

Curing Characteristics of Glycidyl Azide Polymer-Based Binders

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ABSTRACT: The curing of a glycidyl azide polymer (GAP) with a triisocyanate, Desmodur N-100, was followed by measuring the hardness and viscosity. The thermal behavior of the cured samples were investigated by a differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA). Curing causes an increase in the glass transition temperature of GAP. The T_g of gumstocks also increases with an increasing NCO/OH ratio while the decomposition temperature remains practically unchanged. The ultimate hardness of the cured samples increases with an increasing NCO/OH ratio. The binder with a NCO/OH ratio of 0.8 was found to provide the most suitable thermal and physical characteristics for composite propellant applications. The increase in the glass transition temperature of gumstocks upon curing can be compensated by using a 1:1 mixture of bis-2,2-dinitropropyl acetal and formal as the plasticizer. The T_g value of gumstocks can be decreased to -46.7°C by adding 25% b.w. of a plasticizer which does not have any significant effect on the decomposition properties of the gumstocks. Furthermore, a remarkable decrease in the ultimate hardness of the gumstocks is achieved upon addition of a plasticizer, while the curing time remains almost unaffected. The addition of dibutyltin dilaurate as a catalyst reduces the curing time of the gumstocks from 3 weeks to 5–6 days at 60°C . Use of the curing catalyst also results in the hardening of the gumstocks. The decomposition properties of the gumstocks remain practically unchanged while a noticeable increase is observed in the glass transition temperature with an increasing concentration of the catalyst. This can also be compensated by a reverse effect of the plasticizer. The gel time, an important parameter which determines the pot life of a propellant material, can be measured by monitoring the viscosity of the mixture, which shows a sharp increase when gelation starts. The addition of a curing catalyst shortens the gel time remarkably. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 65–70, 2001

Key words: glycidyl azide polymer (GAP); curing; isocyanate; polyurethane; energetic binder; composite propellant; thermal characterization; plasticizer

INTRODUCTION

In the development of high-performance composite solid propellants having minimum smoke, re-

duced pollution, and low sensitivity, glycidyl azide polymers (GAP) can be used as energetic binders.^{1,2} In addition to numerous studies on GAP, including their synthesis,³ structure,⁴ thermal behavior,⁵ and physical, chemical, and explosive properties,⁶ there has been a tremendous continuing effort put forth on the curing of GAP.⁷ It has been shown that GAP can be transformed

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into long-chain polyurethane by using the traditional curing agents: polyisocyanates.⁸ A recent kinetic study on polyurethane formation between GAP and a triisocyanate showed that the reaction needs to be speeded up to a reasonable rate level by using a proper catalyst, for example, dibutyltin dilaurate (DBTDL).⁹ Furthermore, the compatibility of GAP with various energetic materials has also been studied using thermal characterization techniques.^{10–12} A recent article reported the results of a 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 a pure polymer with the main ingredients (plasticizer and curing agent), and the effect of some ingredients on the low-temperature characteristics of the polymeric binder.¹³ Here, we report the results of our continuing study on the curing of GAP, with a special emphasis on the curing characteristics depending on the NCO/OH ratio, and the effect of a catalyst and plasticizer on the thermal and physical properties of the cured GAP.

EXPERIMENTAL

The following materials were used as purchased: GAP (GAP DIOL L-996, 3M, St. Paul, MN; density: 1.3 g/mL; hydroxyl value: 0.83 meq/g; molecular weight (MW_w): 2900 g/mol; viscosity at 25°C: 5000 cps), bis-2,2-dinitropropyl acetal/formal (BDNPA/F, Group Aerojet, Sacramento, CA), biuret triisocyanate (Desmodur N-100, Bayer, Leverkusen, Germany), and dibutyltin dilaurate (DBTDL, Merck-Schuchardt, Hohenbrunn, Germany).

The gumstocks, an acronym used for small-scale samples in binder formulations,¹⁴ were prepared by mixing GAP and Desmodur N-100 at different NCO/OH ratios and curing at 60°C. GAP was first poured into a glass beaker in a given amount (8–12 g). After addition of Desmodur N-100 in an amount calculated to have the desired NCO/OH ratio, it was mixed for about 5 min in a vacuum for degassing. Mixtures were then cured at 60°C. For some samples, a plasticizer and/or catalyst were added to the mixture prior to curing.

