Research paper

Thermal Hazards Studies for the Azidation Process in the Preparation of Tetra Functional Glycidylazide Polymer (t-GAP) Using a Thermal Screening Unit (TSU)

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Abstract: Glycidylazide polymer (GAP) tetraol or tetra functional GAP (t-GAP) is a potential energetic binder, capable of exhibiting superior mechanical properties and better curing behaviour for application in high energy propellants. t-GAP is conventionally prepared through azidation of tetra functional poly-epichlorohydrin (t-PECH). Azidation reactions using a metal azide are known to be sensitive to temperature. The present study was aimed at a systematic evaluation of the safe temperature limit for the preparation of t-GAP and to derive optimized reaction conditions using a thermal screening unit (TSU), through both dynamic and isothermal heating experiments. The thermal hazard studies suggested that the azidation reaction is fairly stable at temperatures above 100 °C as it did not exhibit any abrupt rise in reaction temperature or pressure. The process was validated using laboratory scale batches and completion of the reaction was verified using FTIR spectroscopy.

Keywords: energetic binder, hazard, optimization, t-GAP, thermal screening, composite solid propellant

1   Introduction

Composite solid propellants (CSP) are the major source of chemical energy for rocket/missiles and space vehicles. Polymeric binders are the important ingredients for manufacturing various CSPs [1-5] and plastic bonded explosives (PBX) [6-8]. Binders impart structural as well as mechanical integrity to the propellant and explosive charges. The conventional CSP and PBX formulations employ an inert binder, such as hydroxyl-terminated polybutadiene (HTPB) [9-14], owing to their superior functional behaviour, and easy and low-cost availability. However, the non-energetic nature of such binder polymers is a major concern as it constitutes 10-16 wt.% of the CSP/PBX compositions. Energetic polymers, on the other hand, can significantly enhance the performance of both a CSP and a PBX [15-18]. Glycidylazide polymer (GAP) is an widely reported energetic polymer and is considered to be the most promising candidate as an energetic binder owing to its higher density, positive heat of formation, excellent thermal stability *etc* [19-21]. Furthermore, its glass transition temperature (T_g) of –45 °C makes it useful for propellant and explosive compositions deployable under varied terrain conditions. The azido functionalized polymer GAP with terminal hydroxy functionalization, usually known as GAP-diol, was first synthesized in 1972 [22]. GAP-diol was prepared by azidation of its precursor poly epichlorohydrin (PECH). The general reaction scheme for GAP-diol synthesis is presented in Scheme 1.
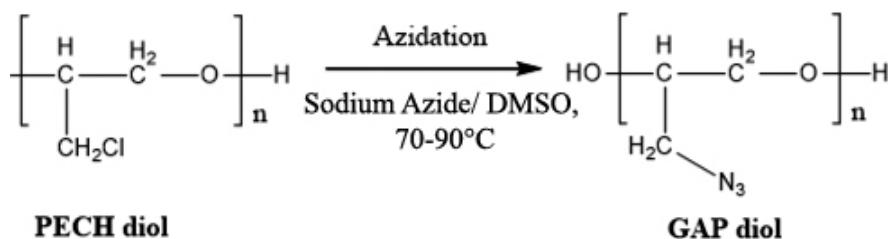
Scheme 1.   Schematic representation of azidation of PECH to form GAP-diol

Since then, numerous publications have reported the use of GAP-diol as an alternative binder [23-25]. Usually, GAP with an average molecular weight in the range of 1000 to 5000 was considered as a suitable candidate for binder application. Recent publications indicate the use of GAP as the preferred binder with green and environmentally friendly oxidizers like and, both in smokeless and aluminized composite propellants [26-32]. In a very recent report, Klapötke *et al.* [33], have presented GAP/TKX-50 based rocket propellant formulation.

