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Composite solid rocket propellant based on GAP polyurethane matrix with different plasticizers

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Abstract: Glycidyl azide polymer (GAP) has been prepared and studied for its application as polymeric matrix for composite solid rocket propellants (CSRP). Different CSRP based on GAP polymeric matrix with different plasticizers were prepared. A cross-linker based on trimethylol propane (TMP) and dibutyltin dilaurate (DBTDL) was added to the GAP matrix to ensure curing completion of the prepared CSRP. The viscosity and shore A of all the prepared CSRPs during the curing process were measured continuously. The mechanical properties of the cured CSRP were determined. The ballistic performance, burning rate at operating pressure and specific impulse were determined using standard a modified six inch rocket motor with 16.25 mm nozzle. By comparing the results, it was concluded that the plasticizer; dioctyl azelate and dibutyl phthalate are not compatible with GAP matrix. In addition, CSRP based on GAP has specific impulse and burning rate slightly higher than the traditional HTPB based CSRP.

Keywords: Glycidyl Azide Polymer (GAP), hydroxyl terminated polybutadiene (HTPB), solid propellants, ballistic performance.

1. Introduction

Glycidyl azide polymer (GAP) is an interesting energetic propellant binders better in performance than hydroxyl terminated polybutadiene (HTPB) which is the currently used propellant binder worldwide [1, 2]. The HTPB propellants have thermal and ballistic performance suitable for its application in rockets [3-7]. GAP polymer has azide group (C-N3 group) along the chain of the polymer. The mixing of GAP with energetic oxidizer like ammonium dinitramide (ADN) can cause improvement of the specific impulse and also chlorine-free exhaust [8-10]. GAP has high heat of formation of +117.2 kJ/mole and the scission of C-N3 group is highly exothermic and could produce high energy of 685 kJ/mol [11-13]. The terminal hydroxyl group in GAP can be reacted with diisocyanate to produce a three dimensional network structure as in the case of HTPB propellant [14]. The binder should have suitable mechanical and physical properties for the application in the field of propellants. HTPB binder has excellent elongation ability at variable range of temperatures and it has high shelf life [15]. As a result, HTPB has several applications in the field of energetic materials as solid propellant and polymer bonded explosives [16-18]. On the other side, GAP has poor mechanical properties and usually cross linkers are added to enhance the mechanical properties [19]. Replacement of HTPB by the energetic GAP is interesting topic for the researchers to obtain high specific impulse and burning rate [20]. In this paper, several plasticizers were used to prepare GAP propellants. The viscosity build-up and shore A of all the prepared samples in addition to traditional HTPB propellant were determined. The mechanical properties and the ballistic characteristics (using 6 inch motor) of the optimum GAP formulation in addition to HTPB propellant were measured.

2. Experimental

2.1. Materials

Hydroxyl-terminated polybutadiene (HTPB R-45M of ARCO Co.; density: 0.9 g/mL; hydroxyl value: 0.84 meq/g; molecular weight (M_n): 2800 g/mol; viscosity at 25°C: 5800 cps), 1,1,1-trimethylol propane (TMP) 97% supplied by SIGMA-ALDRICH (23235-61-2) Germany, 1,4-butane diol 99%, SIGMA-ALDRICH (110-63-4) Germany, dibutyl tin dilaurate (DBTDL) 95%, SIGMA-ALDRICH (77-58-7) Germany, Hexa Metylene Di Isocynate (HMDI), DOA, DOZ and DBP supplied by SIGMA-ALDRICH GERMANY. Aluminum and Ammonium perchlorate (AP) obtained from commercial source were used. Glycidyl azide polymer (GAP) has been prepared according to ref. [11].

2.2. Preparation of composite solid rocket propellant by casting technique

CSRP samples based on HTPB and based on GAP as prepolymers were prepared. From ref. [19], it was concluded that the values of curing ratio (NCO/OH =1.0 - 1.2) with crosslinker ratio of 5% for GAP based PU compositions give optimum mechanical behavior compared with HTPB based PU compositions with curing ratio (NCO/OH =0.8-0.9) which used for large scale CSRP formulations.

