was higher.

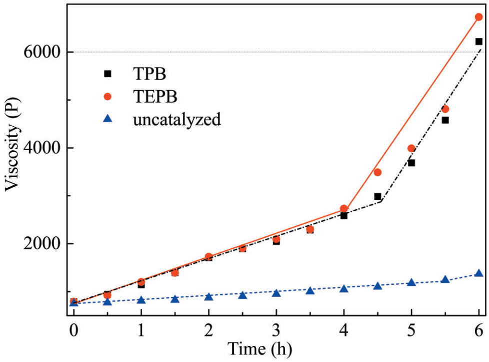


Figure 7. Viscosity build-up of PBX slurries at 60 °C

Application of catalysts in PBX manufacture contributes to a decrease in the manufacture temperature to ambient and to an improvement in the mechanical properties of the PBX grains. Slurries were cast into moulds and maintained at 40 °C to complete the cure process since the catalytic activity of TEPB was high enough under these conditions according to the above analysis. The low reaction rate of uncatalyzed urethane formation at this temperature was the reason that hardness increases in the grain without a catalyst was far below that of the catalyzed grains.

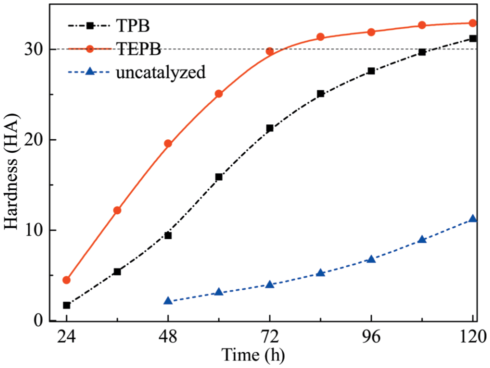


Figure 8. Hardness build-up of the PBX grain during the curing process

As shown in Figure 8, the hardness of the uncatalyzed grain could not be measured until 48 h because of the unformed polymer network and dimensional structure. It was observed that the application of the bismuth complex catalysts effectively enhanced the hardness build-up and shortened the time. There is a slow post-cure process in thermosetting polyurethane [32]. This suggests that PBX grains are cured when the hardness reaches 30 HA. It took approximately 72 h to complete the cure process for the PBX grain containing TEPB and 102 h for the PBX containing TPB, whereas the hardness of the TPB catalyzed grain reached a critical value under this curing condition. It could be assumed that the hardness build-up rate at a lower temperature is unacceptable for a conventional process since the reaction rate constant for urethane formation with TEPB at 30 °C was below the value of the TPB catalyzed one at 40 °C. Thus, HTPE based PBX manufacture at ambient temperature is possible by a readjustment of TEPB concentration.

3.4 Mechanical and thermal characteristics and compatibility

Tensile stress-strain curves of the PBXs cured under different conditions are shown in Figure 9. All of the PBX specimens underwent linear deformation in the initial part until the stress reached a relative extremum. A “dewetting” phenomenon was observed in specimens after the stress extremum. The breaking elongation and maximum stress could be identified directly on the stress-strain curves. It was observed from the curves that the tensile deformation behaviour of the specimens was markably influenced by the catalysts and the curing conditions. The maximum stress of a PBX specimen cured at 60 °C was 0.35 MPa, and the stress decreased with strain after dewetting. This seems to suggest that crosslinking had not been completed during the isothermal curing process. Microcracks rapidly propagated in the incomplete polymer matrix due to the internal residual stress and finally caused fracture of the whole specimen in the tensile test. The maximum stress of a PBX specimen with TPB was much higher than that for the uncatalyzed sample. Obviously, the inferior breaking elongation of the TPB sample suggests that the curing process had also not been complete. However, the low temperature curing process led to reduced residual stress, which contributed to encapsulation of the energetic material particles and delayed the dewetting phenomenon. Two stages were observed in the curve of the TEPB sample, which were a ‘linear elastic’ region [33] and an ‘after dewetting’ region respectively. The sharply reduced Young’s modulus between the two stages demonstrated that the strain of the polymer matrix dominated the second stage. The maximum stress of the PBX specimen with TEPB appeared with the breaking elongation at the second stage, which was different from the other samples. It is obvious that the degree of curing of the TEPB sample is high. The mechanical characteristics of the PBX grain with TEPB is satisfactory due to the low residual stress and high degree of curing.