However, GAP-diol is also reported to exhibit poor mechanical characteristics as compared to HTPB in propellant compositions. In GAP-diol, the terminal –OH groups are attached to a secondary carbon and requires high temperature curing with isocyanates for longer. This in-turn results in the formation of voids in the cured mass and therefore poor mechanical properties. By contrast, primary –OH functionality would enhance the reactivity towards the diisocyanate curing agent, enabling low temperature curing. Therefore, in order to enhance the functionality of GAP, the preparation of tetra-functional GAP or GAP-tetraol (t-GAP) was conceptualized. The most successful method reported for the preparation of t-GAP is from t-PECH, obtained by epoxidation of PECH-diol followed by acid hydrolysis [34]. In a similar way, Soman *et al.* [35] reported a method for the preparation of t-GAP at laboratory scale. In both of these methods, t-PECH had been subjected to azidation with sodium azide in an aprotic polar solvent like DMF or DMSO. The reported parameters suggested maintaining the reaction temperature at 80-100 °C for 20-48 h. It has also been suggested that there is a significant improvement in the mechanical properties of t-GAP as compared GAP-diol. Therefore, a t-GAP based composite propellant is likely to exhibit improved mechanical properties in addition to high performance and superior ballistic properties. Under present study, t-GAP was prepared following the route reported by Soman *et al.* [35]. The adopted reaction scheme for the preparation of t-GAP is shown in Scheme 2.
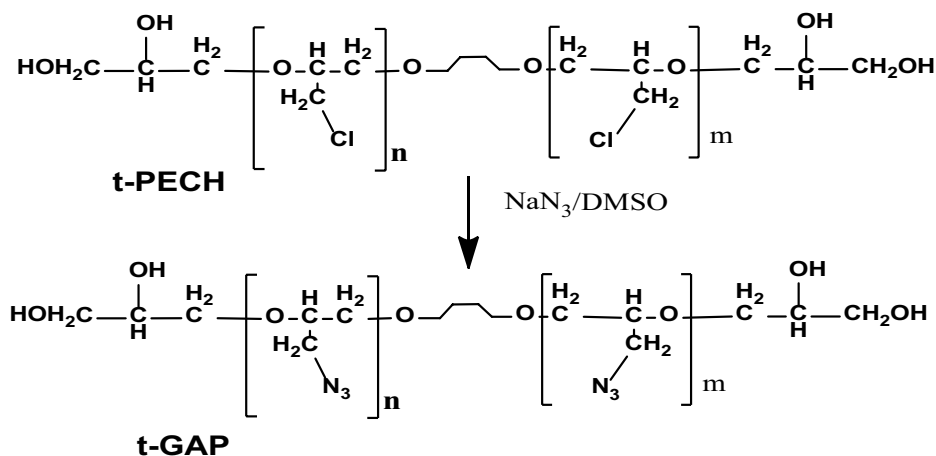
Scheme 2. Schematic representation of the preparation of tetra-functional GAP

Azidation reactions are in general exothermic in nature and therefore the total heat output from such a reaction during the scaled-up preparation is a major concern. Furthermore, the stability of the final product towards prolonged thermal treatment is largely unknown. A relatively large quantity of sodium azide, in 1:1 mass ratio to t-PECH, is used for the azidation. Therefore, a significant amount of un-reacted sodium azide remains suspended in the reaction medium. Sodium azide has an associated explosion hazard when heated in confinement. Prolonged exposure to elevated temperature (>24 h) may be catastrophic during large scale manufacturing when the final product is also explosive in nature. In addition, no literature is available on the optimum process parameters. Therefore, a systematic study was carried out to assess the reaction hazards prior to process optimization and scale-up of t-GAP.

In the present study, a Thermal Screening Unit (TSU) has been employed to study the temperature sensitivity of the azidation reaction. The reaction pressure and temperature were measured as a function of time. The data thus generated were systematically interpreted and used to optimize the reaction parameters in order to reduce the reaction time and eliminate potential explosion or fire hazards. Overall, the present study has led to the development of a scaled-up process for the preparation of t-GAP which is much safer, faster and cost effective.

2   Experimental Section

2.1 Materials

As in the method reported by Soman *et al.* [35], t-GAP was prepared from the precursor tetra functional PECH (t-PECH), through an azidation reaction using sodium azide (NaN$_3$) in DMSO at 80 °C.

t-PECH was obtained from commercial sources prepared through epoxidation of PECH-diol and subsequent acid hydrolysis following the methods described by Soman *et al.* [35]. All other reagents and chemicals, *i.e.* NaN$_3$, ethyl acetate, DMSO, used in this study were of commercial grade with purity >99%. All of these chemical substances were used without any further purification.

2.2 Thermal screening

The screening of the temperature sensitivity of the azidation process was studied using TSU (HEL, UK), a useful tool for thermal hazard analysis. The unit enables rapid and continuous simultaneous measurement of both temperature and pressure of a reaction mixture as a function of time and temperature. The sample under study was placed in a Hastelloy cell attached to the oven lid and fitted with a Pt 100

