



Optimization of Curing Agents for Linear Difunctional Glycidyl Azide Polymer (GAP), with and without Isocyanate, for Binder Applications

**Namdeo Tulshiram Agawane, Ravidra R. Soman,
Rashmi M. Wagh, Javaid Athar,* Mahadev Talawar**

*High Energy Material Research Laboratory,
Sutarwadi, Pune-411021, India
E-mail: jathar786@gmail.com*

Abstract: Glycidyl Azide Polymer (GAP) is one of the most potential energetic binders for rocket propellants and gas generator compositions. In the present paper GAP of molecular weight (M_n) ~2000 was cured with a mixture of di- and tri-isocyanates without a cross linker. The curing profile and time of curing was recorded using a rheometer. The minimum curing time was observed for samples cured with Desmodour N-100 alone, whereas the maximum curing time was observed for samples cured with a mixture of Desmodour N-100 and Isophorone Diisocyanate (IPDI) (1:1 w/w). It was observed that all of the samples cured well and were void or bubble free. The mechanical properties data showed that the tensile strength (TS) of GAP cured with Desmodour N-100 alone was 1.19 kgf/cm², which is a minimum, while the maximum TS (3.66 kgf/cm²) was achieved with a mixture of N-100 and 4,4'-methylenebis(phenylisocyanate) (MDI). The percent elongation for a sample cured with Desmodour N-100 was 160, and was reduced to 64.27 when a mixture of MDI and N-100 was used. In order to study the curing of GAP without an isocyanate, GAP diol was cured with hexanediol di-acrylate. GAP was also cured with an alkyne-based curing agent *i.e.* bis-propargyl succinate (BPS), which showed improved curing. Comparative thermal studies of GAP cured with isocyanate and acrylate was carried out. Differential Scanning Calorimetry (DSC) and Simultaneous Thermal Analysis (STA) curves for all of the cured samples were recorded in order to study and compare the thermal decomposition behaviour of the cured GAP. Isocyanate cured GAP exhibited a single stage decomposition, with larger heat output. Acrylate cured GAP exhibited a two stage decomposition. Finally, a mixture of IPDI and Desmodour N-100 was selected for curing of GAP. Accordingly, curing was carried out and was tested in a small ballistic evaluation motor (BEM) to observe the combustion behaviour and burn rate. From the pressure-time profile it was

found that this composition gave smooth burning with a pressure of ~ 3 kg/sec² for 7 seconds of burn.

Keywords: energetic binder, glycidyl azide polymer (GAP), isocyanate curing agent, non-isocyanate curing agent, insensitive munitions (IM)

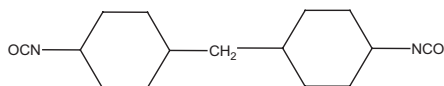
1 Introduction

An energetic insensitive polymeric binder is one of the important ingredients in energetic formulations. These polymers find use in cast-cured 'polymer bonded explosives' as well as cast-cured composite propellants and in gas generating compositions. Energetic binders confer higher energy output over non-energetic conventional binders.

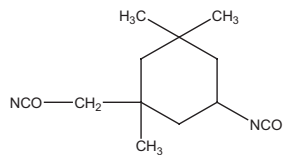
These binders also comply with Insensitive Munitions (IM) criteria [1]. It was reported that the use of low molecular weight azido compounds in solid propellant formulations confers insensitivity and high energy release during ballistic testing [2]. This demonstration of the utility of organic azido compounds led to the extension to synthetic polymers with azido groups. Consequently, research was initiated on the synthesis of azido polymers with hydroxyl end groups, so that they could be used either in conjunction with hydroxyl terminated polybutadiene (HTPB) or alone [3-6]. Among the azido polymers known so far, hydroxyl terminated Glycidyl Azide Polymer (GAP) is the most widely studied due to its high energy release, insensitiveness and thermal stability characteristics [1, 2, 7, 8].

The effective curing of the hydroxyl groups of GAP mixed with di- and tri-isocyanates and the formation of three dimensional networks has been studied by many research groups. The hydroxyl groups of GAP are secondary in nature, which causes a problem with gasification during the curing reactions [9]. In order to overcome these problems during curing with isocyanates, a number of workers have reported curing or crosslinking of GAP by other methods. Azido polymers can undergo dipolar cycloaddition reactions with acrylates resulting in a cross-linked network of polymer containing triazole rings. GAP cured with polyfunctional acrylate has been reported as a binder for gas generating compositions [10-12].

