Thermochimica Acta, 180 (1991) 251–268
Elsevier Science Publishers B.V., Amsterdam

THERMAL CHARACTERISTICS OF GAP, GAP/BDNPA/BDNPF AND PEG/BDNPA/BDNPF AND THE ENERGETIC COMPOSITES THEREOF

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(Received 21 August 1990)

ABSTRACT

The thermal behaviour of the energetic binder systems GAP, GAP/BDNPA/BDNPF and PEG/BDNPA/BDNPF were investigated by thermogravimetry, derivative thermogravimetry, differential scanning calorimetry and Parr bomb calorimetry. The energetic composites of the above-mentioned binder systems with HMX in various particle sizes have been studied and compared with HTPB composites. It was found that the binder systems all have different thermal decomposition properties and that BDNPA/F is more compatible with GAP polymer than with PEG. The thermal decomposition of the GAP binder system was unchanged when BDNPA/BDNPF was used. However, in the PEG binder system, the decomposition temperature and heat of decomposition increased as the ratio of PEG/(BDNPA/BDNPF) decreased. In addition, the decomposition temperatures of the energetic composites of this study are lower than that of pure HMX, and the heats of explosion of these energetic composites are proportional to the size of the HMX particles. The glass transition temperatures of the energetic polymer systems in this investigation were not affected by the addition of the nitroplasticiser BDNPA/BDNPF.

INTRODUCTION

In order to increase the energy content and safety of composite propellants or plastic bonded explosives, more knowledge is needed concerning the thermal behaviour of the energetic ingredients, such as the binder, oxidiser, plasticiser and the composite composed of these [1–6]. The application of thermoanalytical techniques such as differential thermal analysis (DTA),

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thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) to explosives and propellant ingredients is well established. Each individual technique has inherent value, but a combination of two or more has proved to be invaluable for the study of explosives, propellants and other composite systems [7–13].

The object of this study is to investigate the thermal behaviour of the energetic binder systems of glycidyl azide polymer (GAP), GAP/BDNPA/F and PEG/BDNPA/F (BDNPA, bis-2,2-dinitropropyl acetal; BDNPF bis-2,2-dinitropropyl formal) and the energetic composites thereof. All the systems were examined by TG–DTG and DSC. The results from each energetic composite were compared with the results from the HTPB system to demonstrate the energy promotion and thermal compatability of the test's energetic composite systems. In addition, a Parr bomb calorimeter was used to investigate a high-mass sample and to provide a comparison with the DSC results.

EXPERIMENTAL

Materials

The GAP pre-polymer, the nitroplasticiser BDNPA/F and the HMX examined in this study were laboratory synthesised. All PEG pre-polymers were obtained from Wako, Japan.

TABLE 1

Maximum reaction temperature (T_m), onset temperature (T_o) and enthalpy change (ΔH) for DSC measurements

Formulation	Binder (wt.%)			DSC (heating rate 10 °C min^{-1})		
	GAP	PEG	BDNPA/F [c]	T_o (°C)	T_m (°C)	$-\Delta H$ (cal g^{-1})
GAP [a]	100	–	–	233	251	550
GAP [b]	100	–	–	233	240	474
GAP-1	75	–	25	232	239	443
GAP-2	70	–	30	233	239	454
GAP-3	50	–	50	231	237	483
A-1	–	80	20	208	222	99
A-2	–	60	40	209	226	210
A-3	–	40	60	205	233	301
A-4	–	20	80	209	243	369

[a] GAP prepolymer (uncured).

[b] GAP binder (cured).

[c] BDNPA/F: $T_o = 220\,°C$; $T_m = 255\,°C$; $\Delta H = -500$ cal g^{-1}.

TABLE 2

Formulation and thermal measurement results of each system

Formulation	Binder (wt.%) [a]				HMX (wt.%) [b]			T_o	T_m	T_o	T_m	Heat of combustion [c] $-\Delta H$ (cal g^{-1})	Heat of explosion [c] $-\Delta H$ (cal g^{-1})
	I	II	III	IV	A	B	C	30 °C	min^{-1}	10 °C	min^{-1}		
A-1	20	–	–	–	–	–	80	268	283	279	283	2611	1113
A-2	20	–	–	–	–	80	–	250	272	241	252	2620	1096
A-3	20	–	–	–	80	–	–	250	270	245	248	2618	1110
B-1	10	10	–	–	–	–	80	276	285	246	282	2926	1001
B-2	10	10	–	–	–	80	–	244	248	236	239	2813	994
B-3	10	10	–	–	80	–	–	249	254	233	235	2824	975
C-1	–	–	20	–	–	–	80	277	284	280	284	3968	809
C-2	–	–	20	–	–	80	–	273	277	273	274	3898	779
C-3	–	–	20	–	80	–	–	245	250	234	246	3487	807
D-1	–	10	–	10	–	–	80	270	282	243	270	2791	1225
D-2	–	10	–	10	–	80	–	267	279	245	265	2771	1219
D-3	–	10	–	10	80	–	–	265	274	239	259	2758	1181

[a] I, GAP binder, II, BDNPA/F; III, HTPB binder; IV, PEG binder.

