Synthesis and Thermal Decomposition Kinetics of Epoxy Poly Glycidyl Nitrate as an Energetic Binder

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ABSTRACT

An energetic binder epoxy poly glycidyl nitrate (e-PGN) with a molecular weight of about 1244 gr/mol was synthesised via end modified poly glycidyl nitrate (PGN) is presented in the paper. This structure was characterised by the number of epoxy groups, infrared spectroscopy, and nuclear magnetic resonance. The thermal degradation behavior of e-PGN was studied by thermo gravimetric analysis (TG) and differential scanning calorimetry (DSC) under nitrogen atmosphere at different heating rates. The glass transition temperature (Tg) was measured to determine the compatibility of energetic plasticizer with the binder in the mixture of plasticizer/binder and compared with the results of e-PGN, and initial decomposition temperature in e-PGN was studied using the DSC method. The DSC results showed that the glass transition temperature of a mixture of 20 % Bu-NENA/e-PGN mixture (Tg = −56 °C) was lower than e-PGN (Tg = −37.78 °C) that shows the most compatible plasticizer is Bu-NENA. The activation energy of degradation e-PGN and e-PGN-20% Bu-NENA were calculated with DSC by the model-free methods and compared with the results of AKTS software in version 3.51(2013-07-10). The activation energy of exothermic decomposition of the e-PGN and e-PGN-20% Bu-NENA were calculated by the Kissinger, Flynn–Wall–Ozawa, Starink, and AAdvanced kinetics and technology solutions (Friedman) methods. Finally, the half-life prediction of the e-PGN and e-PGN-20% Bu-NENA were investigated.

Keywords: Epoxy poly glycidyl nitrate; End modified; Energetic binder; Energetic plasticizer; Thermal stability; AKTS

NOMENCLATURE

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FWO	Flynn-Wall-Ozawa
AKTS	Advanced kinetics and technology solutions
PGN	Poly glycidyl nitrate
e-PGN	Epoxy poly glycidyl nitrate
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
Tg	Glass transition temperature

1. INTRODUCTION

High energy solid propellants have a long history which has started with the development of gunpowder[1]. Solid propellants are mainly classified into two types homogeneous and heterogeneous[2]. The advantages of heterogeneous (composite) propellants to homogeneous propellants are that the equipment cost is very low and the amount of propellant charge and rocket energy is higher[3]. The main components of composite propellants are binders, fuel, and oxidizer[4]. These components are held together by a binder and form a solid, elastic body with sufficient mechanical properties[5,6]. Binders are classified into two groups, non-energetic and energetic[7]. Hydroxyl-terminated polybutadiene (HTPB) and polyethylene glycol (PEG) are examples for non-energetic binders that have

low energy[8,9]. Energetic binders are polymers that contain functional groups such as nitro, nitrato, azido, and release high energy during combustion and so increase the performance of solid composite propellants[10,11]. Poly glycidyl nitrate (PGN) and glycidyl azide polymer (GAP) are examples of energetic binder[7,12]. The amount of energy is one of the important parameters for solid propellants, so the development of energetic binders is the investigation matter. Among energetic binders, PGN is the most interesting energetic binder (with the heat of explosion 2661 kJ/kg) that is used[7,13,14]. It is a kind of high energetic polymer, but its mechanical properties are low[15].

PGN can be cured rapidly with polyfunctional isocyanates, but after one or two years, a cured sample of PGN is self-decomposed[16]. This elastomer is self-decomposed because rearrangement occurs as shown in Fig. 1(a)[17].

In recent years, many works have been done to modify end-functional groups of PGN. One of the most used methods to modify the PGN is transforming terminal nitrate esters groups to primary hydroxyl groups or chloride groups[16,18,19], and another method is the synthesis of triblock copolymers such as PCL-PGN-PCL as shown in Fig. 1(a) and 1(c)[15,20].

Since binders play a critical role in the mechanical properties of composite propellants, it is important to study the thermal behavior of binders and estimate their lifetime. Although the thermal behavior and kinetics parameters of

(a)

(b)

(c)
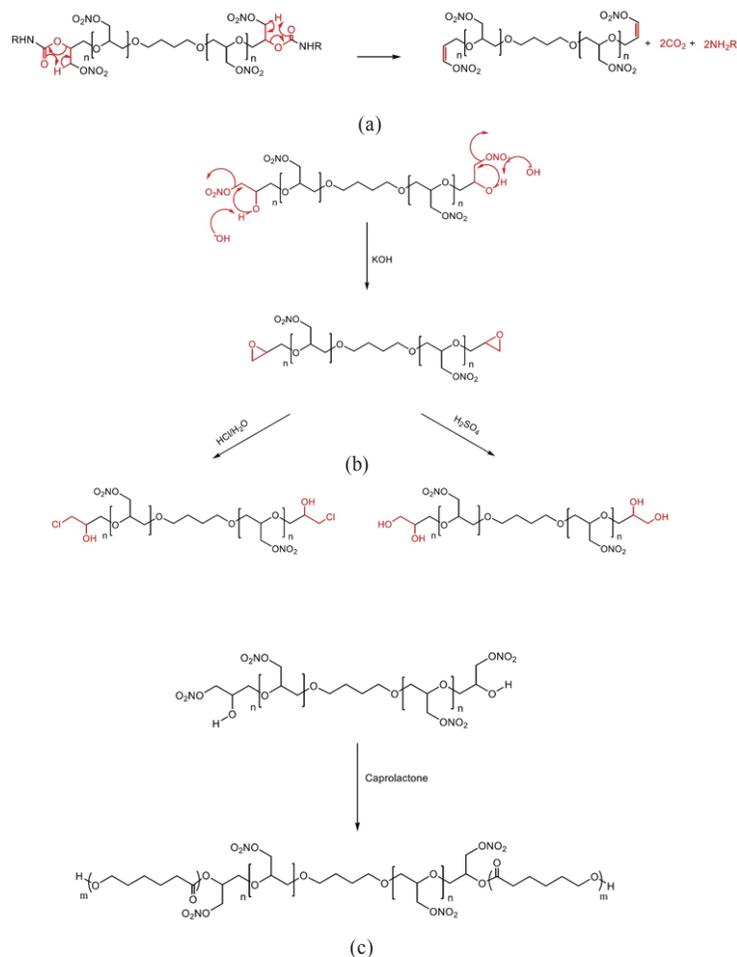
Figure 1. (a) Mechanism of self-decomposition of PGN elastomer, Methods of preparing end-modified of PGN, (b) by eliminating the end-groups, and (c) by triblock copolymer.

