Thermal Characterization of Glycidyl Azide Polymer (GAP) and GAP-Based Binders for Composite Propellants

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ABSTRACT: Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were used to investigate the thermal behavior of glycidyl azide polymer (GAP) and GAP-based binders, which are of potential interest for the development of high-performance energetic propellants. The glass transition temperature (T_g) and decomposition temperature (T_d) of pure GAP were found to be -45 and $242°C$, respectively. The energy released during decomposition (ΔH_d) was measured as 485 cal/g. The effect of the heating rate on these properties was also investigated. Then, to decrease its T_g, GAP was mixed with the plasticizers dioctiladipate (DOA) and bis-2,2-dinitropropyl acetal formal (BDNPA/F). The thermal characterization results showed that BDNPA/F is a suitable plasticiser for GAP-based propellants. Later, GAP was crosslinked by using the curing agent triisocyanate N-100 and a curing catalyst dibuthyltin dilaurate (DBTDL). The thermal characterization showed that crosslinking increases the T_g and decreases the T_d of GAP. The T_g of cured GAP was decreased to sufficiently low temperatures ($-45°C$) by using BDNPA/F. The decomposition reaction-rate constants were calculated. It can be concluded that the binder developed by using GAP/N-100/BDNPA/F/DBTDL may meet the requirements of the properties that makes it useful for future propellant formulations. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 538–546, 2000

Key words: glycidyl azide polymer; energetic binder; composite propellant; thermal characterization; plasticizer

INTRODUCTION

Development of a high-performance propellant requires, first of all, the use of new energetic and environmentally benign oxidizers. New chlorine-free oxidizers have been synthesized for this purpose.[1] However, these materials have to be tested for many aspects such as compatibility, friction, and impact sensitivity before being used in the propellant. The polymer that will be used in the formulation of an energetic and clean propellant is also expected to act as a binder and additional energy source. Glycidyl azide polymers (GAPs) are promising candidates for energetic binders in future composite solid propellants having minimum smoke, reduced pollution, and low sensitivity.[2,3] There have been numerous studies on GAP, including its synthesis,[4] structure,[5] thermal behavior,[6] and physical, chemical, and explosive properties.[7] The pendant azide groups present in the structure of GAP is expected to contribute to some of the energy required from the binder.[8,9]

In the development of energetic binders for solid propellant, GAP should be transformed into a long-chain polyurethane by using a proper curing agent.[10] The choice of an appropriate curing agent is of prime importance to meet the minimum strain, stress, and hardness levels of mechanical properties, which crucially affect the performance of the propellant.[11] In practice, the preparation of a polyurethane binder is not simple to achieve. Side reactions of the curing agent with some impurities including moisture can compete with the polyurethane formation and create some defects in the elastomeric matrix. There has been a tremendous amount of continuing effort on the curing of GAP.[12] It seems that the traditional curing agents, polyisocyanates, can also be used in the polyurethane formation with GAP; however, the use of an effective catalyst is required to speed up the reaction to a reasonable rate level. Furthermore, the propellant application requires extensive knowledge on the influence of ingredients on the thermal, ballistic, and mechanical properties of the binder matrix as well as full characterization of the binder and all ingredients. There exist some studies on the thermal characterization of GAP and GAP-based mixtures.[13–15] In most of the studies, the compatibility of GAP with various energetic materials has generally been studied in terms of changes in the decomposition temperature by using DSC or TGA. However, the low-temperature characteristics of the polymeric binder determine the operational temperature limits of the propellant. There exist also some discrepancies between the results of different studies.[13,14] Therefore, a systematic study on the effect of ingredients on the low-temperature characteristics of the polymeric binder is required prior to a propellant formulation. Here, we report the results of a comprehensive study covering the full thermal characterization of GAP, the thermal stability of the polymer under the conditions of propellant processing and handling, the compatibility of pure polymer with the main ingredients (plasticizer and curing agent), and the ultimate thermal properties of the binder produced by using the selected plasticizer and curing agent.

EXPERIMENTAL

The following materials were used as purchased: glycidyl azide polymer (GAP DIOL L-996, 3M, Minneapolis, Minnesota, USA; density: 1.3 g/mL; hydroxyl Value: 0.83 meq/g; molecular weight: (MW_w):

2900 g/mol; viscosity at 25°C: 5000 cps), dioctyl adipate (DOA, KIMTAŞ, Istanbul, Turkey), bis-2,2-dinitropropyl acetal/formal (BDNPA/F, Group Aerojet, Sacramento, California, USA), triphenylmethane-4,4,4-triisocyanate (Desmodur N-100, Bayer, Leverkusen, Germany), and dibuthyltin dilaurate (Bayer, Leverkusen, Germany).