temperature sensor and a pressure transducer. A tiny magnetic needle placed into the Hastelloy cell ensured thorough mixing of the reaction mass. A temperature program, either dynamic or isothermal heating, was suitably selected for the oven. The operating range of the equipment was from ambient to 400 °C and a pressure up to 172 bar. The key data generated as the onset temperature of the exotherm, rate of temperature and pressure increases, the maximum temperature and pressure, time from the exotherm initiation to maximum rate *etc*. These data are essential for the safe scale-up of chemical processes. A schematic diagram the TSU set-up is shown in Figure 1.
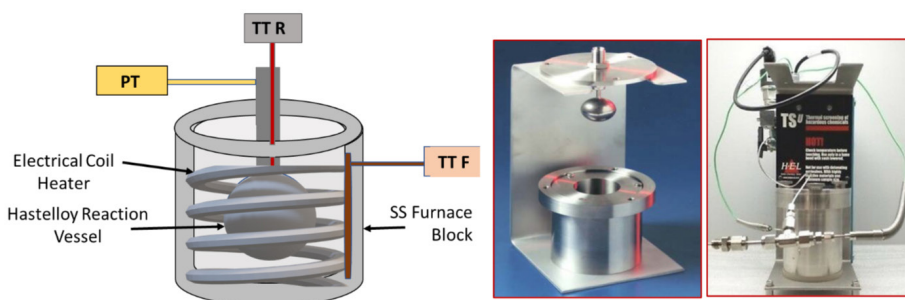

Figure 1.   Schematic representation of the TSU instrumental set-up: PT – pressure transducer, TT R – temperature transducer reactor and TT F – temperature transducer furnace

2.3 Laboratory scale process

The initial laboratory scale experiments, to up 50-100 g/batch, were carried out in a 2 L jacketed glass reactor (HEL, UK), as shown in Figure 2. The reaction temperature (T_r) and jacket temperature (T_j) were logged in real time. The temperature difference ($\Delta T = T_r - T_j$) has been used as an indicator of the process exothermicity and the addition rate of t-PECH was thus controlled accordingly. The HEL laboratory reactor was equipped with controlled liquid feed pump (feed rate: 0-2 L/min) and an anchor blade overhead stirrer.

Figure 2.   Laboratory scale facility used for t-GAP process optimization

2.4 Characterization

The precursor t-PECH and the crude reaction mass obtained after each experiment was characterized using an FTIR spectrometer (Thermo Fisher iS50). Mid-IR range spectra were recorded at a spectral resolution 4 cm^{-1} using a single bounce diamond ATR accessory. PECH exhibits a distinct vibration band at 747 cm^{-1} corresponding to C–Cl stretching. t-GAP shows a strong vibrational band originating from asymmetric stretching of the azide functional group ($-N=N^+=N^-$) at 2088 cm^{-1}, As the reaction proceeds, with replacement of chloride groups by the azide functional group, there is a gradual weakening in intensity of the C–Cl stretching band, and the appearance of the asymmetric stretching band for azide. The completion of the azidation reaction was marked by complete disappearance of the IR band at 747 cm^{-1} and the appearance of a strong asymmetric vibration for the azide functional group.
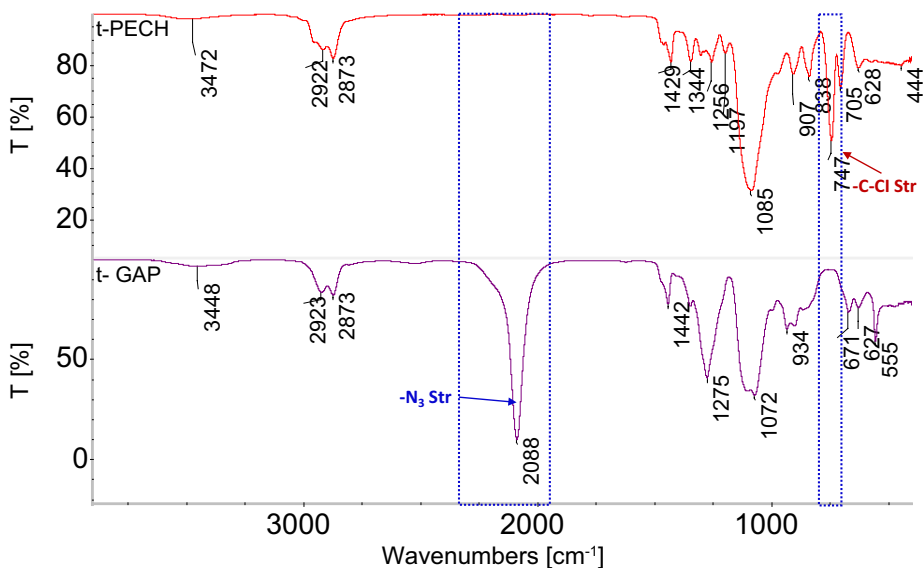
Figure 3.   Comparative FTIR spectra of t-GAP from t-PECH

The hydroxyl value of the polymers was measured using a titrimetric method. A calculated mass of the polymer was reacted with acetic anhydride at about 120 °C in pyridine medium to acetylate the terminal –OH groups. The excess reagent was hydrolyzed with distilled water and the free acetic acid produced by the reaction was determined by titration with standard KOH solution. The hydroxyl value is expressed as mg of KOH required per gram of sample (mg of KOH/g sample).

