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Role of Curing Agents on Decomposition and Explosion of Glycidyl Azide Polymers

Surendra P. Panda,* Sanjay K. Sahu,† Dinkar S. Sadafule,‡
and Jyotsna V. Thakur§
Institute of Armament Technology,
Girinagar, Pune 411 025, India

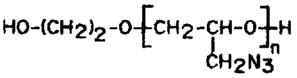
Introduction

GLYCIDYL azide polymers (GAPs) (Fig. 1) cured with diisocyanates have been investigated rather extensively for use as propellants for ram rockets.[1–5] These propellants, in addition to being fuel rich and liberating large amounts of H_2, CO, and gaseous hydrocarbons on their burning in the primary chamber, are greatly insensitive to impact and provide high burning rates.[5] Their decomposition pattern is also not affected by increased pressure.[6] However, the decomposition products of cured GAPs contain HCN, which is highly toxic. Though attempts have been made to suppress HCN in the gaseous decomposition products by using copolymers of GAPs with high hydrocarbon content,[7] no attempt has been made to use diisocyanates to cure GAPs with increasing hydrocarbon content to achieve the same purpose. Further details of the explosive behavior of GAPs and their cured products are not available in the literature. In this Note, hydroxy-terminated GAPs with $\overline{Mn}$, 1100 and 2150 cured with toluene diisocyanate (TDI) (Fig. 2), isophorone diisocyanate (IPDI) (Fig. 3), and 4,4′-dicyclohexylmethane diisocyanate ($H_{12}MDI$) (Fig. 4) have been investigated to elucidate the decomposition mechanism, suppress HCN in the decomposition products, and generate data on their explosive behavior.

Materials and Methods

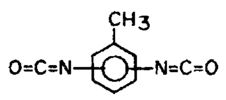
GAPs with two OH groups per molecule with average molecular weights 1100 and 2150 were synthesized by reacting the corresponding polyepichlorohydrin (PECH) with sodium azide in dimethyl sulfoxide (DMSO). Dihydroxy PECHs were in turn synthesized by activated monomer polymerization of epichlorohydrin using BF3-ethylene glycol complex as the catalyst.[8] These polymers were cured with TDI, IPDI, or $H_{12}MDI$ with trimethylol propane (TMP) as a triol crosslinker and dibutyl tin dilaurate (DBTDL) as catalyst at 333 K to be used as ram rocket propellants. TDI, IPDI, and H12MDI (Fluka Chemika, laboratory grade) were obtained commercially and used as received for the cure of the GAPs.

Cured GAP samples were decomposed by taking about 270 mg of a sample in a 100-ml round-bottom flask fitted with a side tube and a vacuum tap and heating it after evacuation in a concentrated H_2SO_4 bath up to 543 K. The gases evolved were collected in an evacuated gas analysis cell of an IR spectrometer fitted with NaCl windows. Fourier transform infrared (FTIR) spectra were recorded using a Perkin–Elmer FTIR spectrophotometer, Model 1605, for the analysis of the gaseous mixture.



$$HO{-}(CH_2)_2{-}O{-}\left[CH_2{-}\underset{\displaystyle CH_2N_3}{\underset{|}{CH}}{-}O\right]_n{-}H$$

Fig. 1 GAP.



(2, 4 isomer, 80% + 2, 6 isomer, 20%)

Fig. 2 TDI

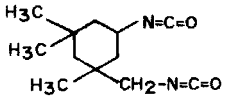


Fig. 3 IPDI.

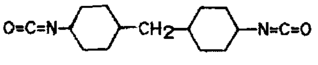


Fig. 4 $H_{12}MDI$.

Ionodes (ion selective electrodes) are simple, potentiometric sensors that respond to the concentration of an ion in a solution. About 1.08 g of cured GAP ($\overline{Mn}$, 2150) was taken in a 100-ml flask fitted with a side tube and a vacuum tap. The flask was heated after evacuation in a concentrated H_2SO_4 bath up to 543 K. The water-soluble and acidic gases evolved were absorbed by 30 ml of 10% NaOH solution to convert HCN to CN^-. Three sets of test solutions with unknown CN^- content were prepared by using GAP cured with TDI, IPDI, and $H_{12}MDI$ separately.

A standard AgCN solution (CN^- content 100 ppm) was taken in a beaker containing a reference electrode (polymer body Ag-AgCl type) and a CN^--sensitive electrode. A digital p_H meter was used to calibrate CN^- concentration in terms of mV. Three more readings were noted for the solutions containing CN^- diluted to 10, 1, and 0.1 ppm. Similarly, the test solutions were measured for their CN^- concentrations by converting mVs produced by the cyanide-specific ion electrode.