Thermal analyses were carried out using a Rheometric Scientific TGA 1000 M and DSC Gold Plus for four different materials: the pure GAP, the plasticised GAP, the cured GAP, and the plasticised-cured GAP. GAP was cured with the trifunctional isocyanate Desmodur N-100 at 65°C using a constant NCO/OH ratio of 1.0. DOA or BDNPA/F was added to the pure GAP as a plasticizer and mixed, followed by curing in the case of the plasticized-cured samples. DSC was calibrated using sapphire, indium, and tin, where the first was used for baseline calibration and the other two were used for temperature calibration. For accurate measurement of the glass transition temperature, T_g, DSC was also calibrated at subambient temperatures using sapphire and mercury. About 2–3-mg samples were used for each experiment, since a greater amount of the sample leads to explosion during the decomposition experiment. Nitrogen gas was purged at a flow rate of 20 mL/min. TGA experiments were carried out in the same manner. It was also calibrated on weight bases. Both nonisothermal with variable heating rates and isothermal methods were used in the characterization tests.

RESULTS AND DISCUSSION

The work is presented in four main parts: Initially, the thermal characterization of the pure GAP (having secondary hydroxyl functions) was carried out to study the effect of heating rate, thermal conditioning, and thermal shock on its thermal properties. By considering the results obtained, the plasticized GAP was thermally analyzed to select a suitable plasticizer and its concentration range for GAP binders. The next part involves the thermal analysis of the cured GAP with and without addition of a plasticizer. The final part deals with the theoretical estimation of the decomposition rate constants of pure and cured GAP.

The typical DSC and TGA thermograms for GAP are given in Figures 1–3, illustrating the determination of the characteristic temperatures and the decomposition energy. To test the repro-
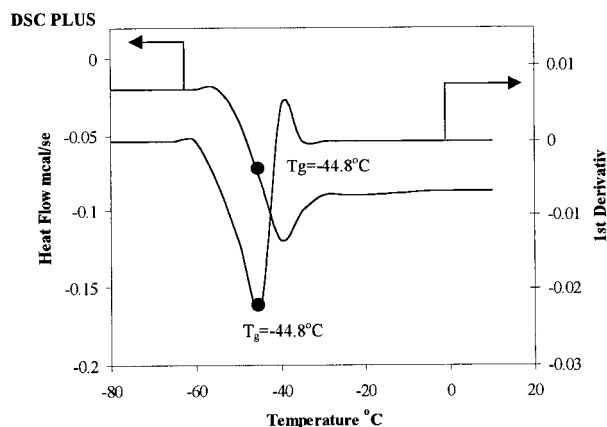
Figure 1   Typical DSC thermogram of pure GAP at subambient temperatures.

ducibility, each experiment was performed at least twice and the average values were taken. The results obtained are within the acceptable limits of deviations.[16] T_g could be determined either from the DSC curve or from its first derivative as shown in Figure 1. The values obtained in both ways are usually in good agreement with each other. The characteristic temperatures of decomposition (namely, T_o, T_{exon}, T_d, and T_f) were determined both from DSC and TGA thermograms as shown in Figures 2 and 3, respectively. The decomposition energy was calculated as the area under the DSC thermogram (Fig. 2).

Thermal Characterization of Pure GAP

From five DSC runs with different amounts of the sample at a ramp rate of 10°C/min, the glass transition temperature of GAP was found to be -44.7 ± 0.7°C, which is in accordance with the
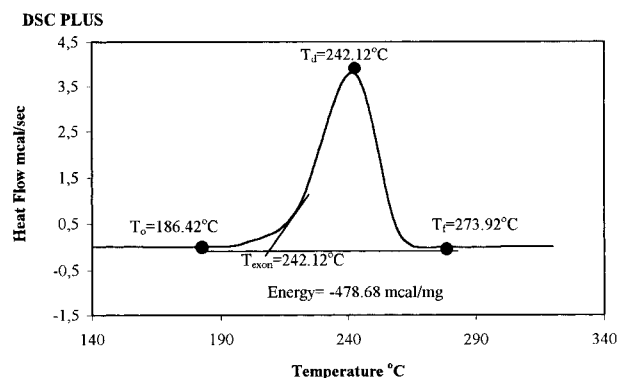