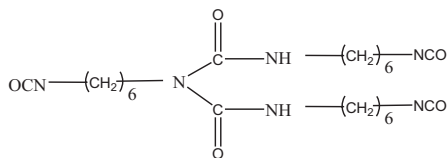
This paper presents data on GAP cured with mixed isocyanates, hexanediol diacrylate and bis-propagyl succinate (BPS). This comparative study is useful for the selection of a formulation for binder application studies (see Schemes 1, 2 and 3).



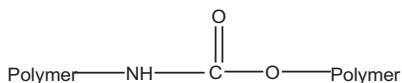
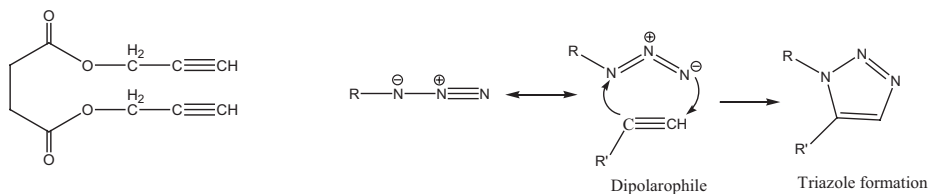
4,4'-Methylenebis(phenylisocyanate) (MDI)



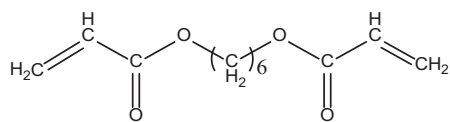
Isophorone di-isocyanate (IPDI)



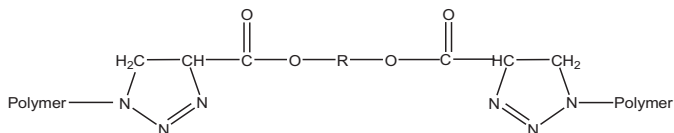
Desmodour N-100

**Scheme 1.** Chain formation reaction of an isocyanate and GAP

Bis-propargyl succinate (BPS)

Scheme 2. Chain formation reaction of BPS and GAP

Hexanediol diacrylate

**Scheme 3.** Chain formation reaction of acrylate and GAP

2 Experimental

GAP diol was synthesized as reported [6, 13]. The molecular weight (M_n) for this linear GAP was 2000, with a polydispersity value of 1.3. The hydroxyl value was determined using the acetylation method and was found to be ~ 2 . The moisture content was determined using the Karl Fisher Method. For the isocyanate curing studies, aliphatic triisocyanates, from Bayer Material Science were used, while IPDI and MDI were from Fluka. For the curing studies the aliphatic triisocyanate Desmodour N100 was used. The rheological studies were performed on a Rheometer Model Rheologica Instruments AB, Sweden, with parallel plate geometry. The mechanical properties, such as TS, % elongation (%E) and E-modulus were determined by using a Hounsfield H25 KS material testing machine, according to ASTM D-638 standard.

For the acrylate curing, hexanediol diacrylate (Fluka) was used. The hardness of the samples was measured using a Durometer Tester, model SHORE-A HARDNESS TESTER MODEL-SHR-A-GOLD. FTIR were recorded on a NICOLET 5700 IR spectrophotometer. The IR spectra were recorded on a smear on NaCl windows. STA was recorded on a WATERS TA Instrument, SDT Q 600. DSC studies were performed using a Perkin Elmer DSC-7, under a nitrogen atmosphere. The gross heat output for all of the samples was recorded in a bomb calorimeter Parr 6300.

2.1 Sample preparation

2.1.1 Isocyanate cured samples

GAP diol (30 g, 0.015 mol) was placed in a beaker and completely dried in an oven at 70 °C for 2 h. The sample was stored in a vacuum desiccator, with evacuation, for 1 hour. The calculation for the quantities of isocyanate were performed on the basis of a mixture of di- and tri-isocyanate for a 1:1 isocyanate:OH ratio. The calculated quantities of N-100 (2.04 g, 0.0043 mol) and IPDI (1.824 g, 0.0082 mol) was added to the beaker and mixed well. The sample was then heated to 70 °C and vacuum was applied to the sample. The sample was brought to room temperature and dibutyltin laurate (0.021 g) was added. Vacuum was again applied until complete deaeration. A small amount of sample was taken for the rheological studies, and the remaining sample was poured into a casting tray and kept in a desiccator, at ambient temperature, for curing. In the same manner GAP diol (30 g, 0.015 mol) was cured with a mixture of MDI (1.71 g, 0.0069 mol) and N-100 (2.04 g, 0.0043 mol). All of the samples cured well and were void free. Dumbbells of the required size were cut out and their mechanical

properties were determined. For the purpose of BEM firing, 50 g castings with mixed isocyanates (N-100 and IPDI) were obtained in a similar manner and the samples were cured in a mould and inhibited with a polyurethane inhibitor system.