PGN polymer and also its compatibility with some energetic plasticizers have been studied[21-23], these items have not been investigated for epoxy poly glycidyl nitrate yet. Regarding the importance of reliable thermal analysis, finding a reliable approach to the kinetic analysis of these materials allows their applications over a considered temperature range to be realised.

The purpose of this study is to synthesis of e-PGN and investigate the thermal behavior and degradation kinetics by using differential scanning calorimetry (DSC) under nitrogen atmosphere at different heating rates. Variation curves of activation energy of e-PGN thermal degradation were evaluated by the model-free methods (Kissinger, FWO, and Starink) and compared with the results of AKTS software. Finally,

kinetic results were used to estimate thermal stability. The compatibility of e-PGN with some energetic plasticizers was studied by DSC. The glass transition temperature obtained for the mixture of energetic plasticizer/binder and compared with the result of e-PGN.

2. EXPERIMENTAL

2.1 Materials

Poly glycidyl nitrate with molecular weight of about 1370 g/mol, 1,2,4-butanetriol trinitrate (BTTN)[24], *N*-butyl-*N'*(2-nitroxy-ethyl) nitramine (BuNENA)[25], nitroglycerin (NG)[26], and trimethylolethane trinitrate (TMETN)[27] were synthesised. The tetrahydrofuran, pyridine, acetic anhydride and ethylene chloride were obtained from Merck and Aldrich and were used without further purification.

2.2 Measurements

The chemical structure of the prepared sample was investigated by infrared (FT-IR) spectroscopy. Infrared spectra were measured with Spectrum One FT-IR spectrometer and wavenumber range of 400–4000 cm^{-1}.

NMR spectra were recorded with a Bruker DRX-300 Avance instrument (300 MHz for ^{1}H and 75.4 MHz for ^{13}C) with CDCl$_3$ as the solvent. Chemical shifts were reported in ppm. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) analysis were performed using a Linseis TGA 1000 instrument under a nitrogen atmosphere with temperature-programmed rates of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min, from room temperature to 430 °C.

Differential scanning calorimetry (DSC) analysis was performed using a METTLER TOLEDO DSC 1 instrument and alumina pans under a nitrogen atmosphere with temperature-programmed rates of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min, from room temperature to 350 °C. The glass transition temperature (*T*g) was determined according to the mentioned test method.

2.3 Synthesis of Epoxy Poly Glycidyl Nitrate (e-PGN)

E-PGN was prepared according to the improved literature method (Fig.1(b))[18].

As shown in Fig. 2, e-PGN was characterised by IR, ^{1}H and ^{13}C NMR spectroscopy. The hydroxyl number of poly glycidyl nitrate and epoxy number of epoxy poly glycidyl nitrate were determined by using the ASTM method, D4274-99 and D1652-04 respectively. Molecular weight was determined using the hydroxy numbermethod[28]. The characterisation results for the synthesised e-PGN are listed in Table 1.

Table 1. Properties of synthesised e-PGN energetic binder

Binder	*T*g*	Molecular weight	^{13}C NMR	^{1}H NMR	Hydroxyl number	Epoxy number
e-PGN	-35.00 to -39.35 °C	1244 g/mol	(75.4 MHz, CDCl$_3$-*d$_1$*): δ 40.8 (CH$_2$-O epoxy), 50.7 (CH-O epoxy), 69.1 (O-CH-epoxy), 72.1 (CH$_2$-O), 75.7 (CH-O), 76.1 ppm (CH$_2$ONO$_2$)	(300 MHz, CDCl$_3$-*d$_1$*): δ 2.55 and 2.74 (2H; CH$_2$-O epoxy), 3.07 (CH-O epoxy), 3.41-3.85 (5H, CH$_2$O-epoxy, CH-O, CH$_2$O) and 4.47-4.60 ppm (2H; CH$_2$-ONO$_2$)	81.5 mg KOH/g PGN	6.08 eq/gr

* The glass transition temperature was measured in the heating rates of 5, 10, 15, and 20 °C/min.

(a)

(b)

(c)