Figure 2   Typical DSC thermogram of pure GAP used to determine the decomposition properties.
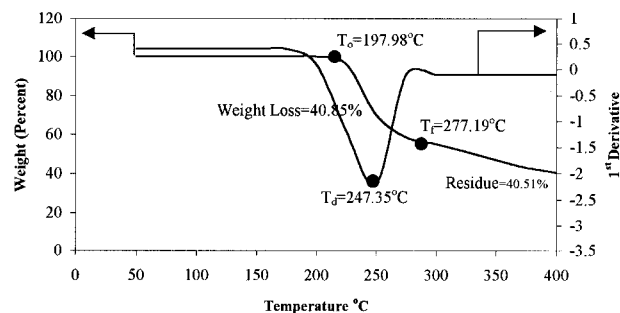

Figure 3   Typical TGA thermogram of pure GAP.

value of -43°C provided by the manufacturer. Since GAP is in rubbery state at temperatures above the T_g, which is lower than the lowest operational temperature (-40°C) for rocket motors, it can be considered as a mechanically safe binder for the composite propellant. However, both the curing and the solid loading increase the T_g of the polymers. Therefore, for being used as binder in composite propellants, the T_g of GAP should be lowered to compensate for the reverse effect of curing and solid loading on the T_g.

The decomposition properties of GAP were determined from the DSC thermograms at different ramp rates in the range of 0.2–5°C/min. A ramp rate higher than 5°C causes violent detonation in the DSC cell. Such explosions are also observed when more than a 3-mg sample is used. Characteristic temperatures of decomposition are shifted to higher values with the increasing ramp rate as shown in Figure 4. Changes in decomposition temperatures with an increasing ramp rate can
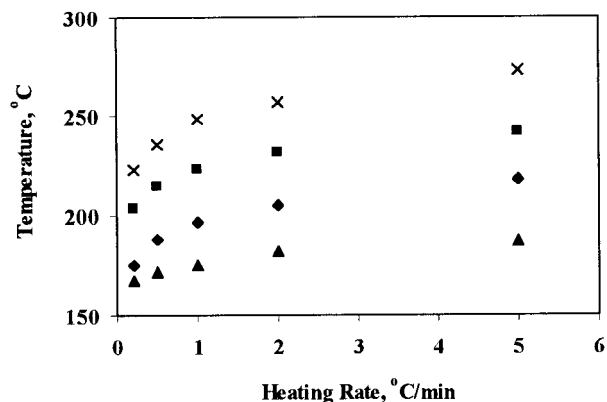

Figure 4   Characteristic temperatures for decomposition of pure GAP determined by DSC at different heating rates: (◆) extrapolated onset temperature; T_{exon}; (■) decomposition temperature, T_d; (▲) decomposition onset temperature, T_o; (x) final temperature, T_f.

be considered as an indication of the necessary molecular reconformation and relaxation of polymer chains taking place before decomposition. Since these molecular motions are time consuming, onset temperatures will increase with an increasing heating rate. Observation of the noticeable changes in T_d as a function of heating rate also indicates a strong temperature dependence of the reaction kinetics. Despite considerable shifts in the decomposition temperatures, the decomposition enthalpy shows only slight changes with the ramp rate (475–486 cal/g). This is not unexpected since the main source of the decomposition enthalpy of GAP is the dissociation of the N_3 groups; once the reaction starts, it should give the same energy during the decomposition. This observation implies that the decomposition pathway is independent of the heating rate or reaction temperature and partial decomposition does not take place.

The decomposition enthalpy of GAP is found to be 485 cal/g at a ramp rate of 5°C/min, which is, to some extent, different from the two values previously reported. One[13] differs slightly, which may be considered to be within the experimental error, while the other[14] shows a noticeable discrepancy. However, these values have been determined for different GAP polymers. Structural differences in the GAP polymers produced by different companies might causes changes in the decomposition enthalpy. In fact, the decomposition enthalpy of the GAP triol has been reported to be 617 cal/g,[17] which is about 30% higher than that of the GAP diol used in this study. This observation suggests that in the development of a propellant-independent determination of the decomposition enthalpy of a polymer is important even if a polymer with a previously investigated chemical structure will be used.