2.1.2 Acrylate cured samples

GAP was initially dried at 50 °C for 2 h on a flash rotary evaporator. Complete removal of volatile matter and moisture was confirmed from the moisture content data (<0.1%). This prepolymer was kept under vacuum in an oven at 50 °C. After cooling, 18 g, 16 g, 14 g and 12 g of GAP were placed in different polypropylene cups, and 2 g (10%), 4 g (20%), 6 g (30%), and 8 g (40%) respectively of hexanediol diacrylate were added to the respective cups; the samples were well stirred and vacuum applied for 1 h. The samples were left overnight to complete the reaction. It was observed that the samples became hard and were removed by cutting the cup. The samples were then taken for further analysis.

2.1.3 BPS cured samples

Dried GAP samples (27 g, 24 g, 21 g, 18 g) were taken in different beakers, mixed with weighed quantities of BPS (3 g, 6 g, 9 g, 12 g, respectively) (10% to 40%) and dissolved at 50 °C. The clear solutions were subjected to deaeration, then poured into casting trays and kept at room temperature for 2 days. These cured samples were post cured at 50 °C for 3 days. Dumbbells were cut for determination of their mechanical properties.

3 Results and Discussion

3.1 Curing time (pot life)

The curing profiles of GAP cured with different isocyanates was recorded on a rheometer and are shown in Figure 1(A-C). From the curing profile, it was observed that the minimum curing time occurred for samples cured with Desmodour N-100 alone, whereas the maximum curing time was observed for samples cured with a mixture of IPDI and Desmodour N-100. Curing times were determined from the curing profile as obtained by the rheometer. The point of sudden viscosity built up in a curing profile was taken as the pot life and this is listed in Table 1.

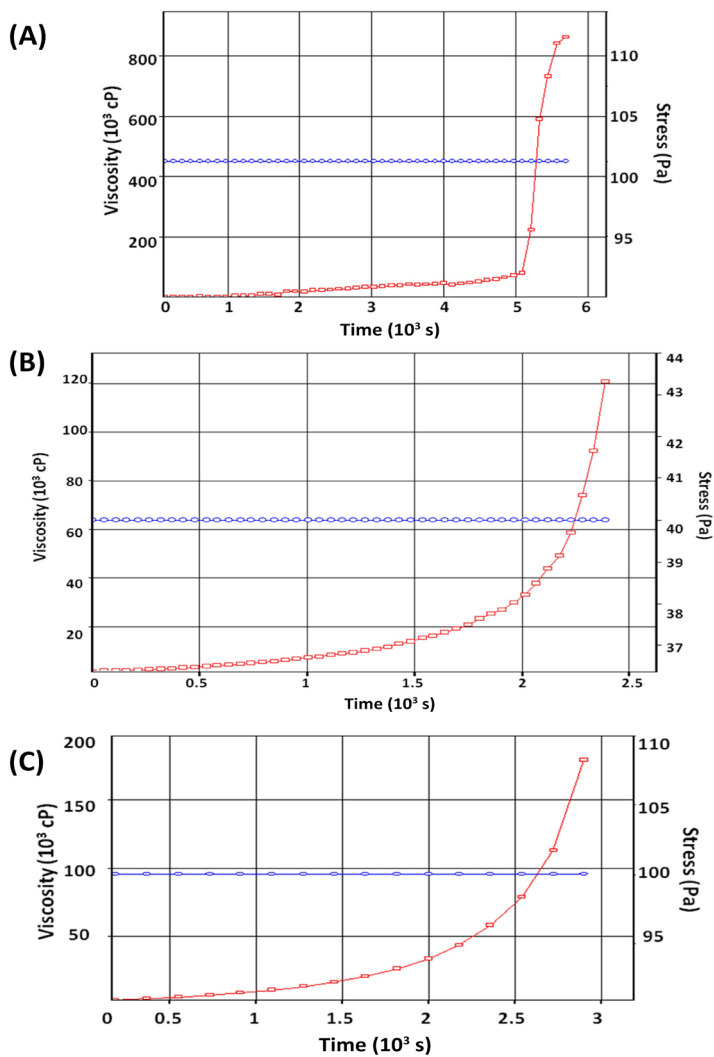


Figure 1. Curing profile for (A) GAP + N-100 (B) GAP + IPDI + N-100 (C) GAP + MDI + N-100