One formulation was traditional named F1 and was based on HTPB binder 14% as a conventional prepolymer while the other formulations were based on GAP as an energetic prepolymer. Formulations F2, F3 and F4 are the same in compositions but include different plasticizers to select the best one which can be compatible with GAP Compositions of the prepared formulations are presented in Table (3).

Table (1) The Compositions of the Prepared CSRP Formulations

Formulation Ingredients (wt %)		F1	F2	F3	F4
Binder	HTPB	10.45	--	--	--
	GAP	--	17	17	17
	Crosslinker mixture	--	0.85	0.85	0.85
	HMDI	0.62	2.59	2.59	2.59
	MAPO	0.3	0.3	0.3	0.3
Plasticizer	DOZ	--	4.25	--	--
	DBP	--	--	4.25	--
	DOA	2.62	--	--	4.25
Oxidizers	AP (400 µ)	38	31	31	31
	AP (200 µ)	16	14	14	14
	AP (7-11 µ)	15	13	13	13
Metal fuel	Al (40 µ)	11	11	11	11
	Al (8-22 µ)	6	6	6	6
Total binder %		14	25	25	25
NCO/OH		0.85	1.1	1.1	1.1

Propellant formulations were prepared by employing casting technique, which begins by mixing of the different ingredients using a stainless-steel mixer of 8 kg capacity and casting under vacuum into the previously prepared 6 inch motors and the JANAF (dumbbell-shaped) samples mold.

2.3. Mechanical Testing

The tensile strength and strain elongation of the optimum samples were measured using LLOYD testing machine measured strength-strain relation for the prepared samples. This test was measured in triple for each sample. The mean value was reported. The test was carried out at normal temperature. The cross head speed was 50 mm/min with cross head speed accuracy of 0.5.

2.4. Characterization of CSRP

Rotational-type digital Anton paar viscometer, Model physica MCR 101 was used to measure the viscosity during the cure reaction (Viscosity build up) at 55°c. Shore A was tested every day for every sample. Samples were taken out from the curing oven for 5 minutes, and then shore A was measured for all samples by using the hardness tester ZWICK (model 3102) by immersing the apparatus needle slowly in the sample and reading the numerical indication shown on the apparatus screen. All the ballistic properties of prepared propellant formulations as burning rate, operating pressure and specific impulse were measured by using 6 inch motor as shown in fig. 1. Large scale motor like 6 inch motor enable us to get more accurate thrust and specific impulse results with less errors. The measurements take place using 16.25 mm 6 inch motor nozzle which secures certain operating pressures and burning rates for each examined formulation to obtain the differences between each formulations at the same nozzle throat. The samples casted in steel cylinders then loaded in the testing motor.

Figure 1 Photo of the 6 inch motor on the test stand.

3. Results and Discussion

3.1. Viscosity build up

The viscosity build-up of the studied sample is presented in Fig. 2. Both DOZ and DBP are incompatible plasticizer with GAP when used in rocket propellant formulations and this affects viscosity build up and curing reaction and as a result the mechanical properties. There was a separation between the solid fillers and binder system noticed after the test. This phenomenon indicates that DOZ is incompatible plasticizer with GAP. The same behavior occurred in formulation F3 when DBP was used as plasticizer but with higher values than F1 and the separation occurred too as what happened in F2 after the test), But DOA is compatible plasticizer with GAP when used in rocket propellant formulations. For 25% binder content propellant have low viscosity and easier processing and casting compared with HTPB based propellant.