The decomposition of pure GAP was also studied by TGA at various heating rates. The characteristic temperatures of decomposition, T_o, T_d, and T_f, obtained from TGA are almost the same as the ones obtained by DSC at the same heating rate. In the case of TGA, violent detonation was observed at heating rates higher than 20°C/min. Although decomposition temperatures also show changes with the heating rate in the TGA, similar to DSC, the weight loss at the decomposition temperature T_d and the residue do not change with the ramp rate. This supports the suggestion that the decomposition pathway is independent of the heating rate and no partial decomposition occurs.
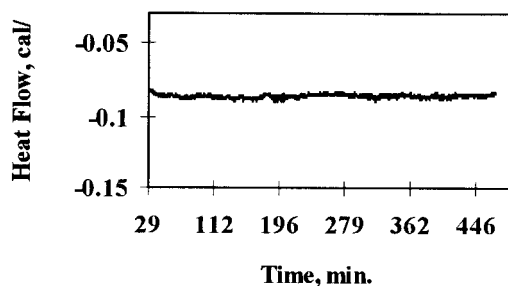

Figure 5   DSC isotherm of pure GAP at 160°C for 8 h.

In accordance with the results of a previous study,[8] these TGA results indicate that GAP decomposes in two stages: The initial weight loss by about 41% corresponds to the abstraction of N_3 groups from the polymeric chain, which is an exothermic decomposition as understood from the DSC thermograms. The second weight loss corresponds to the slow decomposition of the rest of the polymer after the initial N_3 elimination. The latter stage weight loss occurs without any considerable heat liberation as there is no exothermic peak observed after the decomposition of the energetic group.

The TGA thermograms were taken with different final temperatures in the range of 400–900°C at a ramp rate of 10°C/min to determine the temperature dependence of the residue. These thermograms showed that the residue decreases with an increasing final temperature (40.5% at 400, 32.2% at 500, 31.4% at 600, 25.7% at 700, and 22.8% at 900°C). The residue left does not mean that this amount of GAP remains in the rocket motor after combustion. It is obvious that the experimental conditions of TGA do not reflect the actual combustion conditions in the rocket motor. The decomposition of the oxidizer supplies the free oxygen required for the complete combustion of the materials in the propellant.

The nonisothermal DSC and TGA studies of pure GAP showed that characteristic temperatures of decomposition are dependent on the ramp rate. The question arises whether there are rate-limiting steps in the mechanism which determine the starting temperature of decomposition. The DSC and TGA isotherms (Figs. 5–7) were recorded for a long period of time at 160°C (slightly lower than the lowest T_o) and 180°C (slightly lower than the highest T_o) to allow the material to reach thermal equilibrium. The DSC isotherms do not show any significant change at the preset temperature, indicating that T_o is less important
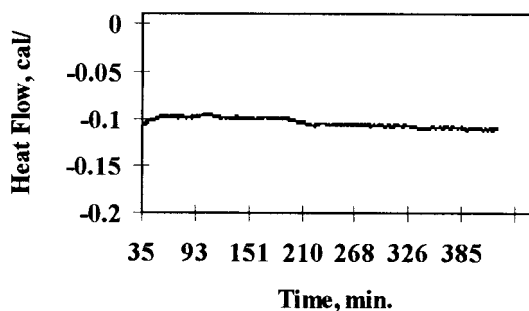
Figure 6   DSC isotherm of pure GAP at 180°C for 7 h.

in the decomposition kinetics than are T_{exon} and T_d. The 3% weight loss at the end of 8 h at 180°C recorded in the TGA isotherm (Fig. 7) indicates that the reaction occurs very slowly at these temperatures.

To test the thermal stability of GAP, the material was left at 100°C (a temperature well above the processing temperatures of polyurethane-based propellants) for 1 week and its thermal properties were followed by DSC and TGA. No significant changes were detected in the thermal properties of pure GAP left at 100°C for 1 week. Thus, GAP has a thermal stability high enough to be used in propellant formulation.

During their service life, propellants are usually faced with thermal cycling because of the wide operational temperature range. The material is expected not to be affected by this type of abrupt temperature changes. To test the effect of the thermal history on the properties of GAP, a thermal shock was applied on the material by keeping it for about 24 h at 100°C, followed by immersing into liquid nitrogen for 10 min. The thermal analysis of the shocked sample by DSC and TGA shows that the thermal properties of the glycidyl azide unity does not seem to be affected by the thermal history of the material.

All the DSC and TGA results given above for the thermal characterization of pure GAP show that its decomposition characteristics, except decomposition enthalpy, are dependent on the heating rate. The thermal history of the material does not affect these characteristics in the temperature range of -100 to 100°C. Therefore, it can be considered to be a suitable polymer for propellant-binder applications at this stage, but requires lowering its T_g for further steps by using a suitable plasticiser.