Table 1. Comparative data of mechanical properties and pot life of GAP cured with different isocyanates

Sample	Pot life [min]	E Mod. [kgf/cm ²]	Tensile [kgf/cm ²]	Max Force [kgf]	Elongation at max [%]	Elongation [%]
GAP + N-100	40	0.802	1.189	0.164	157.9	160
GAP + IPDI + N-100	100	2.14	2.52	0.35	146.61	148.7
GAP + MDI + N-100	58	6.91	3.66	0.49	64.12	64.27

3.2 Shore hardness of GAP cured with acrylate

Cured samples having even surfaces were used as test specimens for measuring the Shore hardness. Each specimen was tested in triplicate at three locations separated by more than 5 mm. The tests were conducted at room temperature. The mean value of the three readings was recorded. The standard deviation was found to be <0.1%. The comparative mean values of the Shore hardness are listed in Table 2.

Table 2. Comparative data of Shore hardness

Sr. No.	Sample details	Mean value of Shore number
1	Isocyanate cured GAP (repeated with different samples)	18
2	Acrylate (10%) cured GAP	17
3	Acrylate (20%) cured GAP	52
4	Acrylate (30%) cured GAP	62
5	Acrylate (40%) cured GAP	71

It is well known that the degree of cross linking or polymerization in a polymer may be affected by the amount of curing agent used to cure the polymer [9-11]. These results indicated that the hardness of the samples increased with the increase in percent of acrylate. As the percent acrylate was increased, it gave increased crosslinking, so the final sample became hard, less elastic and showed the development of cracks during storage. It was observed that IPDI and Desmodour N-100 cured GAP gave Shore hardness values of 18, very close to the Shore hardness value obtained for GAP cured with 10% acrylate. The mechanical properties, as determined for the isocyanate cured samples following the ASTM D-638 standard, for all of the samples are listed in Table 1.

From the Table 1 it was observed that T.S. is maximum (3.66 kg/cm²) for the sample cured with a mixture of Desmodour N-100 and MDI, and is minimum (1.18 kg/cm²) for the sample cured with Desmodour N-100 alone. T.S. for the

sample cured with IPDI and N-100 lies between these two, but elongation in this case is higher. The different mechanical properties observed may be due to structural difference between the different isocyanates. The structure of N-100 consists of linear aliphatic chains, IPDI consists of a single cyclohexane ring, while MDI has two aromatic rings in its structure, hence the polymer network formed after curing shows an increase in TS. The maximum elongation was observed in the case of the sample cured with Desmodour N-100 alone. It was noted that any GAP diol can be cured with a mixture of N-100 and any diisocyanate without the use of a cross linker.

GAP was also cured with an alkyne based curing agent, bis-propargylsuccinate (BPS). GAP cured with BPS was found to be stable even after 1 year. This stability may be attributed to the formation of stable triazole rings, whereas the triazoline ring, formed in the case of acrylate curing, evolves nitrogen gas over time leading to the formation of voids in the finished product [13, 15]. The tensile test was performed on four dumbbell-shaped samples for each composition. The results (Table 3) showed that increasing the BPS content increased the tensile strength but decreased the elasticity. A higher BPS content increases the cross-linking density, which leads to a higher toughness of the cured material. This is consistent with the increased stiffness and strength with increasing cross-linking density in the material. Accordingly, the optimized BPS content was taken as 20% for further work, which gave better TS values, as well as % elongation. GAP cured with acrylate cannot be tested for TS and %E due to its brittle properties. The Shore hardness values of acrylate cured sample are listed in Table 2. The Shore hardness values increased as the percent acrylate was increased from 10 to 40.