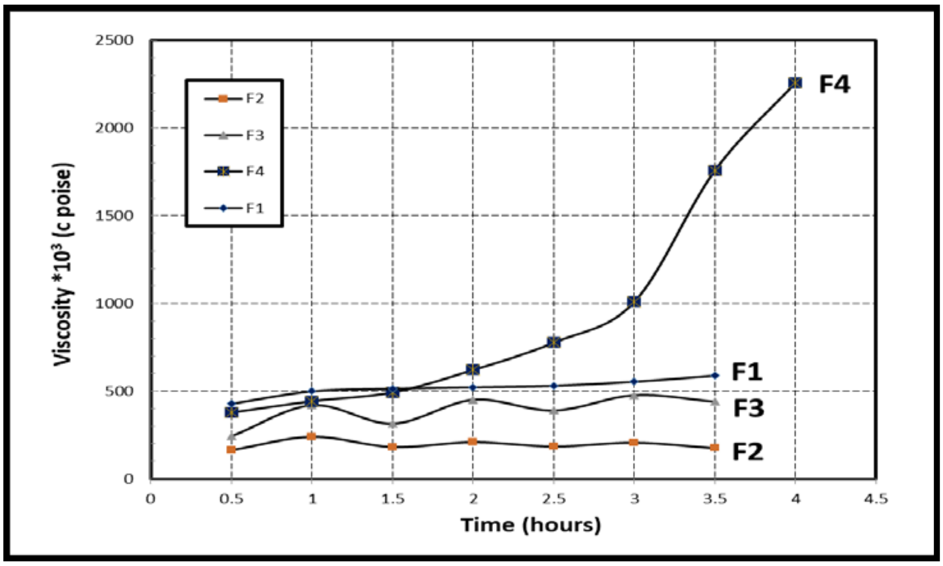

Figure 2 Variation of propellant formulations viscosity build up with time

3.2. *Hardening measurements*

The addition of DBTL as a catalyst reduces the curing time of the propellant formulations based on GAP compared with HTPB formulation from 13 days to 6-7 days at 55°C as shown in Fig. 2. while F2, F3 (GAP based formulations) which containing DOZ and DBP as plasticizer were cured in 14 and 13 days respectively because of incompatibility of both plasticizers with GAP(plasticizer migration on the surface of the propellant).

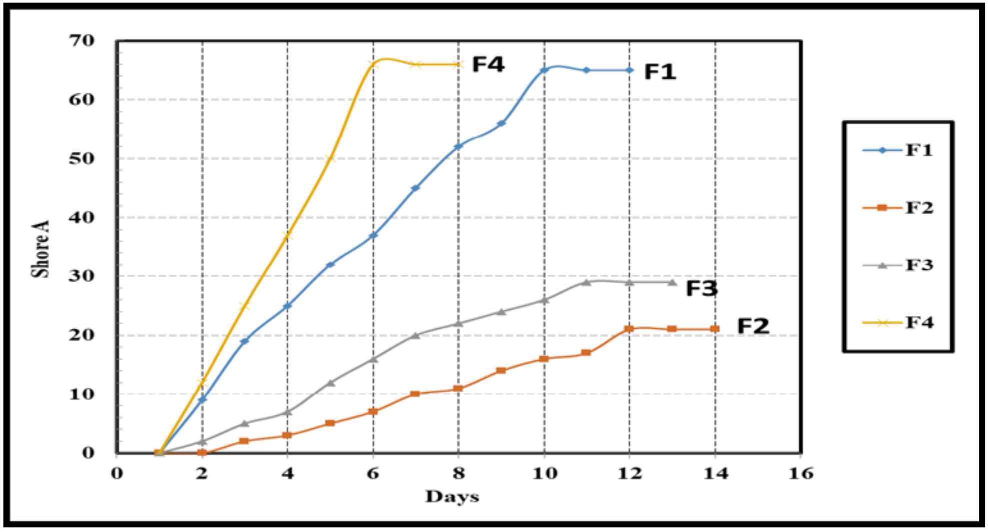

Figure 3 Variation of Hardening measurements (Shore A) with days

3.3. Mechanical properties of propellant samples

By comparing the results of HTPB based propellant F1 (conventional propellant) with the prepared sample F4, it was observed that F4 has higher tensile strength than F1. But in case of the strain measurements, HTPB based formulation F1 has higher strain than GAP based propellant F4 (25%binder). F4 (25%binder) was easily casted and simple in processing. F4 gave good mechanical properties compared with HTPB based propellant F1, as shown in table (2).

Table (2) Results of mechanical properties at 25°C

Formulation	Tensile strength σ (kg_f/cm^2)	Strain Є (%)	Young's modulus E_0 (kg_f/cm^2)
F1 (HTPB)	8.42	47.1	30.3
F4 (25 % GAP binder)	9.29	40.8	33.41

3.4. Ballistic performance of prepared CSRP

As shown in Fig. 1, the 6 inch motor was used to measure the specific impulse and to determine the burning rate. 6 kg of propellant sample was used to obtain thrust and specific impulse with low deviations and accurate measurements. The results are presented in table 3. It is clear that Formulation F4 has burning rate higher than the traditional F1. In addition, the specific impulse of the new propellant F4 is higher than F1. The pressure-time curve of the studied samples is plotted in Fig. 4. It is obvious from this figure that both F1 and F4 have stable burning. Besides, the ingredients of the new propellant based on gap binder are compatible and suitable for its application.