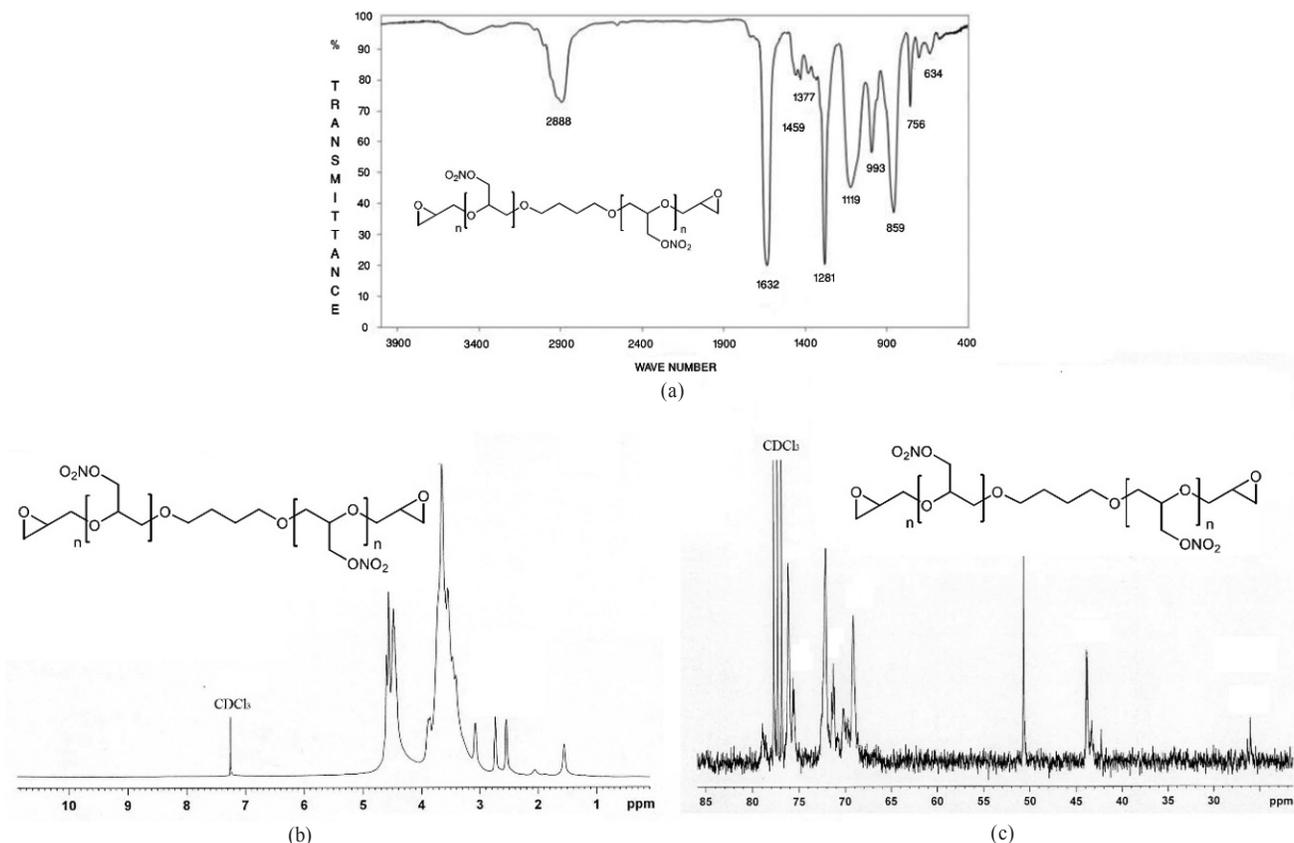**Figure 2. Spectra of e-PGN energetic binder: (a) IR, (b) ¹H NMR, (c) ¹³C NMR.**

2.4 Methods for Determination of the Activation Energy and Half-life Prediction

The kinetics parameter of interest is the apparent activation energy[29]. Numerous analytical methods can be used to determine the activation energy. One of the most valid methods for the calculation of activation energy is model-free iso-conversional methods. Kissinger, FWO, Starink, and AKTS methods are the representatives of it and estimate the activation energy from thermal analysis data[30-31].

In all of the iso-conversion methods, conversion temperature and chosen value of conversion are necessary to determine the activation energy. In the Kissinger method, according to equation 1, activation energy ($E\alpha$) is calculated from the slope of linear representation of $\ln(\beta/T^2)$ against $1/T$. β and T are heating rate and the temperature at conversion degree (α) respectively[30,32,33].

$$\ln\frac{\beta}{T^2} = const - \frac{E_\alpha}{RT} \qquad (1)$$

In the FWO method, according to Eqn. (2), the relationship between the temperature $T\alpha$ and the heating rate β is given by $\log(\beta)$ versus $1/T\alpha$ and plotted. So, activation energy ($E\alpha$) is calculated from the slope of the curve[30,34,35].

$$\log\beta = \log\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567\frac{E_\alpha}{RT_m} \qquad (2)$$

Starink method (the modified Kissinger and FWO methods), according to Eqn. (3), provides high accuracy of activation energy ($E\alpha$), by plotting $\ln(\beta/T^{1.92})$ against $1/T$, and

activation energy ($E\alpha$) is determined for the chosen value of α and β, and T are heating rate and the temperature at conversion degree (α) respectively[30,36,37].

$$\ln\frac{\beta_i}{T_{\alpha,i}^{1.92}} = const - 1.0008\frac{E_{\alpha\alpha}}{RT_\alpha} \qquad (3)$$

Based on the kinetic parameters ($E\alpha$ and A) and assuming a first-order reaction, the value of the reaction rate constant k and half-time prediction for the decomposition of the e-PGN can be calculated using the following equations[35,38]. Parameters of Z, k, T_d, T_p, E_α, $t_{1/2}$, and R, are the pre-exponential factor, the rate constant, desired temperature, peak temperature, the activation energy for decomposition peak, half-time prediction, and molar gas constant, respectively.