[b] A, 5–20 μ; B, 150–300μ; C, 590–840μ.

[c] Measurement with Parr bomb calorimeter.

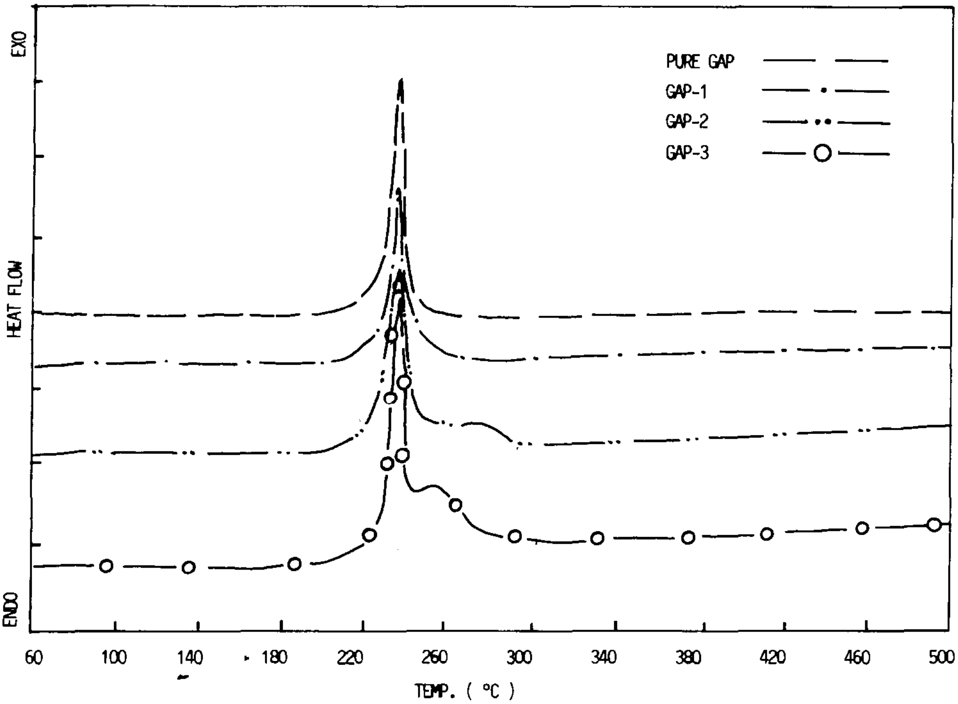

Fig. 1. DSC pattern of GAP polymer binder with and without BDNPA/F.

Sample preparation

The binders were generally formulated to an NCO : OH ratio of 1 : 1. All the binders were prepared by a one-step method. The ingredients were first

TABLE 3

Glass transition temperature of GAP and PEG binder with and without BDNPA/F

Binder (wt.%)			Glass transition temperature [a] (K)
GAP	PEG	BDNPA/F	
0	100	0	225
0	80	20	225
0	60	40	224
0	40	60	223
0	30	70	223
100	0	0	228
50	0	50	224
30	0	70	226
25	0	75	228

[a] DSC measurement results.