Thermal Characterization of Plasticized GAP

Two different plasticizers, DOA and BDNPA/F, were used to reduce the T_g of GAP and to increase

the processibility of the propellant. The former is a common plasticizer used in hydroxy-terminated polybudiene (HTPB) propellants, and the latter is a nitroplasticizer commonly used in gun propellants. Since the plasticizer content in a propellant can be increased up to 35 wt % of the pure polymer, mixtures of GAP and the plasticizers were prepared in different plasticizer concentrations between 0 and 35% by weight. The results of DSC analysis of the plasticized GAP mixtures are listed in Table I for both plasticizers. The characteristic temperatures of decomposition remain practically unchanged when the plasticizer concentration increases. Consequently, both plasticizers can be considered to be compatible with GAP when safety is concerned. The decomposition energy of GAP decreases with an increasing percentage of both plasticizers. However, in the case of BDNPA/F, the decrease in the decomposition energy is more pronounced. This is parallel to a previous observation that the addition of BDNPA/F initially decreases the decomposition energy of GAP, up to a realistic plasticizer concentration.[13]

The effectiveness of a plasticizer for a polymeric system can be measured by the degree of lowering the T_g. Figure 8 shows the variations in T_g as a function of plasticizer percentage. The T_g of GAP is lowered by addition of both plasticizers. However, the lowering of the T_g of GAP from -44.8 to -49.8°C by 30% DOA is not low enough for using in propellant formulations, while a lowering up to -72°C is achieved by adding 35% BDNPA/F. This is in contradiction with a previous report stating that the T_g of GAP would not be affected by the addition of BDNPA/F.[13] However, our results show that BDNPA/F is compatible with GAP, which might be attributed to the strong dipolar interactions between the two materials. This is reflected from the high solubility
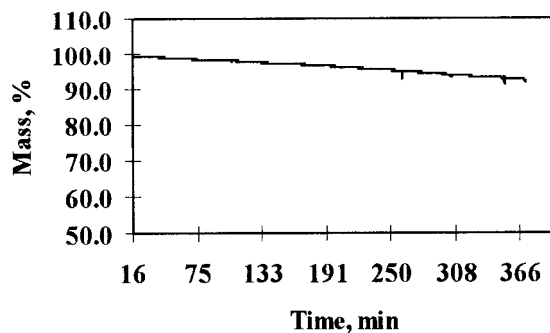

Figure 7   TGA isotherm of pure GAP at 180°C for 7 h.

Table I   DSC Results of GAP + Plasticizer Mixtures with DOA or BDNPA/F

Wt % of Plasticizer	T_g (°C)		T_{exon} (°C)		T_d (°C)		T_o (°C)		T_f (°C)		Energy (cal/g)	
	DOA	BDNP	DOA	BDNP	DOA	BDNP	DOA	BDNP	DOA	BDNP	DOA	BDNP
0	−44.8	−44.8	218	218	242	242	187	187	273	273	−486	−486
5	−48.4	−48.5	219	216	243	242	190	189	271	275	−483	−475
10	−47.9	−50.7	217	218	242	243	191	189	279	275	−483	−459
15	−47.8	−53.9	218	217	243	243	193	189	275	274	−439	−449
20	−47.8	−57.6	217	217	243	243	188	189	273	280	−437	−420
25	−48.4	−65.0	217	217	243	243	190	188	271	275	−448	−384
30	−49.8	−70.5	217	216	243	244	191	191	275	272	−435	−363
35		−72.0		217		244		193		274		−330

parameter of BDNPA/F [provided by the supplier, 11.3 $(cal/cm^3)^{1/2}$], which is considered to be the acceptable measure of compatibility of a plasticizer with polymers. In the literature, the solubility parameter reported for a similar polymeric material[18] is 11.2 $(cal/cm^3)^{1/2}$, which is very close to the value of the plasticizer. Based on this structural expectation and the experimental results obtained from DSC, it can be concluded that BDNPA/F is a suitable plasticizer for GAP when used up to 25% by weight. Although DOA is an effective plasticizer for HTPB-based propellants, it seems not to be suitable for GAP-based propellants.