The hardness of the gumstocks was measured by using Zwick Shore A tester with an accuracy greater than 95% calibrated according to the DIN 53 505 and ASTM D 2240.¹⁵ The needle of the tester was inserted into the specimen and hardness values were read after 15 s. The measure-

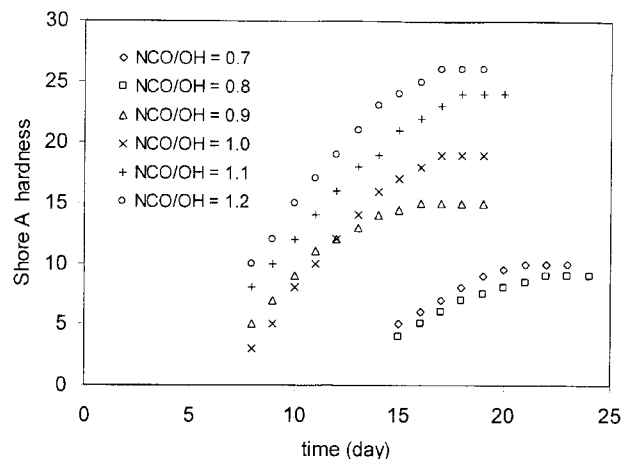


Figure 1 Shore A hardness of gumstocks during the curing reaction of GAP and Desmodur N-100 at 60°C depending on the NCO/OH ratio.

ment was repeated three times on different points of the sample and the average of them was recorded.

The viscosity of the uncured mixtures was measured on a rotational-type digital Brookfield viscometer, Model DV-II, using an SPD-21 spindle at a rotational speed of 10 rpm at 60°C. The viscosity of the samples increased first slightly as the curing reaction proceeded and then showed an abrupt increase at the gel point.

The thermal analyses were carried out by using a Rheometric Scientific TGA 1000 M and DSC Gold Plus. The differential scanning calorimeter (DSC) was calibrated using sapphire, indium, and tin, where the former was used for baseline calibration and the other two were used for temperature calibration. For accurate measurement of the glassy transition temperature, T_g , the DSC was also calibrated at subambient temperatures down to -150°C using sapphire and mercury. About 2–4-mg samples were used for each experiment, since the greater amount of a sample leads to explosion during the decomposition experiment. Nitrogen gas was purged at a flow rate of 20 mL/min. DSC experiments of the gumstocks were carried out at a heating rate of 10°C/min. TGA experiments were carried out in the same manner and were also calibrated on weight bases.

RESULTS AND DISCUSSION

The curing of gumstocks was followed by measuring the Shore A hardness. Figure 1 shows the

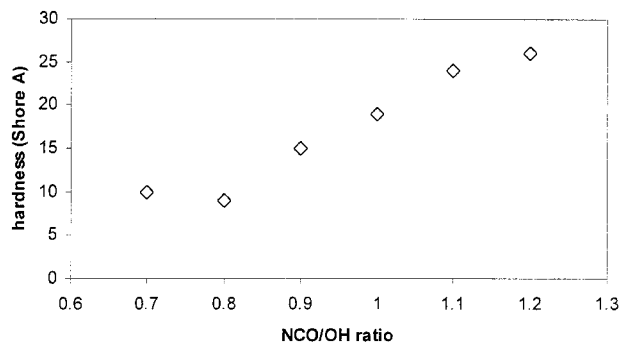


Figure 2 Ultimate Shore A hardness of the gumstocks at the end of the curing reaction of GAP and Desmodur N-100 at 60°C depending on the NCO/OH ratio.

variations in the Shore A hardness during the curing reaction between GAP and Desmodur N-100 depending on the NCO/OH ratio. For all the sample mixtures, the hardness reaches a measurable value after a certain period of time depending on the NCO/OH ratio. The hardness increases as the curing reaction proceeds and reaches a plateau of a constant value, indicating that the curing of GAP is completed. Thus, the curing time of the sample mixture can be determined from the hardness measurement. The curing of GAP is found to be slow. The mixtures having a NCO/OH ratio of 0.7 or 0.8 require a longer time (about 3 weeks) for a complete curing than do the other samples (about 2 weeks). This may be attributed to a significant lack of an isocyanate compound to completely react with GAP molecules, leaving an important amount of GAP unreacted, which had a similar effect as did a plasticizer on the hardness (Fig. 5, *vide infra*). The final hardness value of the cured gumstocks, in general, shows an increase with an increasing NCO/OH ratio as illustrated in Figure 2. However, the sample cured with NCO/OH = 0.7 has a slightly higher hardness compared with that of 0.8, which may be considered as a consequence of the overall uncertainty of the measurement procedure, including the probable effect of a heterogeneous system. It is known that the propellants become harder upon solid loading.¹⁶ Therefore, the gumstock with the NCO/OH ratio that showed the minimum ultimate hardness was selected for the further investigation and propellant development.