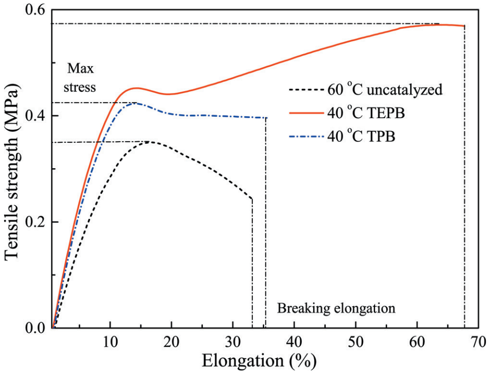


Figure 9. Tensile stress-strain curves of PBXs cured under different conditions

The thermal analysis curves of the HTPE prepolymer, PBX with TEPB and without a catalyst, at a heating rate of 10 °C/min, are shown in Figure 10. The decomposition of the HTPE prepolymer was a two-step process without a violent exothermic peak. The first step was due to depolymerization and slight decomposition, which could be confirmed from the exothermic peak starting from about 200 °C in the DSC curve, and the slight mass loss in the TGA curve, respectively. The second step was due to decomposition of the depolymerized HTPE, corresponding to the main mass loss starting from 350 °C in the TGA curve. The initial temperature of the first decomposition step of HTPE was lower than the decomposition temperature of RDX. A violent exothermic chemical reaction can usually occur when a PBX is exposed to thermal loading, due to the decomposition of the explosive material, such as RDX. This is the major reason why munitions detonate accidentally when subjected to a thermal stimulus. The gaseous products of decomposition of HTPE can accumulate in the warhead shell, or slow cook-off test vehicle, and burst the shell before the violent decomposition of RDX, which decreases the pressure inside the shell and contributes to inhibiting the deflagration-to-detonation transition. The typical initial decomposition temperature of HTPB is about 350 °C [34], which is much higher than that of RDX. This seems to explain the lower thermal sensitivity of HTPE based PBXs and the less severe response in the slow cook-off test for IM compliance.

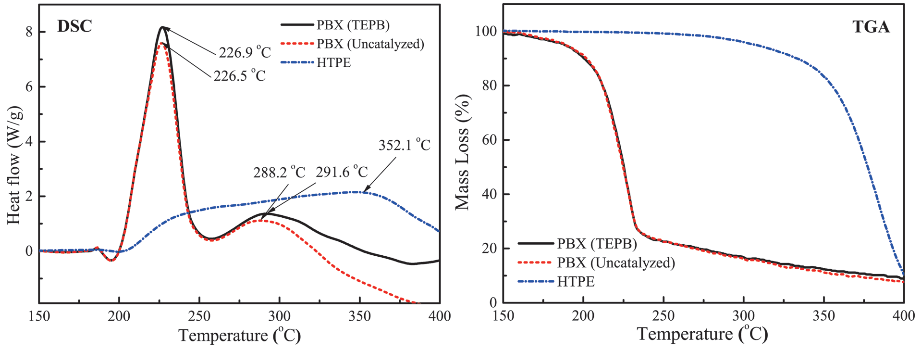


Figure 10. Thermal decomposition curves of the HTPE prepolymer and the substituted PBXN-109 composites with TEPB and without catalyst