Only GAP–BDNPA/F mixtures were studied further by TGA and the results are given in Table II. The TGA results are comparable with the results obtained from DSC up to 25% weight of the plasticizer. There is a slight increase in T_d and a slight decrease in T_o. Due to the presence of a second decomposition process from BDNPA/F, the weight loss of the overall mixture increases (as opposed to pure GAP) with an increasing amount of the plasticizer. Consequently, the amount of residue decreases with an increasing percentage of the plasticizer added. In fact, two weight loss peaks are detectable during decomposition of the mixture with 35% BDNPA/F, similar to the previously observed result.[13] The first-stage weight loss of 29% is observed between 155 and 240°C with a peak of 232°C. The second-step weight loss of 30% is observed between 240 and 277°C with a peak of 250°C. The mixture with 30% BDNPA/F shows a similar but less distinct behavior in TGA. This second peak probably corresponds to the decomposition of the plasticizer since the decomposition temperature of the pure plasticizer was found to be 250°C. These results are in accordance with the fluctuations observed in the DSC thermograms. In fact, at a BDNPA/F concentration higher than 25%, it appears from the observation of the separate BDNPA/F peak in DSC (at 250°C) that the plasticizer becomes
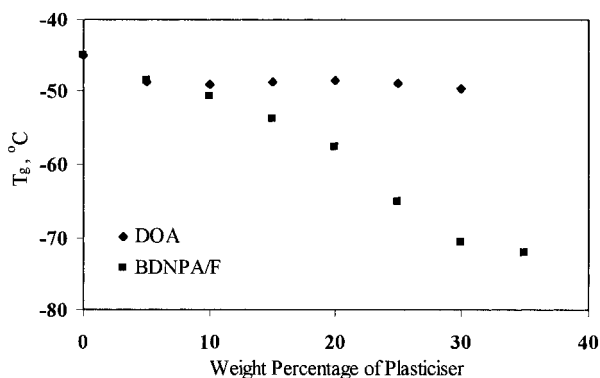

Figure 8   Variation in T_g of GAP as a function of plasticizer content.

Table II   Thermal Properties of GAP/BDNPA/F by TGA

BDNPA/F (wt %)	T_d (°C)	T_o (°C)	T_f (°C)	Weight Loss at First Stage (%)
0	247	196	276	40.5
5	250	188	273	43.8
10	250	177	275	44.4
15	249	176	275	45.9
20	250	161	277	49.6
25	247	170	277	47.9
30	248	167	274	55.1
35	232	155	240	29.3
	250	240	277	30.4

Table III   Thermal Properties of GAP Gumstocks Cured by Using Various Amounts of Catalyst

[Catalyst] (ppm)	T_g (°C)	T_o (°C)	T_d (°C)	Energy (cal/g)
Pure GAP	−44.8	182	232	−484
0	−36.8	182	229	−391
15	−35.3	183	229	−402
43	−34.3	186	228	−383
130	−34.6	182	229	−392
1120	−33.7	186	228	−395

The ramp rate was 10°C/min for the T_g measurement and 2°C/min for the decomposition studies.

Figure 9   Variation in the decomposition energy of GAP gumstocks as a function of BDNPA/F percentage.

Thermal Characterization of Cured GAP

The curing of GAP was achieved using N-100, a trifunctional isocyanate, as the curing agent and dibutyltin dilaurate (DBTL) as the curing catalyst at 65°C and a constant NCO/OH ratio of 1.0. The gumstocks prepared in this way were analyzed by DSC at a ramp rate of 10°C/min for the T_g measurement and 2°C/min for the decomposition studies. Table III shows the DSC results of gumstocks cured using various amounts of the catalyst. The decomposition properties remain practically unchanged, while the T_g value of GAP increases from −44.8 to −36.8°C upon curing without a catalyst, as expected, since by crosslinking, the polymer become more rigid and the molecular motions become more restricted. T_g increases further with an increasing concentration of the catalyst, which enhances the crosslink density up to a saturation point. It is obvious from Table III that the saturation point is achieved at a catalyst concentration of about 43 ppm, which will be used for the preparation of GAP binders with a plasticizer. The increase in T_g of the GAP binder upon curing should be compensated by using a plasticizer in the propellant formulations. In a previous study,[13] the T_g of a GAP binder was reported as −45°C. However, no comparison can be made because it is not clear whether the GAP used there was cured, and if cured, the curing agent was not specified.