Table 3. Mechanical properties of GAP cured with different amount of BPS

Sample (GAP/BPS)	Tensile strength [kg/cm ²]	Elongation [%]
90/10	1.32	110
80/20	2.11	90
70/30	2.85	66
60/40	3.24	52
GAP/Desmodour N100	2.52	146

The IR spectrum of GAP prepolymer is shown in Figure 2(A). The IR spectrum of isocyanate cured GAP and acrylate cured GAP show similar absorption patterns, corresponding to the GAP prepolymer. The IR spectrum of GAP cured with isocyanate is shown in Figure 2(B). The prominent peak

is the absorption at 2100 cm^{-1} for the azido group. The IR spectra of 10% to 40% acrylate cured GAP show a similar pattern, as given in Figure 2(C). The spectra for GAP cured with acrylate shows an absorption peak at 1687 cm^{-1} for C=O stretching. Isocyanate cured GAP shows a C=O stretching (non-hydrogen bonded) peak at 1722 cm^{-1} and an N–H stretching (non-hydrogen bonded) at 3344 cm^{-1} . The acrylate cured GAP shows a characteristic peak at 1445 cm^{-1} , indicating the presence of the N=N stretching band.

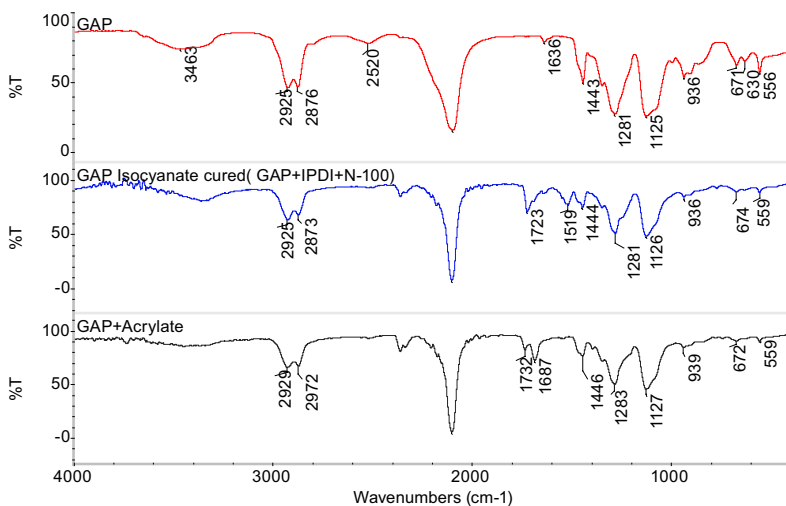


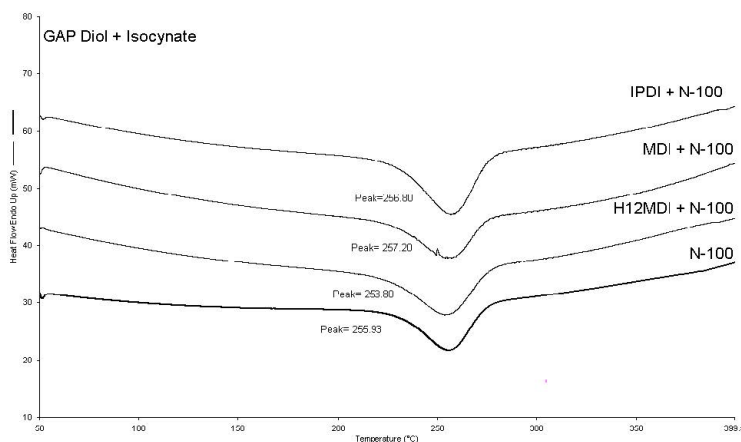
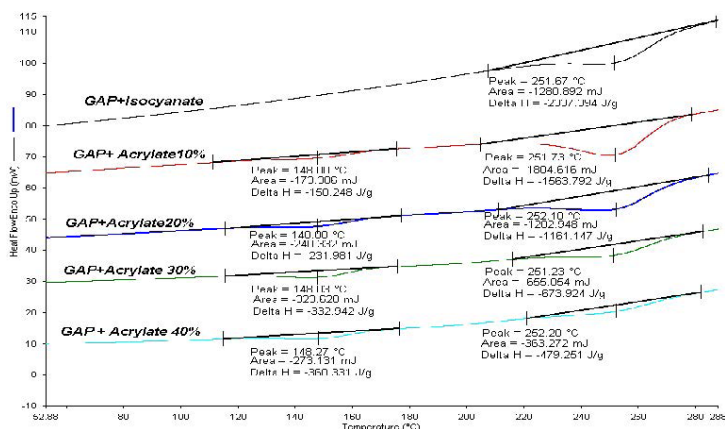
Figure 2. IR Spectra of (A) uncured GAP (B) isocyanate cured GAP (C) acrylate cured GAP