The compatibility of TEPB and the subjected PBXN-109 formulation can be investigated by the decomposition temperature differences (Δ*T*) of the PBX composites according to STANAG 4147 [35]. The first exothermic peak on the PBX curves represents the decomposition of RDX, and Δ*T* was even less than 1 °C. This indicates that TEPB is compatible with RDX. The second exothermic peak represents the decomposition of HTPE. The decomposition temperature of HTPE with TEPB was higher than the uncatalyzed one. It could be speculated that the higher degree of curing of the catalyzed PBX contributed to improving the structural integrity of the PBX grain. Although the hardness reached 30 HA, the incomplete polymer matrix inside the uncatalyzed PBX led to the lower decomposition temperature. It can be determined from the Δ*T*s of the major ingredients in the PBX composites that TEPB is certainly compatible with the substituted PBXN-109 formulation. However, the decomposition temperature of RDX in the HTPE based PBXs was shifted downward by about 10 °C, since the typical decomposition temperature of RDX is about 237 °C according to published research [36]. Therefore, the compatibility of HTPE and RDX is not sure, and relevant results will be discussed in a future publication.

4 Conclusions

Blends of HTPE, TDI and bismuth complex catalysts were prepared to investigate the cure kinetics of the urethane forming reaction by non-isothermal DSC. The catalysts decreased the apparent activation energy and accelerated the cure reaction. FTIR spectra were measured to investigate changes in the corresponding groups and the cure kinetics. Catalyst-hydroxyl group association was formed in the first stage, and a corresponding result was observed simultaneously from the variation tendency of the apparent activation energy at various degrees of curing. The catalytic activities of TPB and TEPB were evaluated by comparing the rate constants at specified temperatures after establishing the reaction kinetic equations. The two bismuth complex catalysts were added in a substituted PBX formulation to verify the possibility of their practical application according to the pot life and the cure process of the PBX slurry. TEPB was shown to be a positively compatible and more effective catalyst with an acceptable pot life, which would allow a significant reduction in the HTPE based PBX manufacturing temperature and time. The mechanical properties and thermal safety of an HTPE based PBX was also markably improved by TEPB.

References

[1] Golofit, T.; Zyśk, K. Thermal Decomposition Properties and Compatibility of CL-20 with Binders HTPB, PBAN, GAP and PolyNIMMO. *J. Therm. Anal. Calorim.* **2015**, *119*(3): 1931-1939.

[2] Chen, F.; Duo, Y.; Luo, S. G.; Luo, Y.; Tan, H. Novel Segmented Thermoplastic Polyurethanes Elastomers Based on Tetrahydrofuran Ethylene Oxide Copolyethers as High Energetic Propellant Binders. *Propellants Explos. Pyrotech.* **2003**, *28*(1): 7-11.

[3] Caro, R. I.; Bellerby, J. M. Synthesis and Characterization of a Hydroxy Terminated Polyether (HTPE) Copolymer for Use as a Binder in Composite Rocket Propellants. *Int. J. Energetic Mater. Chem. Propul*. **2007**, *6*(3): 289-306.

[4] Caro, R. I.; Bellerby, J. M. Characterization and Comparison of Two Hydroxyl-Terminated Polyether Prepolymers. *Int. J. Energetic Mater. Chem. Propul*. **2010**, *9*(4): 351-364.

[5] Daniel, M. A. *Polyurethane Binder Systems for Polymer Bonded Explosives*. Australian Government, Department of Defense, Report DSTO-GD-0492, **2006**.

[6] Lan, Y.; Li, D.; Zhai, J.; Yang, R. Molecular Dynamics Simulation on the Binder of Ethylene Oxide-Tetrahydrofuran Copolyether Cross-Linked with N100. *Ind. Eng. Chem. Res.* **2015**, *54*: 3563-3569.

[7] Kim, K.; Kim, C.; Yoo, J. Test-based Thermal Decomposition Simulation of AP/HTPB and AP/HTPE Propellants. *J. Propul. Power* **2011**, *27*(4): 822-827.