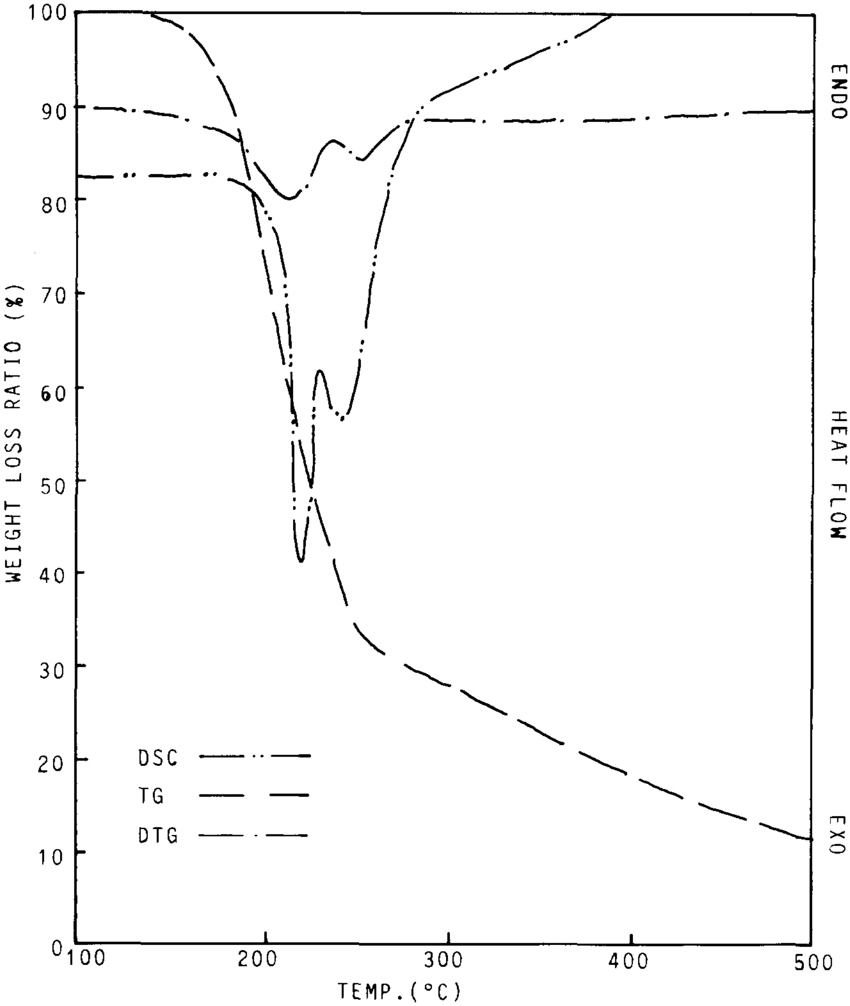

Fig. 2. TG–DTG and DSC results for GAP-3 binder.

dried to a moisture content of less than 0.02% and the test samples of binder and energetic composites were cured in an oven at 60 °C for 7 days.

DSC measurements

DSC measurements were determined using a Dupont 1090 thermal analyser. Samples weighing around 2 mg were heated in an aluminium crucible under a static atmosphere of nitrogen from 225 to 550 °C at a heating rate of 10 or 30 °C min^{-1}. The results are shown on Figs. 1–7 and 14 are listed in Tables 1 and 2. The glass transition temperature (T_g) of GAP

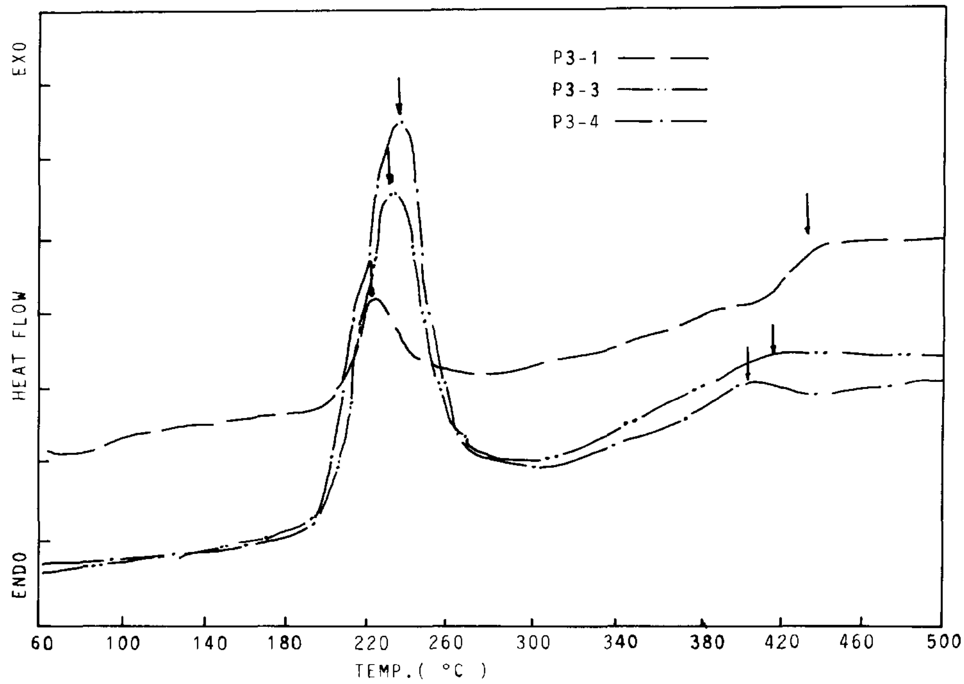

Fig. 3. Comparison of DSC pattern of PEG binder with various ratios of BDNPA/F.