The number average molecular weight was measured using a Kanuer Vapour Pressure Osmometer calibrated using Benzyl as a standard. The measurement is based on the vapour pressure reduction in solution corresponding to Roult's Law, *i.e.* the ratio of lowering of the vapour pressure of the solvent (solution) due to presence of solute to the vapour pressure of pure solvent is equal to the mole fraction of the solute. For this measurement, toluene was used as the solvent.

A calculated amount of the polymer was dissolved in a composition of toluene and dried methanol and titrated against Karl Fisher reagent that contains iodine, sulphur dioxide (SO_2), a pyridine free base and methanol. The moisture measurement was carried out using a Mettler Toledo make Karl Fisher autotitrator. A pair of Pt electrodes sense and measure the sharp change in current when iodine is reduced by SO_2 in the presence of water. The corresponding amount of water is then measured automatically and presented in wt.%.

Density was measured by the liquid displacement method using Archimedes' principle in a density measurement kit (Mettler Toledo). Pieces of glass sinkers of volume 10 mL were weighed in air and then immersed in the polymer. The density was calculated by dividing the weight loss of the sinker in the liquid by the volume of the sinker.

T_g was measured using a Perkin Elmer make DSC 800 Differential Scanning Calorimeter, where about 0.5 mg sample was placed in a hermetically sealed Al pan and cooled to –80 °C using an intercooler. The sample was then heated at a rate of 10 °C/min up to ambient temperature. The temperature of glass transition was measured as the average temperature of the transition in baseline, identified by a sudden change in heat flow.

The characterization results are listed in Table 1.

Table 1. Characterization data of t-GAP

Property	t-GAP
Molecular weight (M_n)	1550
Hydroxyl value [mg KOH/g]	85 ±2
Viscosity [P]	17-20
Density [g/cm^3]	1.35
%VM [%]	<0.1
Moisture [%]	<0.1
T_g [^{0}C]	–47 ±2

3 Results and Discussion

3.1 Thermal screening

The laboratory scale experiments were carried out using TSU to assess the temperature sensitivity of the azidation process on t-PECH. A solution of of t-PECH (0.5 g, 0.04 mmol, M_n = 1165) in DMSO (1.5 mL) and NaN$_3$ (0.5 g, 0.75 mmol) were placed into a 8 mL Hastelloy vessel. The vessel was suspended in the oven cavity of the TSU while attaching a Pt100 temperature sensor and pressure transducer on the top lid. The reaction mass was kept stirring with the help of a tiny magnetic bar needle. The sample was then subjected to programmed dynamic or isothermal heating conditions while the reaction temperature and pressure were measured continuously. Any sharp rise in reaction temperature/pressure indicated an exothermic event and even a runway condition.

3.1.1 Dynamic heating

During the dynamic heating experiment, the reaction mass was subjected to a heating ramp of 0.5 °C/min from room temperature to 110 °C. The upper temperature was chosen based on the fact that commercial DMSO contains a small percentage of water, as high as 0.2-0.5%. On heating commercial DMSO, tiny bubbles were observed on the side of the glass vessel at a temperature slightly above 100 °C due to evaporation of DMSO at a temperature more than 100 °C. The TSU profile obtained from the dynamic heating is as shown in Figure 4.
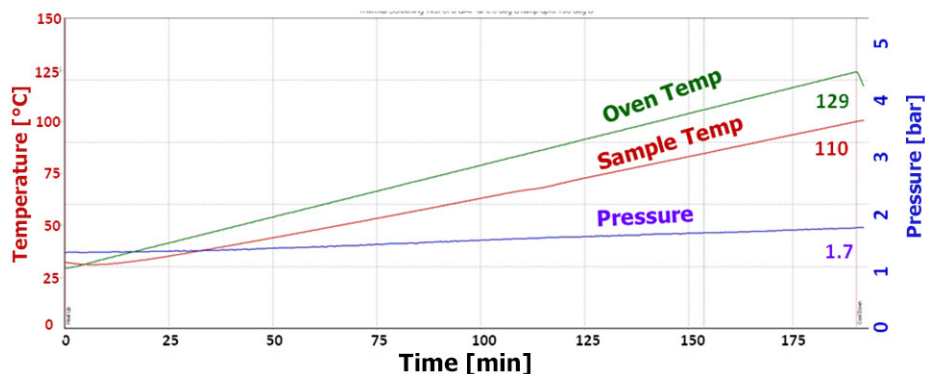

Figure 4.   Dynamic heating profile of the azidation reaction in TSU

The dynamic heating showed a gradual rise in reaction/sample temperature (T_r), maintaining a constant slope similar to that of the oven temperature (T_o). The reaction pressure (P) also showed a linear increase up to 0.7 bar at 110 °C, maintaining a constant slope. The experiment was terminated on attaining 110 °C and no isothermal condition was applied thereafter. No sharp rise either in T_r or P was observed during the dynamic heating of the reaction mass. This implies that, the reaction may be safe to be handled up to 110 °C, in contrast to the reported literature that indicated a safe reaction temperature in the range of 70-80 °C. However, the reaction has to be studied at an increasingly higher but discrete isothermal temperature so as to assess the reaction run away, if any arises from continued heating. Isothermal heating experiments were also essential to establish the reaction time.