Table (3) Ballistic performance results of propellant formulations

Formulations	Pressure (bar)	Burning rate (mm/sec)	Specific impulse Isp (sec)
F1 (HTPB)	107.83	9.45	244.7
F4 (25 % GAP)	112.1	9.72	245.8

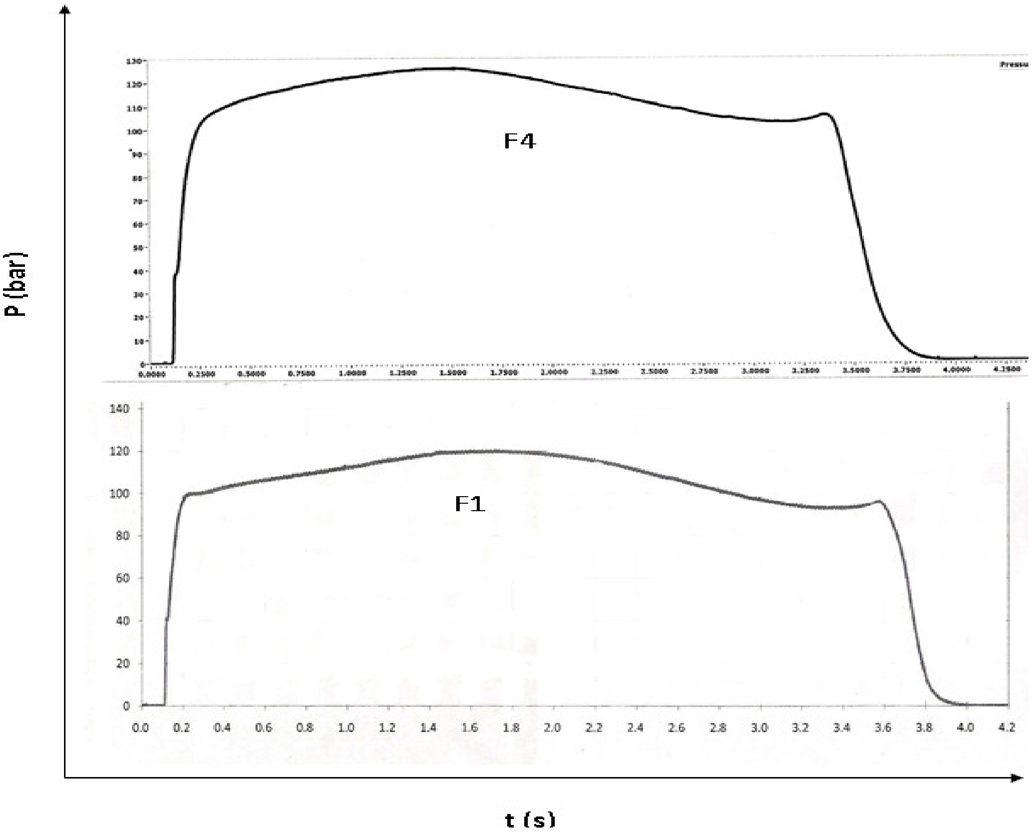

Figure 4 P-t curves obtained by 6 inch motor for the studied samples

4. Conclusion

The results of the viscosity build-up proved that DOZ and DBP are not compatible with GAP binder while GAP sample containing DOA (F4) has viscosity in the range of the traditional HTPB-CSRP until 2 hours. In addition, the GAP propellant containing DOA has shore A in the same range of the traditional HTPB propellant. Also it was concluded that GAP propellant (F4) has slightly higher tensile strength and lower strain compared with HTPB propellant. The 6 inch rocket motor successfully used to determine the ballistic properties of the studied propellants. GAP propellant (F4) has higher burning rate and specific impulse than the traditional HTPB propellant (F1). GAP propellant of 25 wt % polymeric matrix and DOA used as plasticizer is interesting and required more study for its application in the field of Composite propellants.

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