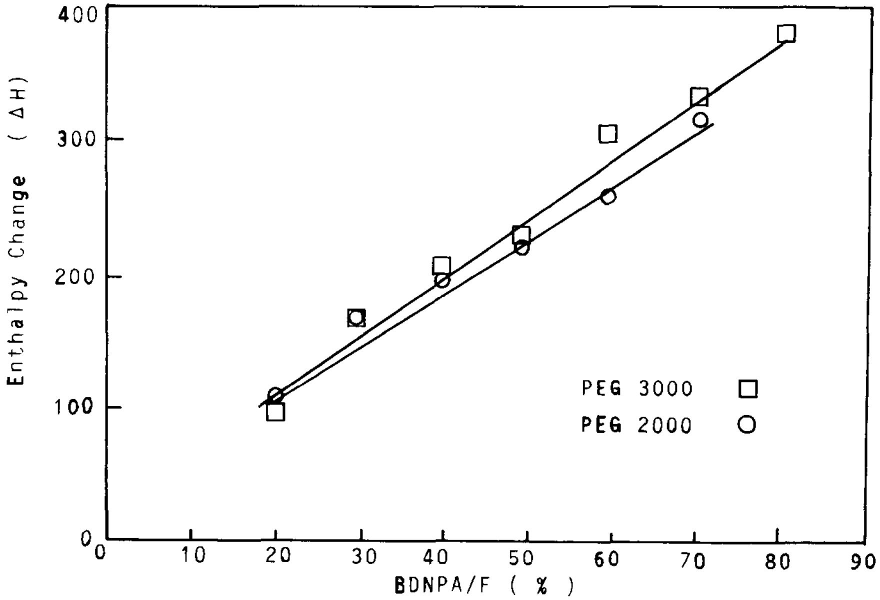

Fig. 4. Enthalpy values of PEG binder with various ratios of BDNPA/F.

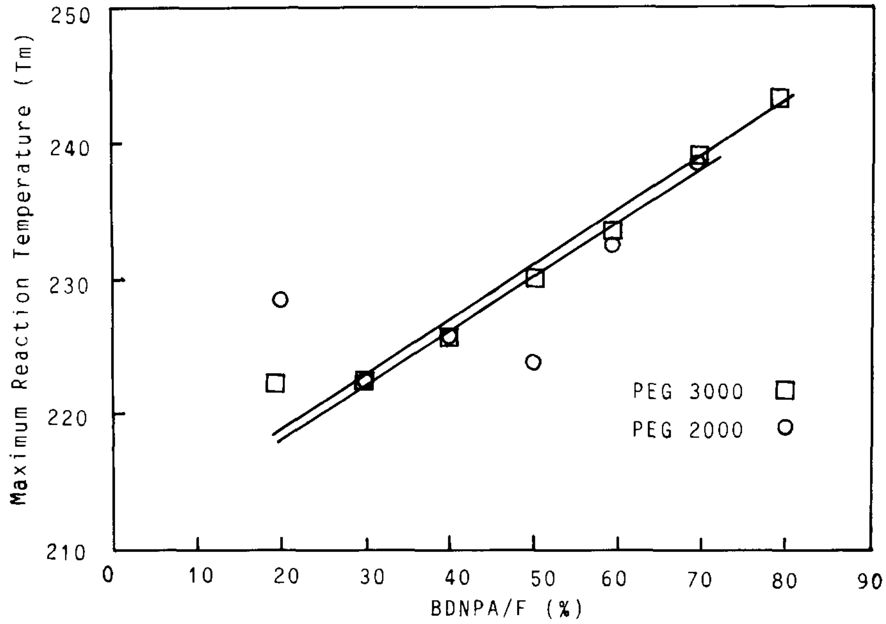

Fig. 5. T_m values of PEG binder with various ratios of BDNPA/F.

and PEG binders, with and without BDNPA/F, were obtained by DSC measurement from 150 to 290 K at the rate of 20 °C min^{-1}. The T_g results are listed in Table 3.