$$Z = \beta\frac{E_\alpha}{RT_p^2}e^{\frac{E_\alpha}{RT_p}} \qquad (4)$$

$$k = Ze^{-\frac{E_\alpha}{RT_p}} \qquad (5)$$

$$t_{1/2} = \frac{0.693}{k} \qquad (6)$$

3. RESULTS AND DISCUSSION

3.1 Activation Energy and Lifetime Prediction

Thermogravimetric analysis technique (TG) and derivative mass loss (DTG) curves of e-PGN samples at a heating rate of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min, from room temperature to 430 °C are shown in Fig. 3. E-PGN is stable
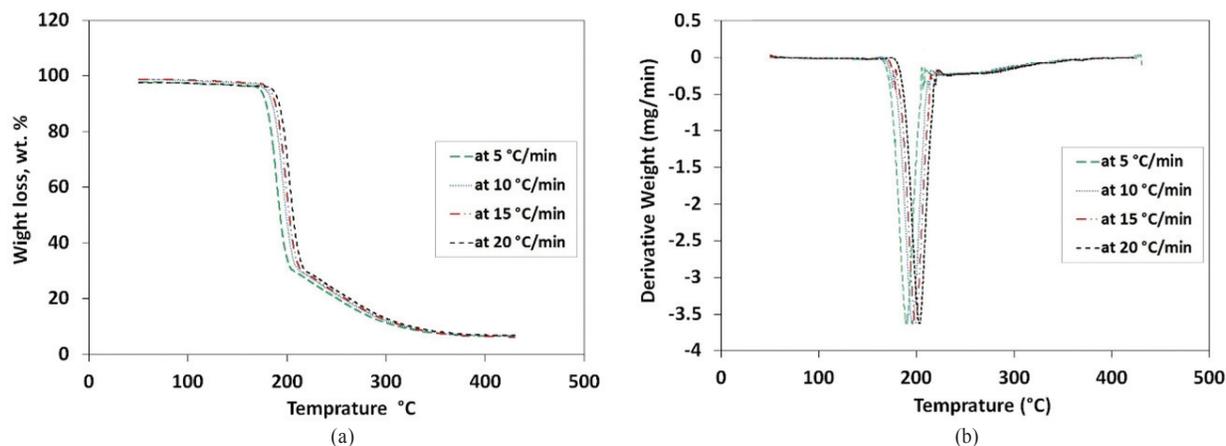
Figure 3. Thermograms of e-PGN sample at various heating rates: (a) TGA, (b) DTG.

to approximately 165 °C and then decomposition occurs in two stages at around 198 °C and 250 °C. The initial mass loss, ~65%, corresponds to the removal of the NO_2, CH_2O, NO, HCN, CH_3NO groups from the e-PGN chain[7,39]. The second mass loss corresponds to the decomposition of the remained polymer chain[7].

As an initial investigation of the thermal analysis of e-PGN, the glass transition temperatures (Tg) were 39.35 °C, 37.78 °C, 37.00 °C, and 36.00 °C for a heating rate of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min, respectively. Based on the DSC runs at a rate of 10 °C/min, the Tg of e-PGN was measured and also to study the plasticising effect on e-PGN binder, the effect of mixing binder/plasticizers on glass transition temperature were investigated by using thermal analysis. The glass transition temperature of a mixture of 20% Bu-NENA/e-PGN ($Tg = -56$ °C) was the lowest.

The kinetics of thermal decomposition of e-PGN was investigated by the differential scanning calorimetry (DSC) technique. DSC curves of e-PGN and 20% Bu-NENA/e-PGN samples, in the heating rates of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min, from room temperature to 350 °C, are shown in Fig. 4. The e-PGN sample showed an endothermic glass transition temperature with a peak temperature of -37.78 °C (related to the heating rate of 10 °C/min) and exothermic decomposition peaks were observed at 207.28

°C, 214.89 °C, 222.13 °C, and 225.05 °C in the mentioned heating rates, respectively. The 20 % Bu-NENA/e-PGN sample showed an endothermic glass transition temperature with peak temperatures of -56.00 °C (related to heating rate 10 °C) and exothermic decomposition peaks were observed at 204.84 °C, 212.82 °C, 219.85 °C, and 220.86 °C in the mentioned heating rates, respectively. These two steps of decomposition in TGA were not seen in DSC thermograms. Because the stages of decomposition were close to each other and thermogram peaks were non-separable.

The corresponding Kissinger plot was depicted to evaluate activation energy for degradation of the energetic binder and mixture of energetic plasticizer/binder. The activation energy of degradation was calculated from the slope of the line that was 151.1 kJ/mol and 141.9 kJ/mol (R^2=0.99) for e-PGN and 20% Bu-NENA/e-PGN, respectively. According to the FWO method, the resulting activation energy for binder and mixture of energetic plasticizer/binder were 151.3 kJ/mol and 142.6 kJ/mol (R^2=0.99), respectively. In theStarink method, the slope of the line was equal to $-E\alpha/R$ and the resulting activation energy for e-PGN and 20 % Bu-NENA/e-PGN were 151.3 kJ/mol and 142.1 kJ/mol (R^2=0.99), respectively. The estimated activation energy by usingAKTS (Friedman method) software was 153.6 and 142.8 kJ/mol (R^2=0.99) for PGN and 20 % Bu-NENA/e-PGN, respectively (Figs. 5(a) - 5(f)).