[8] Hedman, T. D.; Gross, M. L.; Davis, J. J. J.; Davis, N.; Ford, K. P. Experimental Investigation of the Decomposition Preceding Cookoff in a Composite Propellant. *J. Propul. Power* **2014**, *30*(6): 1667-1674.

[9] Caro, R. I.; Bellerby, J. M. Behavior of Hydroxyl-Terminated Polyether (HTPE) Composite Rocket Propellants in Slow Cook-off. *Int. J. Energetic Mater. Chem. Propul.* **2008**, *7*(3): 171-185.

[10] Ahmad, N.; Khan, M.; Ma, X.; Ul-Haq, N. Dynamic Mechanical Characterization of the Crosslinked and Chain-Extended HTPB Based Polyurethanes. *Polym. Polym. Compos.* **2012**, *20*(8): 683-691.

[11] Zhang, P.; Guo, X.; Zhang, J.; Jiao, Q. Application of Liquid Paraffin in Castable CL-20-Based PBX. *J. Energ. Mater*. **2014**, *32*(4): 278-292.

[12] Thibieroz, B.; Lecume, S.; Bigot, Y. Development and Characterization of PBX Cast at Ambient Temperature. *2001 Insensitive Munitions and Energetic Materials Technology Symposium*, Bordeaux, France **2001**, 531-542.

[13] Xu, G.; Zhang, J.; Huang, Z. Effects of Porosity and Mechanic Properties of Explosive Charges Launching Safety. *Proc. 1996 Autumn Seminar on Propellants, Explosives and Pyrotechnics*, Beijing, China **1996**, 101-118.

[14] Huang, Z.; Nie, H.; Zhang, Y.; Tan, L.; Yin, H.; Ma, X. Migration Kinetics and Mechanisms of Plasticizers, Stabilizers at Interfaces of NEPE Propellant/HTPB Liner/EDPM Insulation. *J. Hazard. Mater.* **2012**, *229-230*(3): 251-257.

[15] Fu, X.; Fan, X.; Ju, X.; Qi, X.; Li, J.; Yu, H. Molecular Dynamic Simulations on the Interaction Between an HTPE Polymer and Energetic Plasticizers in a Solid Propellant. *RSC Adv.* **2015**, *5*(65): 52844-52851.

[16] Ou, Y.; Chang, S.; Zhang, B. Effect of Bismuth-containing Catalysts on HTPB Curing Kinetics. (in Chinese) *Chin. J. Energ. Mater*. **2015**, *23*(6): 568-572.

[17] Douglas, W. E.; Overend, A. S. Curing Reactions in Acetylene Terminated Resins-III. DSC, TGA and TMA Study of Catalyzed Cure of an Ethynylaryl-Terminated Monomer. *Eur. Polym. J.* **1993**, *29*(11): 1513-1519.

[18] Hailu, K.; Guthausen, G.; Becker, W.; Konig, A.; Bendfeld, A.; Geissler, E. In-situ Characterization of the Cure Reaction of HTPB and IPDI by Simultaneous NMR and IR Measurements. *Polym. Test* **2010**, *29*(4): 513-519.

[19] Bina, C. K.; Kannan, K.; Ninan, K. N. DSC Study on the Effect of Isocyanates and Catalysts on the HTPB Cure Reaction. *J. Therm. Anal. Calorim.* **2004**, *78*(3): 753-760.

[20] Catherine, K. B.; Krishnan, K.; Ninan, K. N. A DSC Study on Cure Kinetics of HTPB-IPDI Urethane Reaction. *J. Therm. Anal. Calorim.* **2000**, *59*(1): 93-100.

[21] Lee, S.; Choi, J. H.; Hong, I.; Lee, J. W. Curing Behavior of Polyurethane as a Binder for Polymer-Bonded Explosives. *J. Ind. Eng. Chem.* **2015**, *21*(8): 980-985.

