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Technical Notes

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Compatibility of Glycidyl Azide Polymer with Hydroxyl Terminated Polybutadiene and Plasticizers

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I. Introduction

GLYCIDYL azide polymer (GAP) finds application in a number of energetic material formulations due to many positive attributes. GAP is also one of the most thoroughly studied energetic polymers for application as a solid propellant binder [1–3]. A large volume of literature is available on the synthesis of GAP and its different derivatives [4–8]. Detailed studies on the thermal, mechanical, and combustion characteristics of GAP and GAP based formulations are reported in the literature [9–13]. The use of GAP in composite propellant formulations could considerably improve the processability and performance parameters. However, due to the presence of polar azido groups in the polymer backbone, GAP could have compatibility problems with other ingredients such as hydroxyl terminated polybutadiene (HTPB) and plasticizers used in composite solid propellants. GAP and HTPB are not miscible and phase separation occurs when a mix of pure GAP and HTPB is kept undisturbed for a while after dispersion. The authors had shown that the blends of the two polymers with specific concentration levels could be prepared without phase separation [12]. Also in a previous work, the authors had presented the results of thermomechanical and morphological investigation of the blends [14].

In this study, results observed in differential scanning calorimetric (DSC) evaluation of glass transition temperature (Tg) of GAP-HTPB blends are presented. Tg is an important parameter for the solid propellant binder as it strongly influences the transient load bearing capability of the propellant. The compatibility of GAP with nonpolar plasticizers usually used in composite solid propellants is also investigated in terms of gumstock, rheological, and glass transition properties and compared with polar azido plasticizers. The study results could help to realize high strength composite propellants with improved processability and performance.

II. Experimental

A. Materials and Sample Preparation

GAP diol with molecular weight in the range of 1900–2000 [by vapor pressure osmometry (VPO)], hydroxyl value 45–50 mg KOH/g, and viscosity in the range of 2000–2300 cps was prepared by a cationic ring opening polymerization of epichlorohydrin, followed by a reaction with sodium azide under specific conditions and used for the experiments. HTPB with molecular weight ~2500 (by VPO) and hydroxyl value 40–43 mg KOH/g was used. Toluene diisocyanate (a mixture of 2, 4, and 2, 6 isomers 80:20) was used as the curing agent. Dibutyl tin dilaurate in a toluene solution was used as the cure catalyst. The cross-linking agent used was 1, 1, 1-trimethylolpropane and 1, 4-butane diol was used as the chain extender. Dioctyl adipate (DOA), dioctyl phthalate (DOP), isodecyl pelargonate (IDP) and paraffin oil, obtained from commercial sources were used as such. The azido plasticizers used were namely, 1, 6-hexane diol bis (azidoacetate) (HDBAA), 2-ethyl-1, 3-hexanediol bis (azidoacetate) (EHDBAA), and diethylene glycol bis (azidoacetate) (DEGBAA).

A detailed procedure for the preparation of cross-linked GAP and GAP-HTPB specimens is reported elsewhere [12]. A 5% cross-linker content and NCO/OH ratio of unity was used for all the samples. For a preparation of GAP-HTPB specimens without phase separation, a higher reaction rate was employed by an adjustment of catalyst content [12,14]. Cured samples of GAP-HTPB blends were prepared with GAP contents of 10, 30, 50, 70, and 90% for the study.

B. Testing

Tg determination was done using a thermal analysis instrument model DSC 2920 modulated, differential scanning calorimeter. The runs were done at a heating rate of 2°C/min. The miscibility of the different plasticizer systems with GAP was evaluated by vigorous mixing of measured quantities of the materials and visual observation. The mechanical properties were evaluated using a universal testing machine (Instron) as described in ASTM-D 412. Viscosity measurements of the resin-plasticizer mixes were done with a RVDV II$^+$ model Brookfield viscometer.

C. Results and Discussion

1. Glass Transition Characteristics from DSC Data

Figure 1 shows the DSC trace of cross-linked GAP and HTPB. Figures 2 and 3 show the DSC trace of the blends.

For cross-linked GAP, DSC data show a transition region in the range from −46.5 to −40.3°C with Tg taken as the middle point at −43.2°C. In the case of cross-linked HTPB, the Tg was noted at −72.5°C. For the GAP-HTPB blends prepared with different compositions, DSC traces show a clear pattern in the transition. The Tg of the blend is found to shift toward higher values with an increase in the GAP content beyond 30%. Table 1 shows the Tg of the GAP-HTPB blends obtained from the DSC study.