The reaction mass was added to an excess of water and the polymeric product was extracted into ethyl acetate and recovered by distilling off the solvent. The final product (~0.4 g) was characterized using FTIR, when the reaction was found to be complete as no IR absorption was observed at 747 cm^{-1}.

3.1.2 Isothermal heating

On assessing the stability of the reaction mixture through dynamic heating in the TSU to up 110 °C, it was further attempted to establish an optimum higher reaction temperature so as to reduce the reaction time. A reaction mixture of a similar composition to that used in the dynamic heating experiment, was subjected to isothermal heating at a temperature higher than 80 °C. The reaction mixture was initially ramped at 2 °C/min to the desired isothermal temperature, followed by maintaining this temperature for an extended period. Isothermal reactions were conducted at successively higher temperatures 85, 90, 95 and 100 °C over different time periods. After completion of the desired reaction time, the polymeric product was isolated and characterized using FTIR to assess the extent of reaction. A typical isothermal profile of the azidation reaction at 90 °C is shown in Figure 5.
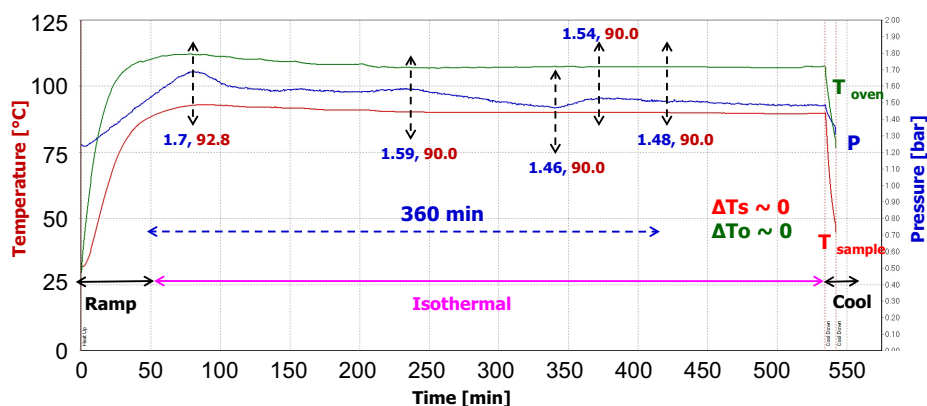

Figure 5. Representative isothermal profile of the azidation reaction at 90 °C

The isothermal experiment at 90 °C in the TSU shows an initial pressure rise up to 1.7 bar at about 82 min. Although the target reaction temperature was achieved at about 50 min, due to the thermal inertia of the heating elements, the temperature continued to rise further up to 92.8 °C causing an overall rise of reaction pressure up to 1.7 bar. This is convincible as the pressure subsided to equilibrium conditions with stabilization of the temperature at 90 °C. As the reaction continued, no further change was observed in the reaction temperature. The reaction pressure became stabilized at about 1.48 bar at around 410 min, indicating completion of the reaction. During this isothermal heating no abrupt rise in temperature or pressure was observed. In order to ascertain the conditions under which the reaction mass undergoes decomposition/degradation of the

product characteristics, the temperature of the reaction mass was dynamically increased until a significant changes/abnormal rise in temperature/pressure was observed. Figure 6 showed that the reaction mass undergoes decomposition at temperature above 250 °C.