[22] Hamshere, B. L.; Lochert, I. J.; Dexter, R. M. *Evaluation of PBXN-109: the Explosive Fill for the Penguin Anti-Ship Missile Warhead*. Australian Government, Department of Defense, Report DSTO-TR-1471, **2003**.

[23] *Standard Test Method for Rubber Property-Durometer Hardness*. ASTM D2240-15e1, ASTM International, West Conshohocken, PA, **2015**, www.astm.org

[24] *Standard Test Method for Tensile Properties of Thin Plastic Sheeting*. ASTM D882-12, ASTM International, West Conshohocken, PA, **2012**, www.astm.org

[25] Wang, J.; An, C.; Li, G.; Liang, L.; Xu, W.; Wen, K. Preparation and Performances of Castable HTPB/CL-20 Booster Explosives. *Propellants Explos. Pyrotech.* **2011**, *36*(1): 34-41.

[26] Luo, S. G.; Tan, H.; Zhang, J.; Wu, Y.; Pei, F.; Meng, X. Catalytic Mechanisms of

Triphenylbismuth, Dibutyltin Dilaurate, and Their Combination in Polyurethane-Forming Reaction. *J. Appl. Polym. Sci.* **1997**, *65*(6): 1217-1225.

[27] Šesták, J. Is the Original Kissinger Equation Obsolete Today: not Obsolete the Entire Non-isothermal Kinetics? *J. Therm. Anal. Calorim.* **2014**, *117*(1): 3-7.

[28] Crane, L.; Dynes, P.; Kaelble, D. Analysis of Curing Kinetics in Polymer Composites. *J. Polym. Sci. Polym. Lett. Ed.* **1973**, *11*(8): 533-540.

[29] Koga, N. Ozawa's Kinetic Method for Analyzing Thermoanalytical Curves. *J. Therm. Anal. Calorim*. **2013**, *113*(48): 1527-1541.

[30] Baker, J. W.; Gaunt, J. The Mechanism of the Reaction of Aryl Isocyanates with Alcohols and Amines. Part III. The "Spontaneous" Reaction of Phenyl Isocyanate with Various Alcohols. Further Evidence Relating to the Anomalous Effect of Dialkylanilines in the Base-Catalysed Reaction. *J. Chem. Soc.* **1949**, *9*: 19-24.

[31] Sekkar, V.; Raunija, T. S. K. Issues Related with Pot Life Extension for Hydroxyl-Terminated Polybutadiene-Based Solid Propellant Binder System. *Propellants Explos. Pyrotech.* **2015**, *40*(2): 267-274.

[32] Carbas, R. J. C.; Da Silva, L. F. M.; Marques, E. A. S.; Lopes, A. M. Effect of Post-cure on the Glass Transition Temperature and Mechanical Properties of Epoxy Adhesives. *J. Adhes. Sci. Technol*. **2013**, *27*(23): 2542-2557.

[33] Wang, Z.; Qiang, H.; Wang, G.; Huang, Q. Tensile Mechanical Properties and Constitutive Model for HTPB Propellant at Low Temperature and High Strain Rate. *J. Appl. Polym. Sci.* **2015**, *132*(24): 42104.

[34] Du, T. Thermal Decomposition Studies of Solid Propellant Binder HTPB. *Thermochim. Acta* **1989**, *138*(2): 189-197.

[35] *Chemical Compatibility of Ammunition Components with Explosives (Non-Nuclear Applications)*. NATO Standardisation Agreement (STANAG) 4147, AC/310 (SG1) D15 (Draft ed. 2) I-96 NAVY/ARMY/AIR.

[36] Jangid, S. K.; Talawar, M. B.; Singh, M. K.; Nath, T.; Sinha, R. K. Experimental Studies on Advanced Sheet Explosive Formulations Based on 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) and Hydroxyl Terminated Polybutadiene (HTPB), and Comparison with a RDX-based System. *Cent. Eur. J. Energ. Mater.* **2016**, *13*(1): 135-147.