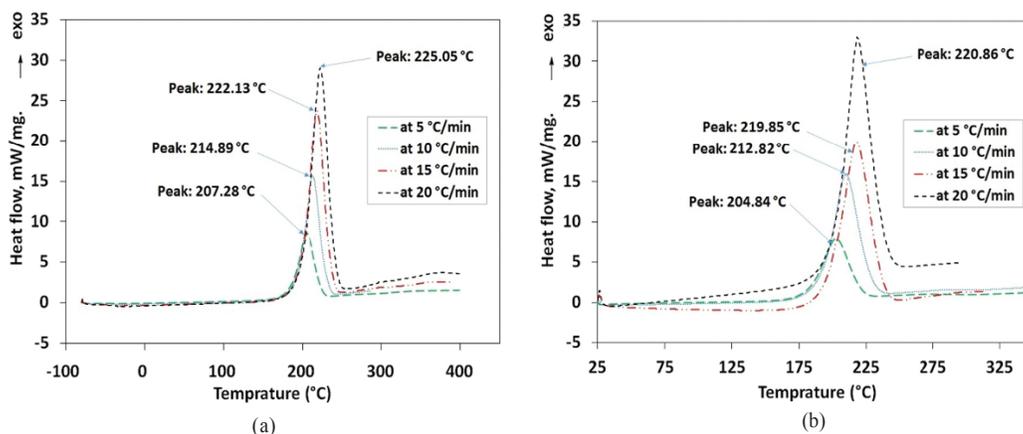Figure 4. DSC thermograms curves under various heating rates: (a) e-PGN, (b) 20% Bu-NENA/e-PGN.
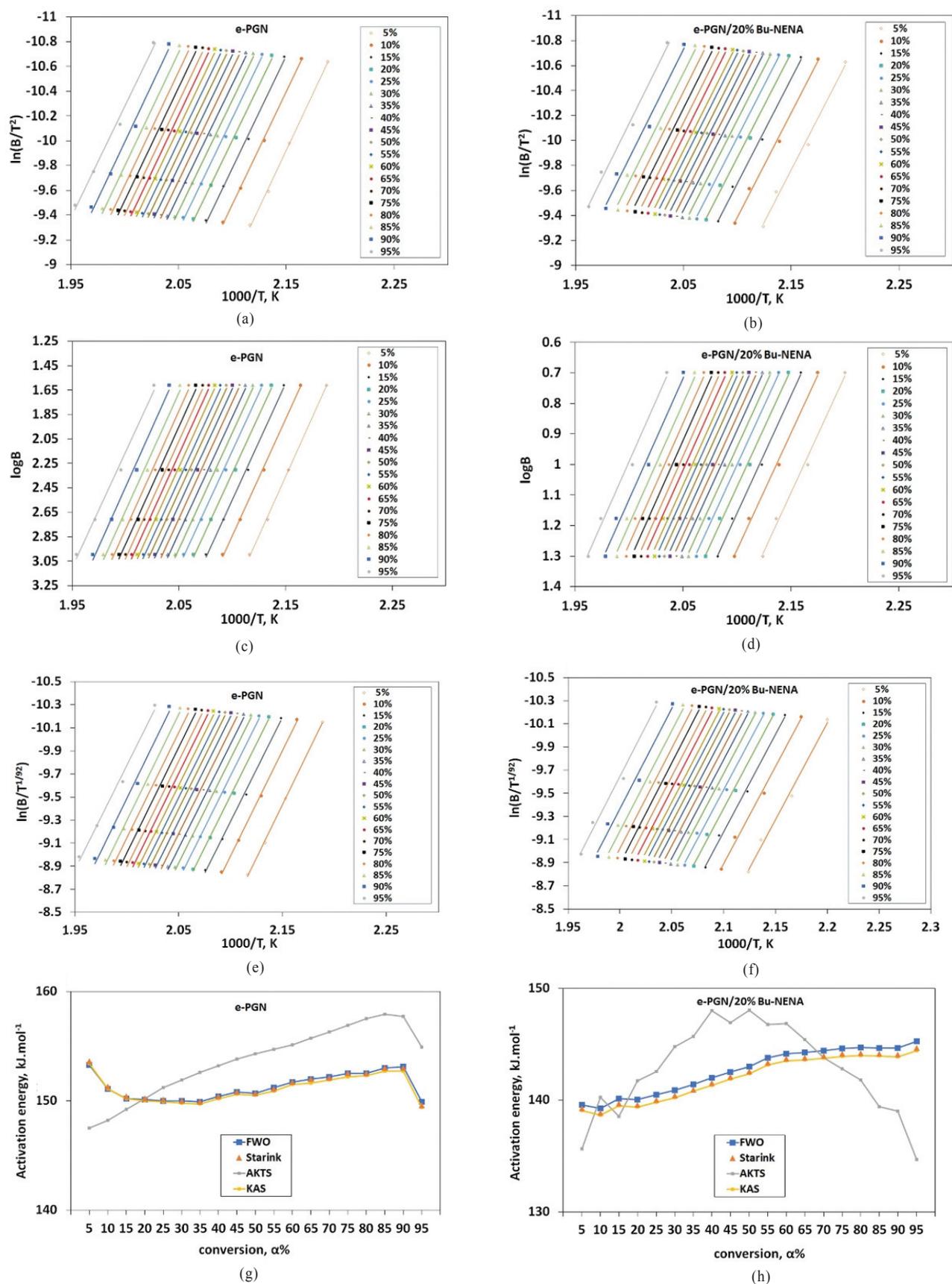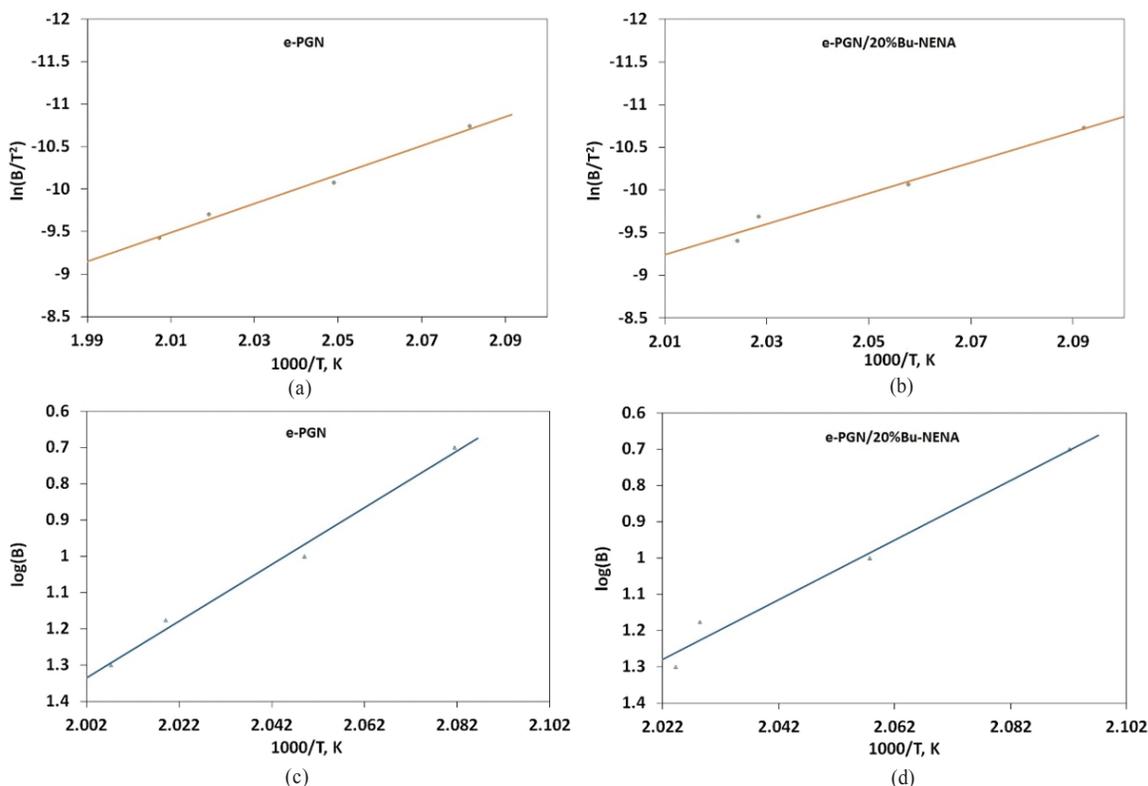
Figure 5. The plots of Kissinger method: (a) e-PGN, (b) 20% Bu-NENA/e-PGN, The plots of FWO method: (c) e-PGN, (d) 20% Bu-NENA/e-PGN, The plots of Starinkmethod: (e) e-PGN, (f) 20% Bu-NENA/e-PGN, Plots of the dependence of the activation energy on conversion rate: (g) e-PGN, (h) 20% Bu-NENA/e-PGN.