3.1.3 Decomposition studies

In order to ascertain the conditions under which reaction mass would undergo decomposition/ degradation, in a separate experiment the temperature of the reaction mass was dynamically increased till significant changes/ abnormal rise in temperature/pressure was observed. The TSU plot of this experiment is shown in Figure 6 where the reaction mass undergoes decomposition at temperature above 250 °C.
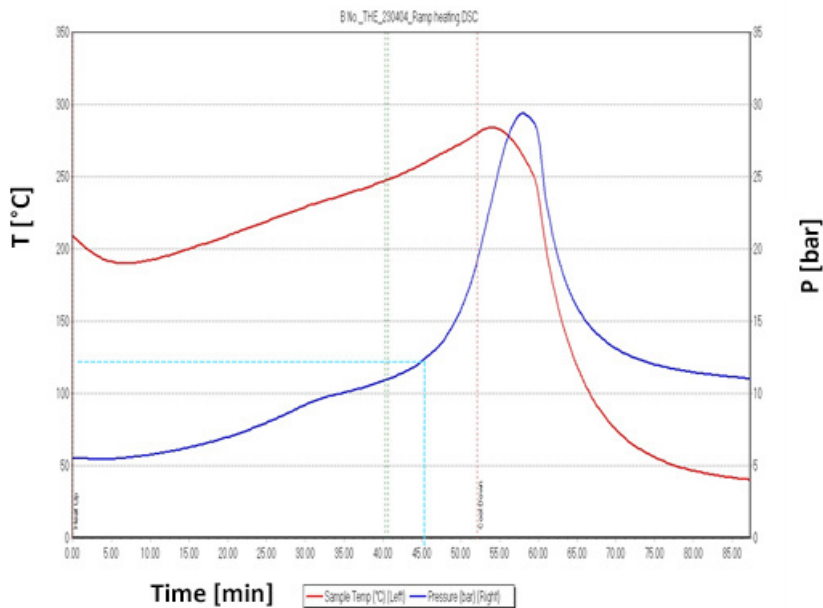

Figure 6. TSU thermograph of the azidation process for the preparation of t-GAP

In order to validate the data obtained from TSU, a similar experiment was carried out using the Differential Scanning Calorimeter DSC-8000 (Perkin Elmer). The DSC profile as shown in Figure 7 showed that it is safe to carry out the reaction up to a temperature of 240 °C, above which it undergoes endothermic

decomposition. In order to validate the results of the TSU experiment, laboratory scale batches at 50 g/batch level were conducted in a laboratory jacketed reactor and the reaction products were isolated and characterized. The final product of each batch was isolated and checked by FTIR for completion of reaction. Table 2 represents the summary of azidation reactions in TSU at different temperatures and time intervals.
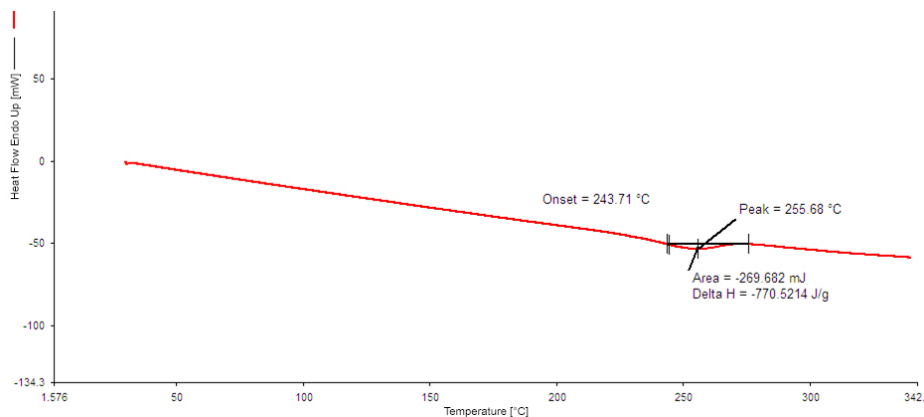

Figure 7. DSC profile for the azidation process for the preparation of t-GAP

Table 2. Summary of reactions in TSU and laboratory scale validation batches

T_r [°C]	Time [h]	Experiment type (TSU or Lab scale)	FTIR band at 747 cm^{-1}	Reaction status
80	20	TSU	No	Complete
85	12	TSU	No	Complete
	8	TSU	Yes	Incomplete
90	6	Lab scale	No	Complete
95	5	TSU	No	Complete
		Lab scale		
100	4	TSU		
		Lab scale		

During the laboratory level experiments at temperatures of 95 and 100 °C, significant evaporation of DMSO solvent vapour was observed. Therefore, a reaction temperature of 90 °C was considered as the optimum temperature, with reaction time of 6 h.

4   Conclusions

♦ Thermal screening of the t-GAP process has been successfully used to assess the temperature stability of the azidation of t-PECH. The reaction was found to be stable up to 110 °C without attaining any runway conditions. Furthermore, isothermal experiments in TSU have enabled a safe process with significantly reduced reaction time to be established . The process was validated with laboratory scale batches using a jacketed glass reactor.

♦ The completion of the reaction was monitored with the disappearance of the IR band at 747 cm^{-1} which corresponds to the C–Cl bond in t-PECH, and the appearance of the IR band at 2088 cm^{-1} due to the asymmetric stretching for azide (–N=N$^+$=N$^-$) functional group.

♦ A reaction temperature of 90 °C was considered as the optimum temperature with a reduced reaction time of 6 h, against a reported duration of about 24 h.