3.3 Thermal studies

The thermal decomposition pattern (DSC curves) for GAP cured with different isocyanates were studied by DSC and are shown in Figure 3. The DSC curves for GAP cured with different proportions of acrylate are shown in Figure 4. The data for the peak temperatures and heat outputs are listed in Table 4. The pattern shows that GAP samples cured with isocyanate decomposed in a single step, with an exothermic peak in the range $253\text{--}257\text{ }^{\circ}\text{C}$ for all samples, with an energy release of 2337 J/g . It has been reported that combustion of the GAP prepolymer is always through N_2 liberation [16-18], and the first exothermic peak is observed at around $250\text{ }^{\circ}\text{C}$. The results obtained from DSC show a single step decomposition with T_{max} of $257\text{ }^{\circ}\text{C}$, with the same energy released by all of the cured samples. The DSC curves revealed that the peak temperature of decomposition (T_{max}) for the cured samples matches the T_{max} obtained for a neat GAP sample, indicating that the decomposition pattern is similar to that of GAP.

Table 4. Comparison of decomposition temperature and heat output for isocyanate and acrylate cured GAP

Sample details	Peak temp.-I [°C]	Heat output-I [J/g]	Peak temp.-II [°C]	Heat output-II [J/g]
Isocyanate cured GAP	—	nil	252	2337
GAP+10% arylate	148	150	252	1563
GAP+20% Acrylate	148	232	252	1161
GAP+30% Acrylate	148	333	252	674
GAP+40% Acrylate	148	360	252	479


Figure 3. DSC curves for isocyanate cured samples

Figure 4. DSC curves of GAP cured with isocyanate and different % acrylate

The decomposition pattern for the acrylate cured GAP was however found to be different. The DSC of acrylate cured samples revealed that the decomposition occurs in two steps, with a first exothermic peak at 148 °C, with evolution of heat in the range 150-361 J/g. The second exothermic peak was at 252 °C, with a heat output of 1563-479 J/g. The first decomposition may correspond to triazole ring cleavage, while second decomposition may correspond to the decomposition of the residual azide groups. The heat output at a peak temperature of 148 °C (1st peak) was 232 J/g for 10% acrylate, which increased up to 360 J/g as the percent acrylate was increased, while the heat output decreased from 1161 J/g to 479 J/g for the second step decomposition. This is due to the gradual decrease in the number of pendant azide ($-\text{CH}_2\text{N}_3$) groups of GAP, which are converted to triazole groups during the crosslinking reaction. The extent of crosslinking is increased as the weight percent of acrylate is increased from 10% to 40%, leading to a decrease in the pendant azide groups of the polymer. Hence the heat output in the second stage decomposition decreases drastically. Furthermore, these samples were also studied by weight loss (STA) in order to understand properly this normal behaviour during decomposition. The STA curves for isocyanate cured GAP and 20%, 30% and 40% acrylate cured GAP samples were recorded. The STA curves are shown in Figures 5, 6(A), 6(B), and 6(C). It has been reported that GAP prepolymer decomposition exhibits second step weight loss. The first weight loss, corresponding to that of a peak temperature of 250-255 °C, is around 40%, corresponding to elimination of nitrogen, while the second stage weight loss corresponds to decomposition of the polymer backbone [7, 9]. Isocyanate cured GAP samples follow a similar pattern. The first stage weight loss was 39%, due to release of N_2 , and the second stage weight loss, corresponding to 48%, was due to slow decomposition of the polymeric backbone. In the case of acrylate cured GAP, the TG pattern was different. Thermogravimetric data showed that the weight loss corresponding to the 1st stage decomposition (148 °C) for 20% acrylate was 3.991%, for 30% acrylate 5.421%, and for 40% acrylate 7.25%. This shows that as the percent acrylate was increased, the curing of acrylate with the azide groups *via* the formation of triazole rings, increased. It has been reported that in the case of the thermal decomposition of polyallylazide cured *via* cyclic dipolar addition by reaction with EGDMA, a two-step weight loss occurs at 155-274 °C and 330-355 °C. It was also reported that weight loss in the case of GAP cured with acrylate occurred in the temperature range 130-280 °C, due to loss of nitrogen from the azide groups [19, 20]. The second stage weight loss starts at around 210 °C and increases from 67% for 20% acrylate, to 85% for 30% acrylate and 90% for 40% acrylate. In the present case, the weight loss starts from 148 °C for acrylate cured GAP in different proportions, whereas isocyanate

cured GAP shows a single step weight loss at around 252 °C, which corresponds to the decomposition temperature of azide-containing polymer.