Table 3. The half-life of e-PGN and 20% Bu-NENA/e-PGN obtained by ASTM (Kissinger and FWO) and AKTS methods

Temperature (°C)	Kissinger ($t_{1/2}$, min)		FWO ($t_{1/2}$, min)		AKTS ($t_{1/2}$, min)	
	e-PGN	20% Bu-NENA/e-PGN	e-PGN	20% Bu-NENA/e-PGN	e-PGN	20% Bu-NENA/e-PGN
100	44915	76536	45203	76788	96605	226300
125	2558	3728	2569	3736	4512	3778
150	204.4	259.5	204.9	259.8	303.5	214

Figure 6. ASTM method, The plots of Kissinger method: (a) e-PGN, (b) 20% Bu-NENA/e-PGN, The plots of FWO method: (c) e-PGN, (d) 20% Bu-NENA/e-PGN.

Table 2. Activation energy and frequency factor parameters of e-PGN and 20% Bu-NENA/e-PGN obtained by Kissinger and FWO methods

Methods	Activation energy (kJ/mol)		Frequency factor (1/min)	
	e-PGN	20 % Bu-NENA/e-PGN	e-PGN	20 % Bu-NENA/e-PGN
Kissinger	141.587	149.311	1.02×10^{15}	7.22×10^{15}
FWO	141.680	149.359	1.04×10^{15}	7.31×10^{15}

The calculated activation energy for different conversion values by the Kissinger, FWO, Starink, and AKTS (Friedman) methods are shown in Fig. 6(g) and 6(h). In the e-PGN of the Kissinger, FWO, and Starink methods, their progress is obviously similar. In first, the calculated activation energy values decreased with the degree of conversion until it reached about 35 % conversion. Thereafter, the activation energy increased to a 90 % conversion rate. After that, the activation energy decreased versus conversion until it reached 153 kJ·mol⁻¹ at 95 % of conversion. According to AKTS

(Friedman) method, activation energy values increased with the degree of conversion until about 85% conversion and again decreased.

In the 20% Bu-NENA/e-PGN of the Kissinger, FWO, and Starink methods, their progress is obviously similar. At first, the calculated activation energy values decreased with the degree of conversion until it reached about 10% conversion. Thereafter, the activation energy increased to 85% conversion rate. After that, the activation energy decreased by 90% then increased to 95 % conversion rate. According to AKTS (Friedman) method, investigation of activation energy changes is complex. Approximately, activation energy increased with the degree of conversion until about 50 % conversion and again decreased.

In determining the half-life, the thermokinetic parameters correlating to the non-isothermal decomposition of the e-PGN and 20% Bu-NENA/e-PGN were determined by DSC data, using the ASTM method E698 and E2890. The data of Fig. 5 were used to plot Kissinger Eqn. (1) and FWO Eqn (2), (Fig. 6), Which implies that the mechanism of a thermal

decomposition reaction is first order, the slopes of the lines are equal to $-E\alpha/R$ for Kissinger method and $-0.4567E\alpha/R$ for FWO method and the pre-exponential factor in the Arrhenius equation is computed according to equation 4 by ASTM E698 and E2890. The calculated values of activation energy and frequency factor for e-PGN are listed in Table 2. The half-life prediction of energetic binder e-PGN was predicted by the Eqn. (6) and the results compared[35]. Half-life was calculated by using ASTM and AKTS methods at three different temperatures. The resulting values are given in Table 3.