♦ Dynamic heating experiments using TSU until decomposition of the product occurred indicated that it is safe to carry out the process up to a temperature of 240 °C under closed conditions. The same had been confirmed with a DSC thermograph of the process.

References

[1] Williams, F.A.; Barrere, M.; Huang, N.C. *Fundamental Aspects of Solid Propellant Rockets.* Technovision Services, No. 116, Slough, UK, **1969**.

[2] *Explosives, Propellants & Pyrotechnics.* (Bailey, C.M.; Hartley, F.; Lee, R.G.; Murray, S.G., Eds.) Brassey's UK Ltd., **1989**.

[3] Perez, D.; Ramohalli, K. A Scientific Approach to Composite Propellant Processing. *Proc. 26th AIAA/ ASME/SAE/ASEE, Joint Propulsion Conf.*, Orlando, **1990**.

[4] Kishore, K.; Sridhara, K. *Solid Propellant Chemistry.* DESIDOC, Defense R&D Organisation, **1999**.

[5] Folly, P.; Mäder, P. Propellant Chemistry. *Chimia* **2004**, *58*: 374-382.

[6] Gharia, J.S.; Sinha, R.K.; Tadas, V.V.; Prakash, V.; Phadke, V.K. Studies on Physico-Mechanical and Explosive Characteristics of RDX/HMX Based Castable Plastic Bonded Explosives. *Def. Sci. J.* **1998**, *48*(1): 125-130; https://doi.org/10.14429/dsj.48.3877.

[7]   Antic, G.; Lasevic, V.D.; Stankovic, M.; Borkovic, Z. Explosive Characteristics of Cast PBX Based on HMX, Ammonium Perchlorate and Aluminium. *Sci. Tech. Rev.* **2004**, *64*(3-4): 38-44.

[8]   Kumar, A.S.; Rao, V.B.; Sinha, R.K.; Rao, A.S. Evaluation of Plastic Bonded Explosive (PBX) Formulations Based on RDX, Aluminum, and HTPB for Underwater Applications. *Propellants Explos., Pyrotech.* **2010***, 35*(4): 359-364; https://doi.org/10.1002/prep.200800048.

[9]   Muthiah, R.M.; Manjari, R.; Krishnamurthy, V.N. Rheology of HTPB Propellant: Effect of Mixing Speed and Mixing Time. *Def. Sci. J.* **1993**, *43*(2): 167-172.

[10] Muthiah, R.M.; Krishnamurthy, V.N.; Gupta, B.R. Rheology of HTPB Propellant: Development of Generalized Correlation and Evaluation of Pot Life. *Propellants Explos., Pyrotech.* **1996**, *21*(4): 186-192; https://doi.org/10.1002/prep.19960210405.

[11] Muthiah, R.M.; Krishnamurthy, V.N.; Gupta, B.R. Rheology of HTPB Propellant: Effect of Solid Loading, Oxidiser Particle Size, and Aluminum Content. *J. Appl. Polymer Sci.* **1992**, *44*(11): 2043-2052; https://doi.org/10.1002/app.1992.070441120.

[12] Nair, C.P.R.; Prasad, C.H.D.V.; Ninan, K.N. Effect of Process Parameters on the Viscosity of AP/Al/HTPB Based Solid Propellant Slurry. *J. Energy Chem. Eng.* **2013**, *1*(1): 1-9.

[13] Jawalkar, S.N.; Mehilal; Kurva, R.; Singh, P.P.; Bhattacharya, B. Influence of Bicurative on Processability of Composite Propellant. *Def. Sci. J.* **2007**, *57*(5): 669-675.

[14] Bandgar, B.M.; Krishnamurthy, V.N.; Mukundan, T.; Sharma, K.C. Mathematical Modeling of Rheological Properties of Hydroxyl-terminated Polybutadiene Binder and Dioctyl Adipate Plasticizer. *J. Appl. Polymer Sci.* **2002**, *85*: 1002-1007.

[15] Provatas, A. *Energetic Polymers and Plastics for Explosive Formulations – A Review of Recent Advances.* Commonwealth of Australia, DSTO-TR-0966, Canberra, **2000**.

[16] Agrawal, J.P.; Hodgson, R. *Organic Chemistry of Explosives.* John Wiley & Sons Ltd. Chichester, **2007**; ISBN-13: 978-0-470-02967-1.

[17] Kubota, N. *Propellants and Explosives, Thermochemical Aspects of Combustion.* 2nd ed., Wiley-VCH Verlag GmbH & Co. KG, Weinheim, Germany, **2007**; ISBN: 978-3-527-31424-9.

[18] Agrawal, J.P. *High Energy Materials, Propellants Explosives and Pyrotechnics.* Wiley-VCH Verlag GmbH & Co. KG, Weinheim, Germany, **2010**; ISBN 978-3-527-32610-5.