Measurements of temperature of explosion of uncured and cured samples of GAPs were carried out in a special apparatus. This apparatus consists of a 10-cm-diam cylindrical copper block with a 2.5-cm-diam and 7-cm-depth cavity. It contains Wood's metal with a melting point of 338 K as the bath material, which can be heated up to 623 K. Approximately 5 mg of sample material was taken in an aluminum cup with a 5-mm diam and 2-mm height. The cup was covered with an aluminum cap. The Wood's metal bath was then electrically heated. The heating rate was controlled by a dimmerstat, and the bath temperature was monitored by a thermometer. When the desired temperature was reached, the current was controlled. The aluminum cup containing the sample was introduced into the bath, and a stopwatch was started. After a certain time interval the sample exploded with flash, and the stopwatch was instantly stopped. This reading represented the explosion delay. Thus, readings were taken at successive temperature intervals of 1 K until a temperature was reached at which the explosion delay was less than 5 s. The temperature corresponding to the 5-s explosion delay is usually referred to as the explosion temperature.

Energy of activation for explosion was calculated by using the equation

$$t = Ce^{E/RT} \tag{1}$$

where t is explosion time lag, E is energy of activation, T is absolute temperature, C is a constant (depending on the composition of the explosive), and R is universal gas constant (1.986 cal/g). This expression can be rewritten as

$$\log t = B + E/(2.303 \times 1.986)T \tag{2}$$

where B is a constant.

On plotting $\log t$ against $1/T$, a straight line is obtained. The slope of the plot is equal to E/R, from which the energy of activation for explosion can be calculated.

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*Associate Director and Dean, and Chairman, Faculty of Explosives and Applied Chemistry; panda@iat.ernet.in.

†Senior Research Fellow, Faculty of Explosives and Applied Chemistry.

‡Technical Officer 'B,' Faculty of Explosives and Applied Chemistry.

§Technical Assistant 'B,' Faculty of Explosives and Applied Chemistry.

Impact sensitivity of cured and uncured GAP samples was measured by an indigenous drop weight tester (disk diameter = 16.5 mm). The maximum weight used was 2 kg, and the maximum height from which the weight could be dropped was 170 cm. The Julius Peters Berlin 21 Friction Tester (maximum load used, 36 kg) was used to determine the friction sensitivity of various cured and uncured GAPs.[9]

Results and Discussion

Chen and Brill[10] have previously studied the FTIR spectrum of the decomposition products of GAPs. However, the diisocyanate-cured products were not similarly studied by them. Study of the composition of the gaseous decomposition products of the cured samples of GAP is vital for its applications as a ram-rocket propellant. In our study, the two varieties of GAPs and their TDI-, IPDI-, and H_{12}MDI-cured products decomposed and eliminated HCN in each case. The cyanide absorption is most predominant in the FTIR spectra of the mixtures of the decomposition products. It appeared in the range 2340–2360 cm^{-1} as a doublet. Interestingly, the intensities of the doublet were at maximum for the gaseous products obtained by decomposing TDI-cured GAPs. This indicates that the concentration of HCN in the gaseous mixture released by TDI-cured GAPs is distinctly higher than those in similar mixtures released by other samples of GAPs.

Thus it became necessary to make a quantitative measurement of the amount of HCN liberated from GAP cured with different diisocyanates to correlate it with increasing the hydrocarbon content of the diisocyanates. Using an ion selective electrode, the cyanide contents of TDI-, IPDI-, and H_{12}MDI-cured GAP were calculated to be 22.5, 7.5, and 3.9×10^{-3} mg, respectively. Thus, it can be seen that the higher hydrocarbon content of the diisocyanates considerably suppresses HCN liberated from the cured GAPs. In addition, by replacing GAP diol- by hydroxy-terminated polybutadiene (HTPB; $\overline{Mn}$, 2300, and 2 OH per molecule) to the extent of 5, 10, and 15% without changing the curing agents described in this Note, we have achieved suppression of HCN generation by another order. However, HTPB addition adversely affected the burning rate of GAP-based ram-rocket propellants (Panda, S. P., Sahu, S. K., and Thakur, J. V., Institute of Armament Technology, Pune, India; 7 June, 1999; unpublished results).

GAPs and their studied cured products were found to be stable up to 433 K and completely decomposed between 521 and 553 K, with a two-stage decomposition mechanism producing N_2 in the first stage and H_2, CO, CO_2, H_2O, CH_4, and other hydrocarbons subsequently.[11] In the present study, absorption peaks between 3740 and 3558 cm^{-1} were assigned to the various stretching absorptions of OH, CH, and NH groups present in H_2O, CH_4, and NH_3, and absorption peaks between 1694 and 1470 cm^{-1} were assigned to CH_2O, CO, and aliphatic compounds having an imine group (>NH) present in the gaseous mixture being analyzed. Two discrete absorptions were detected in the FTIR spectra of all of the samples of GAPs and their cured products around 966 and 930 cm^{-1}. They were assigned to NH_3 after Pfeil and Lobeecke.[7] The presence of polymeric nitrene as an intermediate was detected by us[11] by decomposing GAPs photochemically under intense UV irradiation and having the intermediate nitrene react with an unsaturated polymeric hydrocarbon to get a crosslinked and insoluble product. Thus, the overall mechanism of decomposition of GAPs and their cured products can be described as follows:

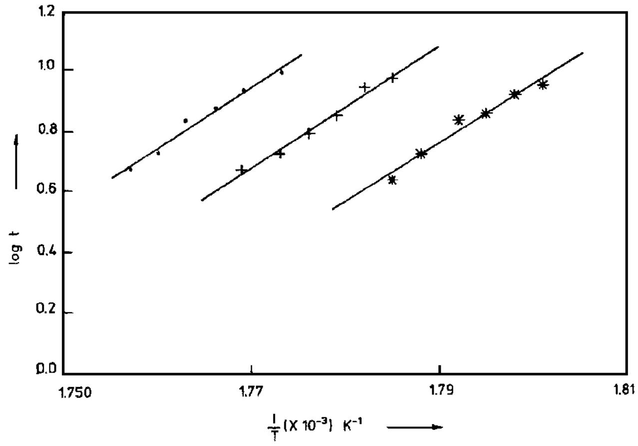
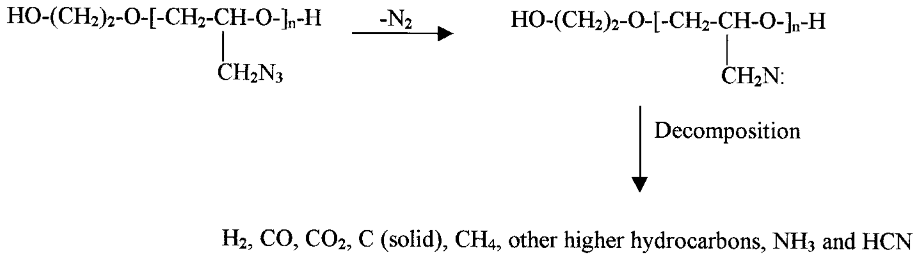


Fig. 5 Energy of activation for explosion of GAP ($\overline{Mn}$, 2150) cured with TDI(+), IPDI(*), and H_{12}MDI(●).



$$HO\text{-}(CH_2)_2\text{-}O\text{-}[\text{-}CH_2\text{-}\underset{\displaystyle CH_2N_3}{\underset{|}{CH}}\text{-}O\text{-}]_n\text{-}H \xrightarrow{-N_2} HO\text{-}(CH_2)_2\text{-}O\text{-}[\text{-}CH_2\text{-}\underset{\displaystyle CH_2N:}{\underset{|}{CH}}\text{-}O\text{-}]_n\text{-}H \xrightarrow{\text{Decomposition}} H_2, CO, CO_2, C\text{ (solid)}, CH_4, \text{other higher hydrocarbons}, NH_3 \text{ and } HCN$$

Two samples of GAPs ($\overline{Mn}$, 1100 and 2150) and their cured products with TDI, IPDI, and H_{12}MDI were found to be insensitive to explosion with 2 kg of weight dropped from a height of 170 cm in the drop test and a weight of 36 kg used in the Julius Peters friction test. However, under confined heating as described under the determination of heat of explosion, GAP with $\overline{Mn}$, 1100 and 2150 exploded at 556 and 534 K, respectively. Their diisocyanate-cured samples exploded relatively at higher temperature between 560 and 572 K. Figure 5 gives the relation between log t (t-time needed for explosion in seconds) against $1/T$ (T-temperature of explosion in K) for different diisocyanate cured GAPs with $\overline{Mn}$, 2150. The energy of activation calculated from the curve for GAP ($\overline{Mn}$, 2150) cured with TDI, IPDI, and H_{12}MDI is 388.5, 372.3, and 360.21 kJ/mol, respectively. Similarly, the energy of activation for explosion for GAP ($\overline{Mn}$, 1100) cured with TDI, IPDI, and H_{12}MDI is 383.76, 366.21, and 397.8 kJ/mol, respectively. These values are high in magnitude but cannot be correlated to any structural features of cured GAPs with a good measure of accuracy.

Conclusion

Concentration of HCN in the decomposition products of cured GAP could be considerably decreased by using IPDI and H_{12}MDI, which are alicyclic and contain a higher percentage of hydrocarbon than TDI as curing agents. Cured products of GAP were found to be highly insensitive to impact and friction. However, they exploded between 560 and 572 K under confined conditions with activation energy for explosion varying from 360.21 to 397.8 kJ/mol.