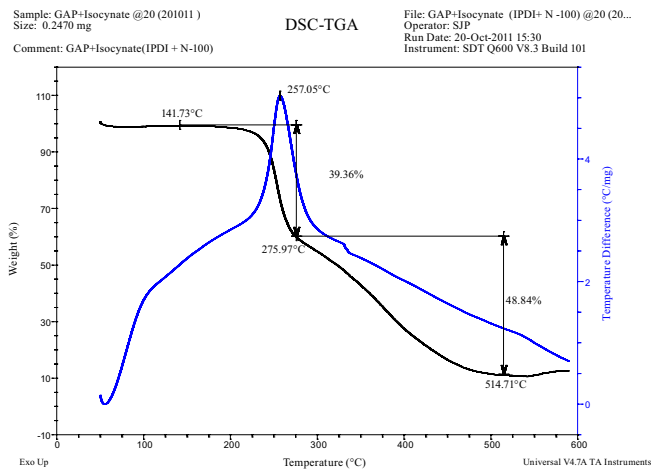
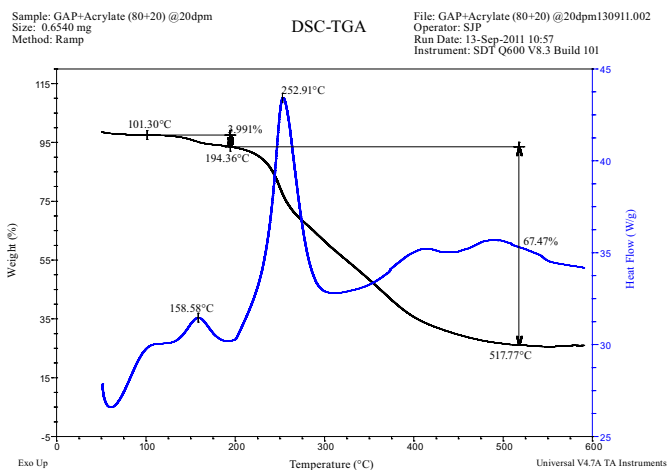
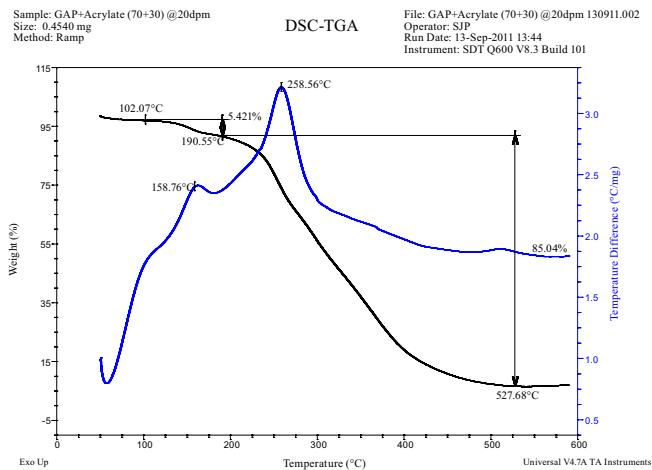


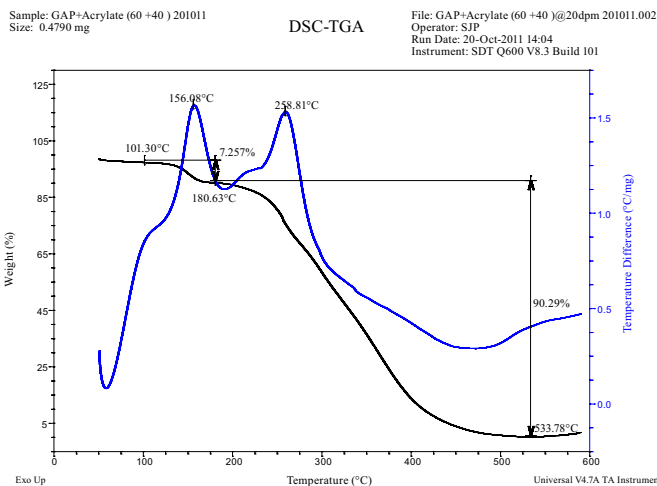
Figure 5. STA curve for GAP cured with isocyanate



(A)



(B)



(C)

Figure 6. STA curve GAP cured: (A) with 20% Acrylate; (B) with 30% Acrylate; (C) with 40% acrylate

The above data indicates that isocyanate cured GAP is more thermally stable, up to 252 °C, than acrylate cured GAP where decomposition starts at around 148 °C in the first step.