4. CONCLUSION

The energetic binder of e-PGN was synthesised and prepared according to the improved literature method. The thermal behavior of the binder was investigated using DSC diagrams. The results showed that the glass transition temperature of a plasticizer/binder mixture is less than the pure binder (37.78 °C) and the glass transition temperature of a plasticizer/binder mixture of 20% Bu-NENA/e-PGN (Tg = −56°C) was the lowest. Thermoanalytical data for e-PGN and 20% Bu-NENA/e-PGN showed that decomposition peak temperatures increase with increasing heating rates. The calculated activation energy of exothermic decomposition of the e-PGN by using the Kissinger, FWO, Starink, and AKTS (Friedman method) was 151.1, 151.3, 151.3, and 153.6 kJ.mol^{-1} respectively and for 20% Bu-NENA/e-PGN was 141.9, 142.6, 142.1, and 142.8 kJ.mol^{-1} respectively. Based on the results of the activation energy and reaction progression, the half-life (50% conversion) of the e-PGN and 20% Bu-NENA/e-PGN were calculated at three different temperatures.

REFERENCES

1. Bunyan, P.; Cunliffe, A.V.; Davis, A. & Kirby, F.A. The degradation and stabilisation of solid rocket propellants. *Polym. Degrad. Stab*., 1993, **40**(2), 239-250. doi:10.1016/0141-3910(93)90211-Z

2. Chaturvedi, S. & Dave, P.N. Solid propellants: AP/HTPB composite propellants. *Arab. J. Chem*., 2015. doi: 10.1016/j.arabjc.2014.12.033

3. Huggett, C. Bartley, C.E. & Mills, M.M. Solid propellant rockets. Princeton University Press, United States of America, 2016. 176 p.

4. Kuo, K.K.Y. & Acharya, R. Applications of turbulent and multiphase combustion. Wiley, Canada, 2012. 600 p.

5. Reshmi, S.; Arunan, E. & Nair, C.R. Azide and alkyne terminated polybutadiene binders: Synthesis, cross-linking, and propellant studies. *Ind. Eng. Chem. Res*., 2014, **53**(43), 16612-16620. doi:10.1021/ie502035u

6. Wingborg, N. Improving the mechanical properties of composite rocket propellants. Akademisk Avhandling, Department of Fibre and Polymer Technology, Royal Institute of Technology, Stockholm, Sweden, 2004. (PhD thesis).

7. Ang, H.G. & Pisharath, S. Energetic polymers: Binders and plasticizers for enhancing performance. Wiley-VCH, Germany, 2012. 234 p.

8. Perut, C.; Lacroix, G.; Orlandi, O. & Franson, C. New solid propellants developments at snpe materiaux energetiques.

Int. J. Energ. Mater. Chem. Propul., 2009, **8**(6), 515-530. doi:10.1615/IntJEnergeticMaterialsChemProp.v8.i6.40

9. Willer, R.L. Binders for high-energy composition utilizing cis-, cis-1, 3, 5-tri (isocyanatomethyl) cyclohexane. US Patent 5240523, 31 August 1993.

10. Badgujar, D.M.; Talawar, M.B.; Zarko, V.E. & Mahulikar, P.P. New directions in the area of modern energetic polymers: An overview. *Combust. Explos. Shock Waves*., 2017, **53**(4), 371-387. doi:10.1134/S0010508217040013

11. Hinshaw, C.J.; Wardle, R.B. & Highsmith, T.K. Propellant formulations based on dinitramide salts and energetic binders. US Patent 5741998, 21 April 1998.

12. Provatas, A. Energetic polymers and plasticisers for explosive formulations-A review of recent advances. Defense Science and Technology Organization Melbourne Australia, No. DSTO-TR-0966. April 2000.

13. Astuti, E.; Supranto, S.; Rochmadi, R.; Prasetya, A.; Ström, K. & Andersson, B. Determination of the temperature effect on glycerol nitration processes using the HYSYS predictions and the laboratory experiment. *Indones. J. Chem*., 2014, **14**(1), 57-62. doi:10.22146/ijc.21268

14. Dong, Q.; Li, H.; Liu, X. & Huang, C. Thermal and rheological properties of PGN, PNIMMO and P (GN/NIMMO) synthesized via mesylate precursors. *Propellants Explos. Pyrotech*., 2018, **43**(3), 294-299. doi:10.1002/prep.201700201

15. Bayat, Y.; Razghi, M.A.; Ghorbani, M.; Ghadiri, A.; Mossahebi, M.M. & Dehghani, H. Synthesis of Tri-Block Polycaprolactone-Poly Glycidylnitrate Polycaprolactone as Polyol Propellant Binder. *J. Energ. Mater*., 2015, **10**(2), 25-34. https://www.sid.ir/en/journal/ViewPaper.aspx?id=480873

16. Leeming, W.B.H.; Marshall, E.J.; Bull, H.; Rodgers, M.J. & Paul, N.C. An investigation into polyGLYN cure stability. *In* Proceedings of the 27th In International Annual Conference of ICT, Karlsruhe, Germany, 1996, pp. 99/1–99/5.

17. Kim, J.S.; Cho, J.R.; Lee, K.D. & Kim, J.K. 2-nitratoethyl oxirane, poly (2-nitratoethyl oxirane) and preparation method thereof. US Patent 7288681, 30 October 2007.

18. Paraskos, A.J.; Dewey, M.A. & Edwards, W. One pot procedure for poly (glycidyl nitrate) end modification. US Patent 7714078, 11 May 2010.