DSC runs of the cured gumstocks were carried out at subambient temperature with a ramp rate of 10°C/min to determine the glass transition

temperature, T_g , which determines the lower limit of the operational temperature range in the propellant applications. The T_g of pure GAP was found to be $-44.7 \pm 0.7^\circ\text{C}$, which is in agreement with the literature value of 45°C .¹³ The glass transition temperatures of the cured gumstocks are given in Figure 3. It is interesting to note a linear relationship between the T_g value of the gumstocks and the NCO/OH ratio within the range studied. Curing increases the T_g value of GAP by 6–9°C depending on the NCO/OH ratio. This increase in the T_g value of GAP on curing can readily be attributed to the crosslinking which restricts the molecular motions and makes the polymeric material more rigid.

The decomposition properties of the gumstocks were determined from the TGA and DSC thermograms taken at higher temperatures with a ramp rate of 10°C/min. The decomposition temperature of gumstocks were found to be slightly lower than that of pure GAP ($T_d = 242^\circ\text{C}$)¹³ and shows only small variations with the NCO/OH ratio between 240.5 and 237.2°C. While the decomposition characteristics of GAP remain practically unchanged upon curing, the glass transition temperature increases on curing and with the increasing NCO/OH ratio. Since GAP is in rubbery state at temperatures above the T_g , which is lower than the lowest operational temperature 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 the reverse effect of curing and solid loading on the T_g .

A previous article reported that the glass transition temperature of GAP can be decreased by

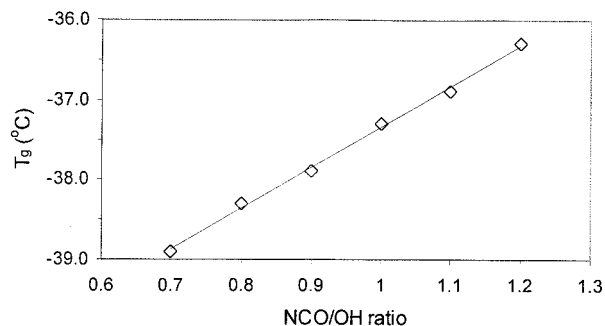


Figure 3 Glass transition temperature of the cured gumstocks as a function of the NCO/OH ratio in the mixture of GAP and Desmodur N-100.

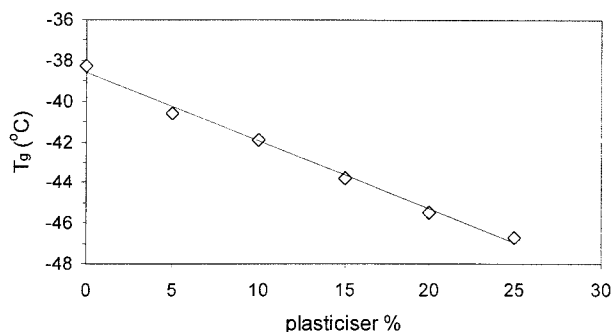


Figure 4 T_g value of the gumstocks having NCO/OH ratio of 0.8 as a function of the plasticizer percentage.

using a 1:1 mixture of bis-2,2-dinitropropyl acetal and bis-2,2-dinitropropyl formal (BDNPA/F) as a plasticizer.¹³ BDNPA/F was also used as a plasticizer in the gumstocks having a NCO/OH ratio of 0.8 and its effect on the T_g of the gumstocks was studied by DSC. Figure 4 shows that the T_g value of the gumstocks also decreases with an increasing percentage of the plasticizer. By addition of the plasticizer to the gumstocks, the T_g value of the cured samples can be decreased to -46.7°C , which is low enough to produce a rubbery propellant at operating conditions.

In a previous article, we showed that a plasticizer does not affect the decomposition characteristics of GAP.¹³ DSC and TGA studies on plasticized gumstocks having a NCO/OH ratio of 0.8 showed that the addition of a plasticizer does not affect the decomposition properties of cured GAP significantly. Only the decomposition temperature of the gumstocks increases slightly with an increasing amount of a plasticizer to 25% (less than 5°C).