The dominant single glass transition observed in the DSC trace for the blends prepared with different compositions confirms the microheterogeneous morphology of the interpenetrating network

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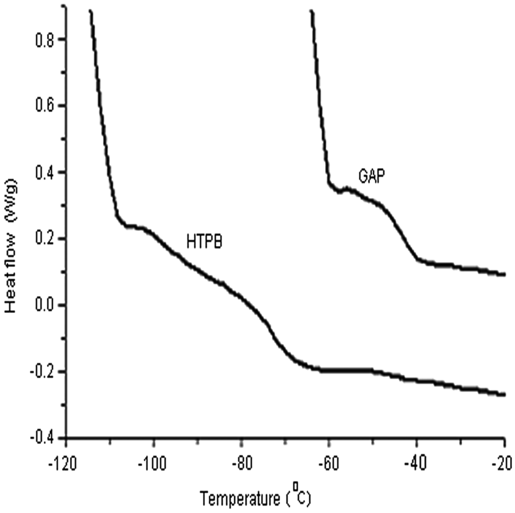

Fig. 1 DSC traces of cross-linked GAP and HTPB.

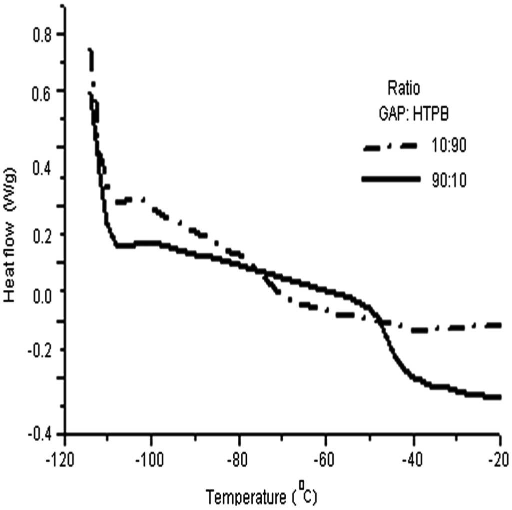

Fig. 2 DSC traces of GAP-HTPB blends.

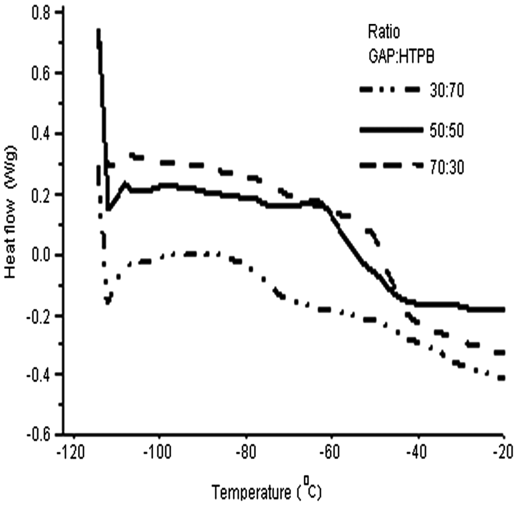

Fig. 3 DSC traces of GAP-HTPB blends.

Table 1 Glass transition temperature of GAP-HTPB blends prepared with different compositions

Composition of the blend GAP, %	HTPB, %	Tg, °C
100	0	−43.2
90	10	−45.5
70	30	−47.0
50	50	−57.0
30	70	−74.0
10	10	−74.2
0	100	−72.5

structure formed by the polymer networks as reported earlier [12]. At 10 and 30% GAP content, the Tg of the blend was found to be lower than that of pure cured HTPB, indicating good compatibility of the polymer networks at specific concentration levels. This observation is in agreement with the dynamic mechanical analysis results reported earlier [14].

2. *Compatibility Evaluation by Miscibility*

Miscibilities of different plasticizer systems were evaluated by preparing blends of GAP with varying concentration of plasticizers. The concentrations of the plasticizers were varied in the range of 0 to 50% by weight in the mix. DOA, DOP, IDP, and paraffin oil were evaluated for the study. Three azido compounds, namely, HDBAA, EHDBAA, and DEGBAA, were used for comparison. After vigorous mixing of measured quantities of the components, the mixes were visually inspected for phase separation for extended periods. When IDP and paraffin oil were used poor miscibility and phase separation were observed. DOA and DOP were found to be miscible with GAP and no phase separation was observed. The three azido plasticizers were also found to be miscible with GAP at all proportions.