Comparison of the heat output of acrylate cured GAP samples at the second stage of decomposition indicated that as the percent acrylate was increased the

heat output was reduced. This is due to the decrease or conversion of the energetic free/pendant azido groups to triazole rings. It reveals that the formation of the triazole rings dilutes the heat output of cured GAP during its decomposition.

The gross heat output for all of the samples was recorded in a bomb calorimeter Parr 6300. The results are listed in Table 3. The values for the heat output are comparable, as the value corresponds to the decomposition of the polymer backbone. For acrylate cured GAP, the heat output marginally increased from 10% to 40%. This increase may be due to the increase in the percent acrylate used for curing. The value for isocyanate cured GAP was comparable to that of the acrylate cured.

In order to observe the burning characteristics of cured GAP, 50 g of GAP was cured with a mixture of IPDI and N-100. This combination of mixed isocyanates was selected on the basis of the observed curing profile so as to obtain void-free cured grains. The P-T profile was recorded for this sample. This showed smooth burning with constant pressure of $\sim 3 \text{ kg/s}^2$ for up to 7.5 s burn time.

The DSC curve of BPS cured GAP is shown in Figure 7, and is similar to isocyanate cured GAP, with a single decomposition at a peak temperature of 256°C .

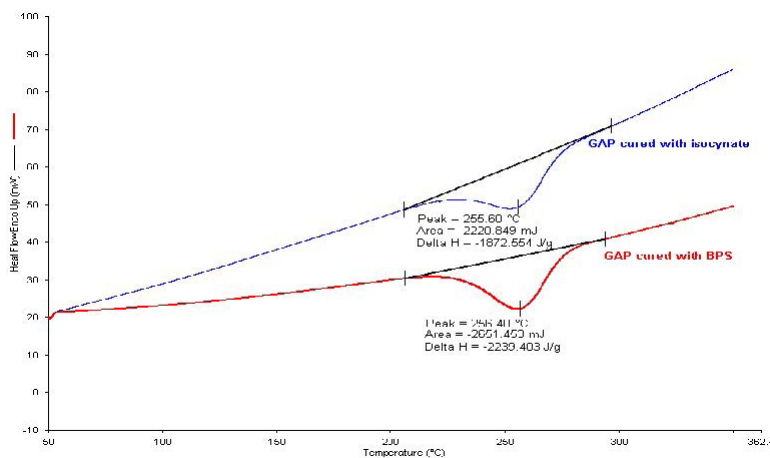


Figure 7. DSC curve for GAP cured with BPS and isocyanate

Table 5. Gross heat output value of samples

Sr. No.	Sample details	Gross heat output [cal/g]
1	Isocyanate cured GAP	4909
2	Acrylate cured GAP (10%)	4744
3	Acrylate cured GAP (20%)	4882
4	Acrylate cured GAP (30%)	5061
5	Acrylate cured GAP (40%)	5156

4 Conclusions

A detail study of the curing of GAP has been performed. GAP diol can be cured with different isocyanates, mixtures of isocyanates, as well as isocyanate free curing agents. The TS and elongation of these cured samples revealed good rubbery properties. The curing time for these samples varied with the type of isocyanate used in the mixed isocyanates. The cured binder gave smooth burning and can be further used with different solid loading. GAP was also cured with hexamethylene diacrylate and bis-propargyl-succinate (BPS), at room temperature, but acrylate curing exhibited the development of cracks during storage. However, better curing without any void development on storage was achieved with BPS. The hardness of acrylate cured GAP was found to increase with increases in the percent acrylate. The thermal analysis data for the cured samples revealed that isocyanate cured GAP is stable up to 252 °C and releases a higher heat output in a single stage. In the case of acrylate cured GAP, decomposition starts at 148 °C, with a second stage decomposition starting at 252 °C; the heat output was found to be lower. Because of the better mechanical properties when compared with BPS cured GAP, and also its stability and ease of processing, the use of mixed isocyanates (Desmodour N-100 + IPDI) may be the better option for curing of GAP in propellant compositions.

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