The addition of a plasticizer affects the mechanical properties of the gumstocks significantly. Figure 5 shows the variations in the Shore A hardness of the gumstocks having a NCO/OH ratio of 0.8 with the plasticizer concentration during the cure reaction between GAP diol and Desmodur N-100 at 60°C . Especially at a high percentage of a plasticizer, the hardness is quite low. However, the curing time of the gumstocks is not much affected by the addition of BDNA/F. The ultimate hardness observed may correspond to an apparent curing completion of the samples, but not a true chemical completion of the curing, since there might be large numbers of GAP molecules that remained unreacted due to both the lack of an isocyanate compound and the diffusional control effect.

Since the polyurethane formation between GAP and Desmodur N-100 is slow, the curing of GAP needs to be speeded up by using a catalyst. DBTDL has been shown to be an effective catalyst for the curing of GAP.⁹ Therefore, the effect of a catalyst on the mechanical and thermal properties of the gumstocks was investigated for the samples prepared by adding DBTDL into the mixtures of GAP and Desmodur N-100 having NCO/OH ratio of 0.8 and containing 25% b.w. of the plasticizer and curing at 60°C . The gumstocks prepared in this way were studied by measuring the hardness and by DSC and TGA. By using a catalyst, the curing time is remarkably reduced, from 3 weeks to 2–5 days depending on the catalyst concentration. Furthermore, an ultimate Shore A hardness of 13 was achieved at the end of the curing period of the gumstocks containing 25% of the plasticizer, which normally makes the mixture soft. Please recall that the uncatalyzed gumstock with 25% of the plasticizer has an ultimate hardness of 3. The decomposition properties remain practically unchanged, while the T_g value of the gumstocks increases slightly with the increasing concentration of the catalyst as illustrated in Figure 6. The uncatalyzed gumstock having a NCO/OH ratio of 0.8 and 25% of the plasticizer has a T_g value of -46.7°C . The same gumstock but cured by using 75 ppm of DBTDL as a catalyst has a T_g value of -43.5°C . This is still low enough to be used in the development of an energetic binder. The low value of the ultimate hardness and the lower T_g observed for the uncatalyzed sample compared to that of the catalyzed one can be explained by considering that monitoring the hardness gives an apparent curing completion of the samples but not a true

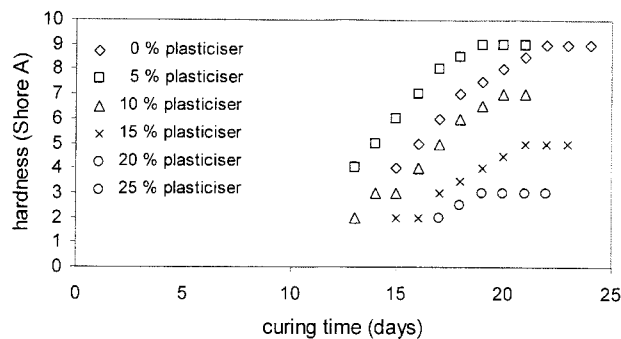


Figure 5 Shore A hardness of gumstocks having NCO/OH ratio of 0.8 and various amounts of BDNPA/F as a plasticizer during the curing reaction of GAP and Desmodur N-100 at 60°C .

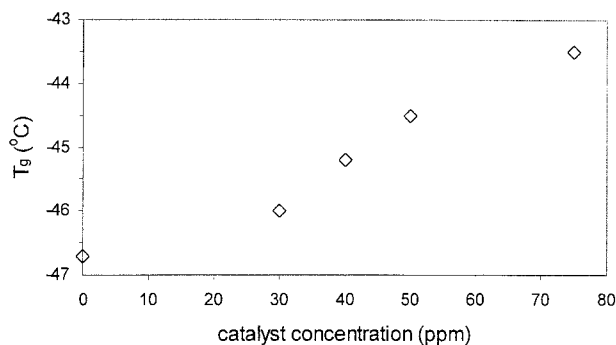


Figure 6 T_g value of the cured gumstocks having NCO/OH ratio of 0.8 and 24% of the plasticizer as a function of the catalyst concentration.

chemical completion of the curing since there might be large numbers of GAP molecules that remained unreacted due to the diffusional control effect, especially if the curing reaction is initially fast when catalyzed.