[19] Frankel, M.B.; Grant, L.R.; Flanagan, J.E. Historical Development of Glycidyl Azide Polymer. *J. Propul. Power* **1992**, *8*: 550-563; https://doi.org/10.2514/3.23514.

[20] Nazare, A.N.; Asthana, S.N.; Singh, H. Glycidylazide Polymer (GAP) – An Energetic Component of Advanced Solid Rocket Propellants – a Review. *J. Energ. Mater.* **1992**, *10*: 043-063; https://doi.org/10.1080/07370659208018634.

[21] Frankel, M.B.; Ranagan, J.E. *Energetic Hydroxy Terminated Azide Polymer.* Patent US 4268450, **1981**.

[22] Vandenburg, E.J. *Polymers Containing Azidomethyl Side Chains*. Patent US 3645917, **1972**.

[23] Ahad, E. *Process for the Preparation of Alkyl Azide-substituted Hydroxy-terminated Polyethers.* EU Patent 0274213, **1987**.

[24] Gettwert, V.; Bohn, M.A.; Fischer, S.; Weiser, V. Performance of ADN/GAP Propellants Compared to Al/AP/HTPB. *Proc. Insensitive Munitions & Energetic Materials Technology Symp. (IMEMTS),* Rome, Italy, **2015**.

[25] Hussein, A.K.; Elbeih, A.; Zeman, S. The Effect of Glycidylazide Polymer on the Stability and Explosive Properties of Different Interesting Nitramines. *RSC Adv.* **2018**, *8*: 17272-17278; https://doi.org/10.1039/C8RA02994F.

[26] Nguyen, C.; Morin, F.; Hiernard, F.; Guengant, Y. High Performance Aluminized GAP-based Propellants – IM Results. *Insensitive Munitions & Energetic Materials Technology Symp.,* Munich, Germany, **2010**.

[27] Da Silva, G.; Rufino, S.C.; Iha, K. Green Propellants: Oxidizer. *J. Aerosp. Technol. Manage.* **2013**, *5*(2): 139-144; https://doi.org/10.5028/jatm.v5i2.229.

[28] Wingborg, N.; Andreasson, S.; de Flon, J.; Johnsson, M.; Liljedahl, M.; Oscarsson, C.; Petterssons, Å.; Wanhatalo, M. Development of ADN-based Minimum Smoke Propellants. *AIAA Paper 2010-6586, IMEMTS*, **2015**, pp. 1-10; https://doi.org/10.2514/6.2010-6586.

[29] Gettwert, V.; Franzin, A.; Bohn, M.A.; DeLuca, L.T.; Heintz, T.; Weiser, V. ADN/GAP Composite Propellants with and without Metallic Fuels. *Proc. 10th Int. Symp. on Special Topics in Chemical Propulsion & Energetic Materials (10-ISICP),* Poitiers, France, **2014**.

[30] DeLuca, L.T.; Palmucci, I.; Franzin, A.; Weiser, V.; Gettwert, V.; Wingborg, N.; Sjöblomc, M. New Energetic Ingredients for Solid Rocket Propulsion. *Proc. 9th Int. High Energy Materials Conf. and Exhibit (HEMCE),* Thiruvananthapuram, Kerala, India, **2014**.

[31] Gettwert, V.; Fischer, S.; Menke, K. Aluminized ADN/GAP Propellants – Formulation and Properties. *Proc. 44th Int. Annu. Conf. of Fraunhofer ICT*, Karlsruhe, Germany, **2013**, P57.

[32] Menke, K.; Heintz, T.; Schweikert, W.; Keicher, T.; Krause, H. Formulation and Properties of ADN/GAP Propellants. *Propellants Explos., Pyrotech.* **2009**, *34*(3): 218-230; https://doi.org/10.1002/prep.200900013.

[33] Klapötke, T.M.; Suceska, M. Theoretical Evaluation of TKX-50 as An Ingredient in Rocket Propellants. *Z. Anorg. Allg. Chem.* **2021**, *647*: 572-574; https://doi.org/10.1002/zaac.202100053.

[34] Ampleman, G. *Glycidyl Azide Polymer.* Patent US 5359012, **1994**.

[35] Soman, R.R.; Athar, J.; Agawane, N.T.; Shee, S.; Gore, G.M.; Sikder, A.K. Synthesis, Characterization and Rheology of Tetrafunctional Glycidylazide Polymer vis-a`-vis Difunctional GAP. *Polym. Bull.* **2016**, *73*: 449-461; https://doi.org/10.1007/s00289-015-1500-7.

Contribution

Prasanta Kumar Adak: methods
Mrinal Ghosh: foundations
Ashish Kumar Meena: methods
Mukesh Jain: methods
Shaibal Banerjee: methods