19. Wei, W.; Shi-min, H.; De-liang, Z.; Jin-qiang, X.; Bing-kun, S.; Yan-lu, X. & Bo, W. Synthesis and Curing of Epoxy-terminated Poly(glycidyl nitrate). *Chin. J. Energ. Mater*., 2017, **25**(1), 49-52. doi:10.11943/j.issn.1006-9941.2017.01.008

20. Abrishami, F.; Zohari, N. & Zeynali, V. Synthesis and kinetic study on the thermal degradation of triblock copolymer of polycaprolactone-poly (glycidyl nitrate)-polycaprolactone (PCL-PGN-PCL) as an energetic binder. *Polym. Adv. Technol*., 2019, **30**(3), 640-647. doi:10.1002/pat.4500

21. Shee, S.K.; Reddy, S.T.; Athar, J.; Sikder, A.K.; Talawar, M.B.; Banerjee, S. & Khan, M.A.S. Probing the compatibility of energetic binder poly-glycidyl nitrate with energetic plasticizers: thermal, rheological and DFT

studies. *RSC Adv*., 2015, **5**(123), 101297-101308. doi:10.1039/c5ra16476a

22. Chen, J.K. & Brill, T.B. Thermal decomposition of energetic materials: Part 51. Kinetics of weight loss from nitrate ester polymers at low heating rates. *Thermochim. Acta*., 1991, **181**, 71-77. doi:10.1016/0040-6031(91)80413-D

23. Chen, J.K. & Brill, T.B. Thermal decomposition of energetic materials 50. Kinetics and mechanism of nitrate ester polymers at high heating rates by SMATCH/FTIR spectroscopy. *Combust Flame.*, 1991, **85**(3-4), 479-488. doi:10.1016/0010-2180(91)90149-6

24. Gouranlou, F. & Kohsary, I. Synthesis and characterization of 1, 2, 4-butanetrioltrinitrate. *Asian J. Chem*., 2010 **22**(6), 4221-4228.

25. Rao, K.P; Sikder, A.K.; Kulkarni, M.A.; Bhalerao, M.M. & Gandhe, B.R. Studies on n-Butyl Nitroxyethylnitramine (n-BuNENA): Synthesis, Characterization and Propellant Evaluations. *Propellants Explos. Pyrotech*., 2004, **29**(2), 93-98. doi:10.1002/prep.200400035.

26. Liu, J. Nitroglycerin. *In* Nitrate Esters Chemistry and Technology. *Springer,* Singapore, 2019. pp. 281-340. doi:10.1007%2F978-981-13-6647-5_6

27. Wang, Y.L.; Liu, W.X.; Wang, W.; Zhu, Y.; Li, B.D.; Chen, B.; Ding, F. & Ji, Y.P. Synthesis of insensitive nitrate plasticizers TMETN and PGDN by micro reaction technology. *Chin. J. Explos. Propellants*., 2018, **04**, 359-368. doi:10.14077/j.issn.1007-7812.2018.04.007

28. Rezaei, M.; Shahidzadeh, M. Synthesis and Characterization of Poly(2,2-Bis(azidomethyl)-1,3-Propylene Adipateas as Energetic Binder. *J. Energetic. Mater.,* 2016, **11**, 47-57.

29. Xie, C.; Gan, Y.; Ben, C. & Li, C. Pyrolysis kinetics analysis on FRP rod of composite insulators by DSC. *In* 2016 IEEE International Conference on High Voltage Engineering and Application, pp. 1-4. IEEE, 2016. doi:10.1109/ICHVE.2016.7800647

30. Vyazovkin, S.; Burnham, A.K.; Criado, J.M.; Pérez-Maqueda, L.A.; Popescu, C. & Sbirrazzuoli, N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim. Acta*., 2011, **520**(1-2), 1-19. doi:10.1016/j.tca.2011.03.034

31. Guo, S.; Wan, W.; Chen, C. & Chen, W.H. Thermal decomposition kinetic evaluation and its thermal hazards prediction of AIBN. *J. Therm. Anal. Calorim*., 2013, **113**(3), 1169-1176. doi:10.1007/s10973-013-2993-7

32. Jangid, S.K.; Singh, M.K., Solanki, V.J., Sinha, R.K. & Murthy, K.P.S. Studies on Sheet Explosive Formulation Based on Octahydro-1, 3, 5, 7-Tetranitro-1, 3, 5, 7-Tetrazocine and Hydroxyl Terminated Polybutadiene. *Def. Sci. J*., 2017, **67**(6), 617-622. doi:10.14429/dsj.67.10533

33. Shi, X.; Wang, J.; Li, X.; An, C.; Wang, J. & Ji, W. Preparation and Properties of 1, 3, 5, 7-Tetranitro-1, 3, 5, 7-Tetrazocane-based Nanocomposites. *Def. Sci. J*., 2015, **65**(2), 131-134 doi: 10.14429/dsj.65.7843

34. Krishnan, K.; Viswanathan, G.; Kurian, A. & Ninan, K.

Kinetics of decomposition of nitramine propellant by differential scanning calorimetry. *Def. Sci .J*., 1992, **42**(3), 135-139.

35. Bayat, Y. & Chizari, M. Synthesis, Characterization and Stability of Triblock Copolymer Based on Tetrahydrofuran and Glycidylazide as Binder. *Polymer Science Series B*., 2018, **60**(5), 621-628. doi:10.1007/s10973-017-6351-z.

36. Kizilca, M. & Copur, M. Thermal dehydration of colemanite: Kinetics and mechanism determined using the master plots method. *Can. Metall. Q*., 2017, **56**(3), 259-271. doi:10.1080/00084433.2017.1349023

37. Starink, M.J. A new method for the derivation of activation energies from experiments performed at constant heating rate. *Thermochimica. Acta*., 1996, **288**(1-2), 97-104. doi:10.1016/S0040-6031(96)03053-5

38. Tompa, A.S. & Boswell, R.F. Thermal stability of a plastic bonded explosive. *Thermochim. Acta*., 2000, **35**, 169-175. doi:10.1016/S0040-6031(00)00386-5

39. Maharrey, S.; Highley, A.; Weise-Smith, D. & Behrens, R. Thermal Decomposition Mechanisms in Poly-Glycidyl Nitrate (PGN) Prepolymer. Sandia National Lab (SNL-CA), Livermore, CA (United States), No. SAND2006-7332C. November 2006.

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