Another characteristic of gumstocks is the gel time, which is related to the formation of crosslinking and therefore affects the processing of an uncured propellant. During casting of a composite propellant, the slurry must have rheological properties that permit the uncured mixture to flow into all parts of the motor case. An adequate flow of the slurry during casting can create voids or other defects, causing an increase in burning surface area, which results in increased pressure and malfunctions of the motor. Therefore, the propellant slurry should have a reasonably low viscosity and long enough pot life to make it castable. Pot life is strongly dependent on the rate of the curing reaction, which should be controlled for the mixture to remain fluid for a sufficient time. Gel time of the uncured gumstocks can be determined by a viscosity measurement. Such measurements were performed only for the slurries having 25% BDNPA/F as a plasticizer and DBTDL as a catalyst in various concentrations because of the reduced curing time. The gel time could be determined for these gumstocks. The time at which there is a sharp increase in the viscosity is considered as the gel time of a gumstock, beyond which a gumstock does not flow.

The viscosity values were monitored as a function of time after the curing reaction was started for three various gumstocks having a NCO/OH ratio of 0.8, 25% BDNPA/F as a plasticizer and DBTDL as a catalyst in three different concentrations of 30, 50, and 75 ppm. As can be seen from

Figure 7, the viscosity increases slightly during the curing reaction up to the gel time. At the gel time, one observes a sudden sharp increase in the viscosity. The gel time of the gumstocks was determined to be 903, 224, and 103 min for the gumstocks having a catalyst concentration of 30, 50, and 75 ppm, respectively. As expected, the gel time is strongly dependent on the amount of the curing catalyst. The higher the catalyst concentration, the shorter the gel time.

CONCLUSIONS

Curing of GAP could be achieved using a triisocyanate, Desmodur N-100, at 60°C. The hardness of the GAP/Desmodur N-100 mixtures increases during the curing process, reaching the highest value at the end of curing. The ultimate hardness value of gumstocks increases with an increasing NCO/OH ratio. The gumstock having a NCO/OH ratio of 0.8 exhibits the lowest ultimate hardness value and, therefore, is selected for the further studies and development of the energetic binder. Curing causes an increase in the glass transition temperature of GAP. The T_g of gumstocks also increases with an increasing NCO/OH ratio, while the decomposition temperature remains practically unchanged.

The increase in the glass transition temperature of gumstocks upon curing can be compensated by using BDNPA/F as a plasticizer. The T_g value of gumstocks can be decreased to -46.7°C by adding 25% b.w. of the plasticizer, which does not have any significant effect on the decomposition properties of the gumstocks. Furthermore, a remarkable decrease in the ultimate hardness of

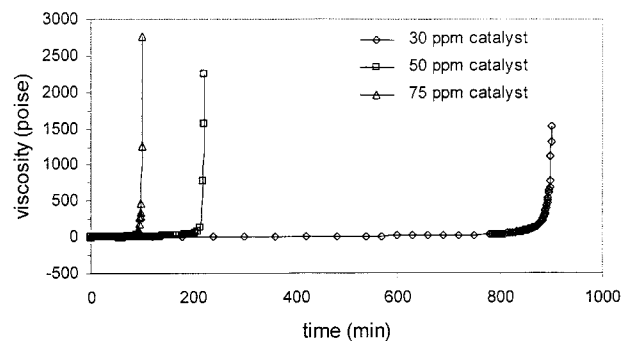


Figure 7 Viscosity of the gumstocks having NCO/OH ratio of 0.8, 25% of the plasticizer, and DBTDL as catalyst in various concentrations as a function of time during the curing process.

the gumstocks is achieved upon addition of a plasticizer, while the curing time remains almost unaffected.

Since the curing of GAP is too slow for being used as energetic binder in the composite propellants, the reaction needs to be speeded up by using a catalyst. The addition of DBTDL reduces the curing time of the gumstocks from 3 weeks to 5–6 days. Use of DBTDL as a curing catalyst results in the hardening of gumstocks since the catalyst does not only affect the rate of the polyurethane formation between GAP and Desmodur N-100, but also exerts considerable influence on their mechanical properties. The decomposition properties of the gumstocks remain practically unchanged while a noticeable increase is observed in the glass transition temperature with an increasing concentration of the catalyst. This can also be compensated by a reverse effect of the plasticizer. Thus, the gumstocks having a NCO/OH ratio of 0.8, 25% b.w. of the plasticizer, and DBTDL as a curing catalyst in concentrations up to 75 ppm will have T_g values lower than the operation limit.

Use of both the catalyst and the plasticizer affect the curing characteristics of GAP-based binders including the processibility of the material during the curing period. The gel time, an important parameter which determines the pot life of a propellant material, can be measured by monitoring the viscosity of the mixture which shows a sharp increase when gelation starts. The addition of a curing catalyst shortens the gel time remarkably. This point must also be taken into account in developing an energetic binder for the composite propellants.

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