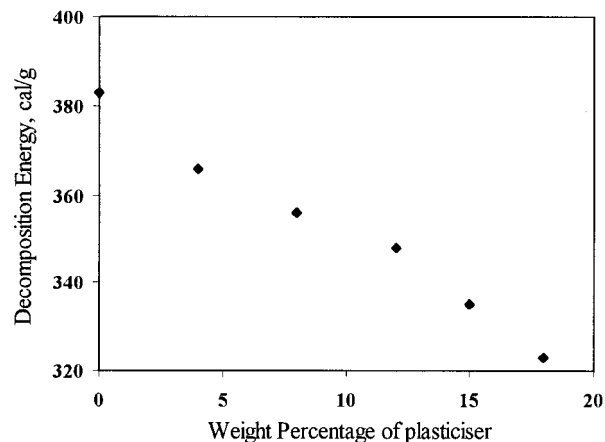The effect of the plasticizer on the thermal properties of cured GAP was studied by DSC analysis of the GAP gumstocks containing various amounts of BDNPA/F and being cured by using a constant NCO/OH ratio of 1.0 and a constant catalyst concentration of 43 ppm. The characteristic temperatures of decomposition remain almost unchanged, while the decomposition energy and the glass transition temperature of the cured GAP show variations with increasing concentration of the plasticizer. Figure 9 shows that decomposition energy of the cured GAP decreases with an increasing percentage of BDNPA/F in the binder. However, opposite to the effect of curing which lowers the decomposition energy of GAP from 486 to 383 cal/g, the addition of a plasticizer causes only a slight change in the decomposition energy of the cured GAP. The T_g of the cured GAP decreases linearly with an increasing percentage of BDNPA/F in the binder as shown in Figure 10. When the plasticizer concentration reaches 18%
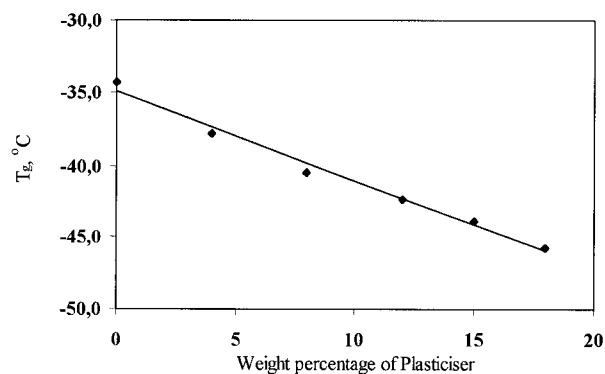

Figure 10   Variation in T_g of GAP gumstocks as a function of BDNPA/F percentage. Gumstocks were cured by using a constant NCO/OH ratio of 1.0 and a constant catalyst concentration of 43 ppm.
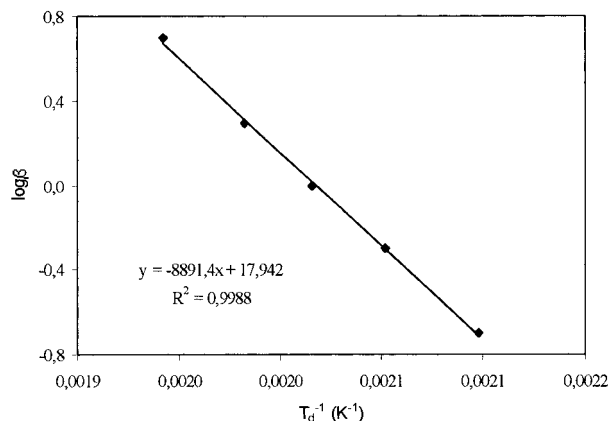
Figure 11 Arrhenius plot for the decomposition of pure GAP.

weight of the total binder, the T_g is lowered to $-45°C$, which is low enough to have a rubbery propellant at the operating conditions. Contrary to our finding, a previous study[13] reported that BDNPA/F has no effect on the T_g. This could be due to the use of a much higher percentage of the plasticizer, which was probably not homogeneously mixed with GAP at this high level. Consequently, it can be concluded that BDNPA/F is also compatible with the cured GAP from a safety point of view and a GAP binder having appropriate thermal properties can be prepared by using GAP as the polymer, Desmodur N-100 as the curing agent, DBTL as the curing catalyst, and BD-NPA/F as the plasticizer, amounting up to 1:2 weight ratio of BDNPA/F to GAP.