The complete lack of miscibility of paraffin oil with GAP could be assigned to the nonpolar long chain hydrocarbon nature of paraffin oil and resulting incompatibility with the polar polyether backbone of GAP. The phase separation seen with the GAP-IDP system is also a result of a nonpolar long hydrocarbon configuration of IDP compared to DOA or DOP. In the case of DOA and DOP the miscibility observed is the result of the compatibility of polar ester linkage with GAP. The good compatibility shown by azido plasticizers with GAP could be assigned to the presence of ester groups and also azido groups similar to GAP.

3. *Gumstock Property Evaluation of Plasticised GAP*

Gumstock properties of a cross-linked GAP network plasticized with DOA and DOP were evaluated. The plasticizer content was varied from 0 to 20%. It was observed that DOA and DOP strongly influence the mechanical properties. Increasing the plasticizer content from 0 to 20% reduced the tensile strength from 0.75 to 0.4 MPa and increased the elongation from 235 to 300%. Hardness shore A was found to decrease with increasing plasticizer content. The data show that DOA and DOP are compatible with GAP at these concentration levels. Figures 4–6 show graphical representations of the data.

4. *Effect of Plasticizer on the Viscosity of GAP*

The variation in viscosity of GAP evaluated with different plasticizers clearly indicates the advantage of azido plasticizers. Figures 7 and 8 show a comparison of the effect of concentration of ester and azido plasticizers on the viscosity of GAP resin. The study showed that the azido plasticizers are more effective in reducing the viscosity of GAP. The observation of better compatibility of azido plasticizers could be explained from the fact that the presence of polar azido groups in both the systems leads to better chemical and thermodynamic feasibility of mixing. It was noted that for a 50% concentration of azido plasticizer, the viscosity of GAP was reduced to nearly 6.3% of the initial value.

5. *Effect of Plasticizer on the Glass Transition Characteristics of GAP*

The use of DOA and bis-2, 2-dinitropropyl acetal/formal as a plasticizer with GAP formulation has been reported [11]. Different

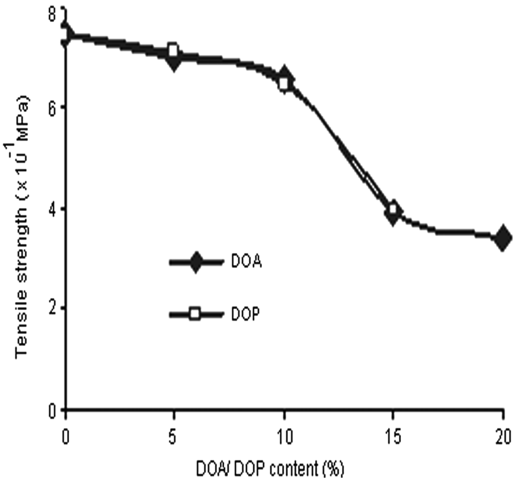

Fig. 4 Effect of plasticizer content on the tensile strength of cross-linked GAP networks.

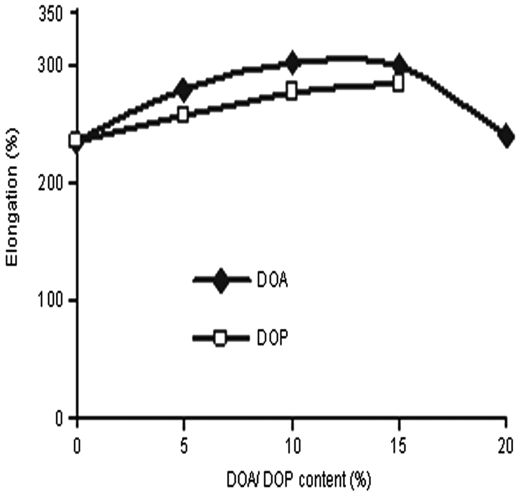

Fig. 5 Effect of plasticizer content on the elongation of GAP cross-linked networks.