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Numerical Simulation of Axisymmetric Solid Rocket Motor Ignition Transient with Radiation Effect

In Hyun Cho*
Korea Aerospace Research Institute,
Yusung-ku, Taejon, 305-600, Republic of Korea
and
Seung Wook Baek†
Korea Advanced Institute of Science and Technology,
Gusung-dong, Yusung-ku, Taejon 305-701,
Republic of Korea

Introduction

THE solid rocket ignition transient representing a short period right after starting the rocket motor consists of propellant ignition, flame spreading, and chamber filling/pressurization. High-temperature and high-pressure gases ejected from the ignitor at the fore-end section of the rocket chamber heat up the solid propellants. As the heat flux to the propellant surface increases, the propellant starts to burn and releases a large amount of thermal energy in the combustion chamber. Propellant ignition is begun at the head end of the chamber, and the flame spreads toward the end of the rocket, finally burning along the whole propellant surface. The detailed analysis of this ignition transient phenomenon is very important to the efficiency and safety of the solid rocket motor. Inside the rocket motor, radiation is considered to affect the thermal characteristics that will finally change the fluid dynamics. However, its analysis presents a formidable challenge inasmuch as the radiative transfer equation (RTE) is a form of integro-differential equation. Even if there were numerous methods to solve the RTE, the recently proposed finite volume method[1] is considered a good choice for application because this method can easily be applied to complex geometries and be coupled with the other discritized equations.

In this study a more refined model is developed to examine the ignition transient in an axisymmetric solid rocket motor by solving an unsteady turbulent flowfield. In contrast to previous studies,[2,3] the effects of gas radiation are taken into account. Whereas the radiative transfer equation is solved using the finite volume method, the other governing equations are numerically solved using the SIMPLER algorithm in generalized coordinates.

Mathematical Model

Conservation Equations

When the ignitor located at the center of the port is activated as shown in Fig. 1a, the ejected plume starts momentum and heat transfer to the solid propellant. The Favre averaged, two-dimensional axisymmetric Navier–Stokes equations with k–ε turbulent transport model governing this turbulent transport phenomena are developed as follows.

Mass:

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial}{\partial x_i}(\bar{\rho}\tilde{u}_i) = 0 \tag{1}$$

Momentum:

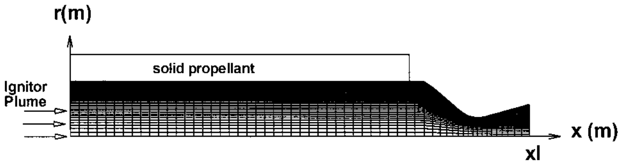
$$\frac{\partial}{\partial t}(\bar{\rho}\tilde{u}_i) + \frac{\partial}{\partial x_j}\left(\bar{\rho}\tilde{u}_i\tilde{u}_j - \mu_{\text{eff}}\frac{\partial \tilde{u}_i}{\partial x_j}\right) = -\frac{\partial \bar{p}}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} \tag{2}$$

Energy:

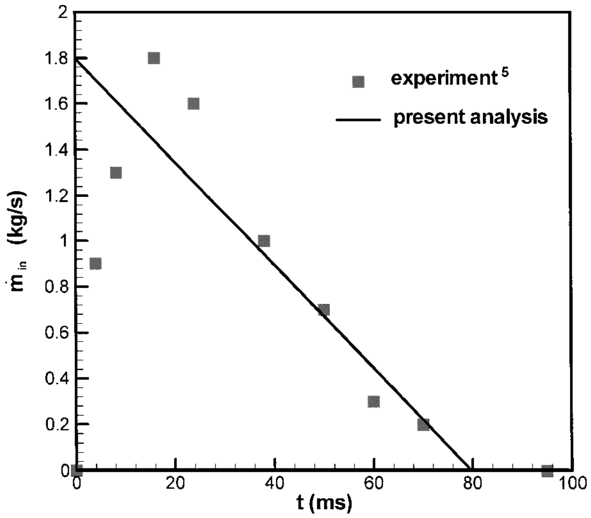
$$\frac{\partial}{\partial t}(\bar{\rho}\tilde{h}) + \frac{\partial}{\partial x_j}(\bar{\rho}\bar{u}_j\tilde{h}) = \frac{\partial \bar{p}}{\partial t} + \tilde{u}_j\frac{\partial \bar{p}}{\partial x_j} - \nabla\cdot q - \nabla\cdot q^r + \Phi \tag{3}$$

Laminar and turbulent heat flux:

$$q = -\left(\frac{\mu_l}{Pr_l} + \frac{\mu_t}{Pr_t}\right)\frac{\partial \tilde{h}}{\partial x_j} \tag{4}$$



a) Grid system



b) Ignitor plume mass flow rate $\dot{m}_{\text{in}}$

Fig. 1 Grid system and mass flow rate by ignitor.

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*Senior Researcher, Department of Space Propulsion System.

†Professor, Department of Aerospace Engineering. Senior Member AIAA.