Decomposition Kinetics

The rate constant for the decomposition reaction of GAP was calculated using the method ASTM E 698[19] by assuming that the decomposition is a first-order reaction. To determine the effect of curing on the decomposition rate, DSC thermograms were run at various ramp rates for both pure GAP and cured GAP. The plot of the logarithm of the ramp rate ($\log \beta$) versus the reciprocal decomposition temperature ($1/T_d$) gives a straight line for both pure GAP and cured GAP as shown in Figures 11 and 12, respectively. The slope of the straight lines gives the Arrhenius activation energy of decomposition. The activation energy of cured GAP (178 kJ/mol) is slightly higher than is the activation energy of pure GAP (166 kJ/mol), which may be attributed to the re-

stricted molecular motions of the chains because of crosslinking.

The intercept of the straight lines gives the Arrhenius coefficient $Z = 8.9 \times 10^{15}$ and 5.0×10^{17} for pure and cured GAP, respectively. By having the activation energy (E) and the Arrhenius coefficient (Z), one can calculate the rate constant (k) for the decomposition of the pure and cured GAP at any temperature by using the Arrhenius equation $k = Ze^{-E/(RT)}$, where R is the ideal gas constant. The activation energy estimated for the decomposition of pure GAP is slightly higher than the previously reported value based on a TGA study; thus, the rate constant obtained is slightly lower than the literature value.[14] This might arise from the use of different GAP polymers and different techniques. DSC is a more suitable technique than is TGA for determining the decomposition rate constants since the decomposition temperatures can be detected more accurately by DSC, which is less affected by external factors such as vibrations.

CONCLUSIONS

Thermal properties of pure GAP were determined by TGA and DSC analysis: $T_g = -45°C$; 242°C $\Delta H_d = -485$ cal/g. The decomposition enthalpy shows only slight changes with the increasing ramp rate while the characteristic temperatures of decomposition are shifted to higher values, which can be considered as an indication of the necessary molecular reconformation and relaxation of polymer chains taking place before de-
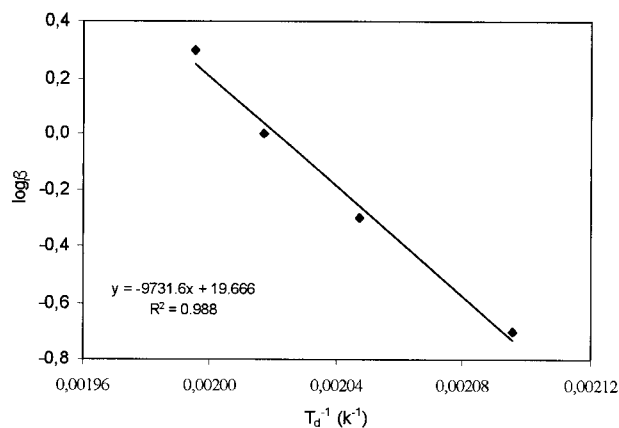

Figure 12 Arrhenius plot for the decomposition of GAP binder cured by using a constant NCO/OH ratio of 1.0 and a constant catalyst concentration of 43 ppm.

composition. The thermal conditioning studies show that GAP is thermally stable for 1 week at 100°C and the thermal history of the material does not change its properties. Thus, GAP has a thermal stability high enough to be used in propellant formulations.

The thermal analysis results showed that DOA is not a suitable plasticizer for GAP since no significant lowering of T_g is achieved. The T_g of GAP is decreased from −45 to −65°C with a 25/75 plasticizer/polymer weight ratio with BDNPA/F, which shows that BDNPA/F is a suitable plasticizer for GAP-based propellants.

Curing causes an increase in the T_g (−37°C) and a decrease in the T_d (228°C) due to the crosslinking of GAP with N-100. Using the curing catalyst causes a further increase in the T_g of GAP up to −34°C. However, the T_g of cured GAP can be decreased to −45°C by using BDNPA/F as a plasticizer. BDNPA/F is also found to be compatible with cured GAP from a safety point of view and a GAP binder having appropriate thermal properties can be prepared by using GAP as the polymer, Desmodur N-100 as the curing agent, DBTL as the curing catalyst, and BDNPA/F as the plasticizer, amounting up to a 1:2 weight ratio of BDNPA/F to GAP.

DSC thermograms taken at different heating rates can provide a convenient way to study the kinetics of the decomposition reaction of pure and cured GAP. The activation energy of cured GAP (178 kJ/mol) is slightly higher than is the activation energy of pure GAP (166 kJ/mol), which may be attributed to the restricted molecular motions of the chains because of crosslinking. Thus, the decomposition of GAP is slowed upon curing.

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