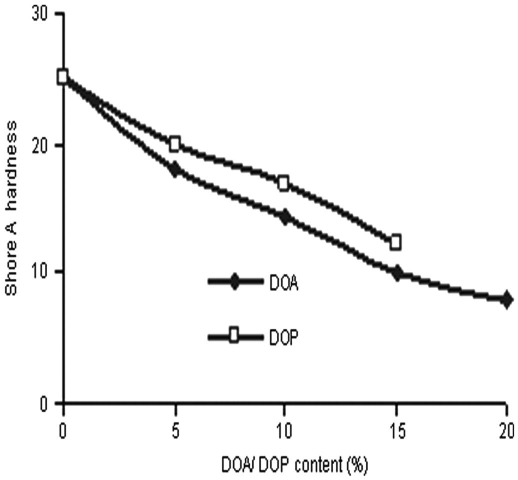

Fig. 6 Effect of plasticizer content on the shore A hardness of cross-linked GAP networks.

types of plasticizers were found to differ considerably with respect to the effect on the Tg of cross-linked GAP. Table 2 shows the effect of DOA content on the Tg of the cross-linked GAP samples and Table 3 shows the Tg values of cured GAP with azido plasticizers.

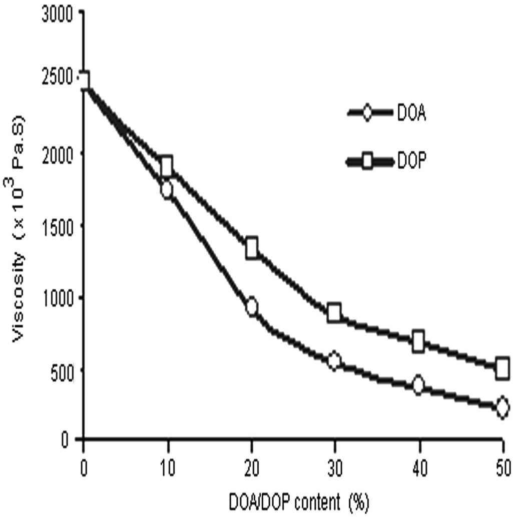

Fig. 7 Effect of DOA and DOP content on the viscosity of GAP resin.

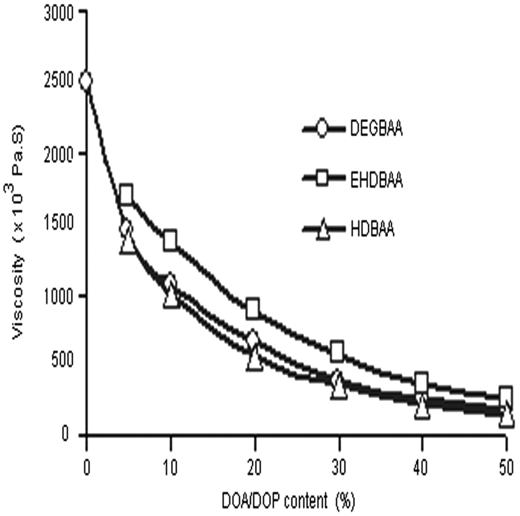

Fig. 8 Effect of azido plasticizers on the viscosity of GAP resin.

The Tg values of cross-linked GAP were found to be significantly affected by the presence of DOA as a plasticizer. The Tg values were found to decrease from −45.5 to −48.2°C, for 10% DOA content, beyond which no impact was seen. Among the three azido plasticizers used, HDBAA was found to be most effective, as the Tg

Table 2 Effect of DOA content on Tg of cross-linked GAP

DOA content, %	Tg, °C
0	−43.2
5	−47.5
10	−48.2
20	−48.2

Table 3 Effect of azido plasticizers on the Tg of cross-linked GAP

Plasticizer	Tg, °C
HDBAA	−52.3
DEGBAA	−46.8
EHDBAA	−44.5

was reduced to −52.3°C with the incorporation of 20% HDBAA in the formulation.

III. Conclusions

The DSC studies carried out for the cross-linked blends prepared with different concentrations of GAP and HTPB indicated a predominantly single glass transition region indicating the absence of total phase separation. The microheterogeneous morphology resulting from the interpenetration of the networks could be the reason for this phenomena. The marginal decrease in Tg of the blends at low concentration of GAP (10 and 30%) indicates good compatibility of the polymer networks at specific concentration levels. The results indicate that GAP can be effectively used as an additive in HTPB formulations.

A compatibility study shows that the polar and chemical nature of GAP and a plasticizer influence the solubility. Comparison of the results of evaluation of miscibility, gumstock properties, viscosity, and Tg of a plasticized GAP network shows good compatibility between GAP and ester-type plasticizer systems such as DOA and DOP, and azido plasticizers.

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