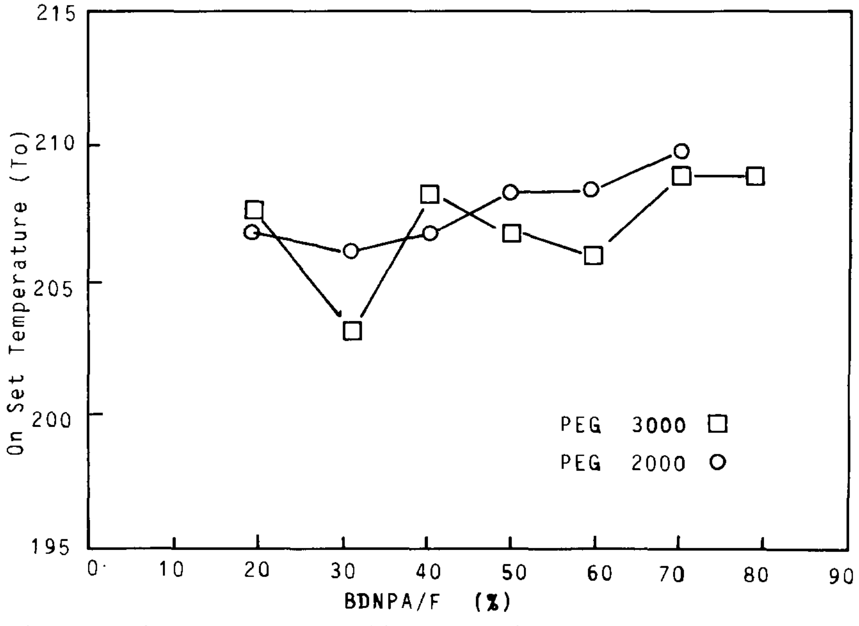

Fig. 6. T_o values of PEG binder with various ratios of BDNPA/F.

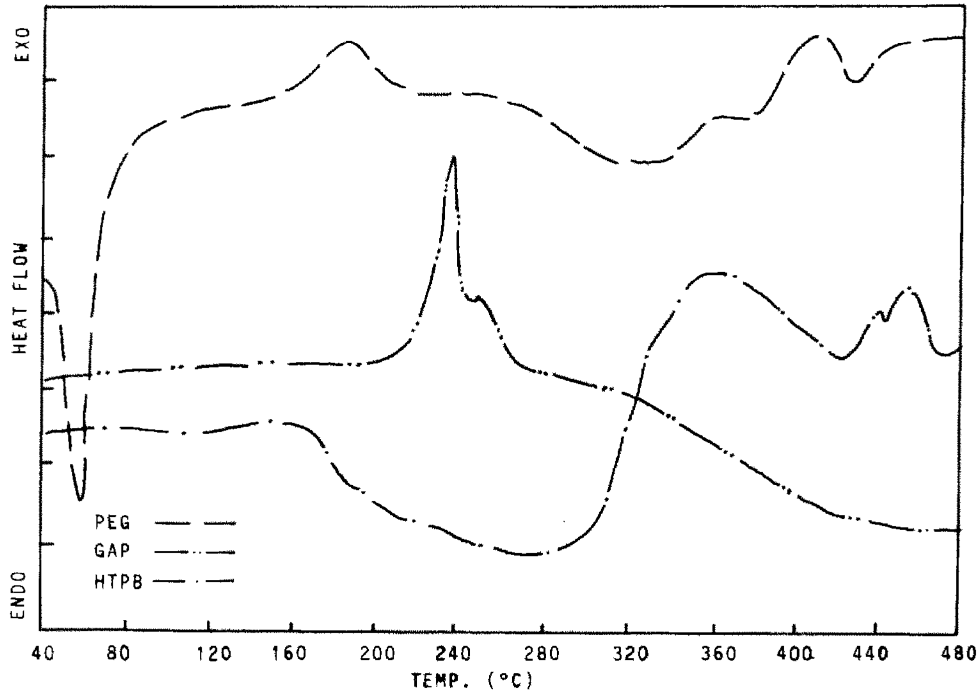

Fig. 7. DSC pattern of GAP, PEG and HTPB.

TG–DTG measurements

TG–DTG measurements were carried out on a Perkin–Elmer thermal analyser. Samples weighing around 5–7 mg were heated under a static atmosphere of nitrogen at 20 °C min^{-1} from 25 to 700 °C. The results are shown in Figs. 8–13 and are listed in Table 4.

Parr bomb calorimetry

A sample of around 1 g was used in this measurement. In order to confirm the interrelation trend observed in the DSC measurements, a comparison of the ΔH values obtained by Parr bomb calorimetry and by DSC measurements was made.

RESULTS AND DISCUSSION

It is recognised that the results obtained for the measurement of the thermal sensitivity of energetic material are affected by the testing conditions such as heating rate, testing pressure, container-seal condition, mass of testing material, etc., but that the sample shape and particle size affect the

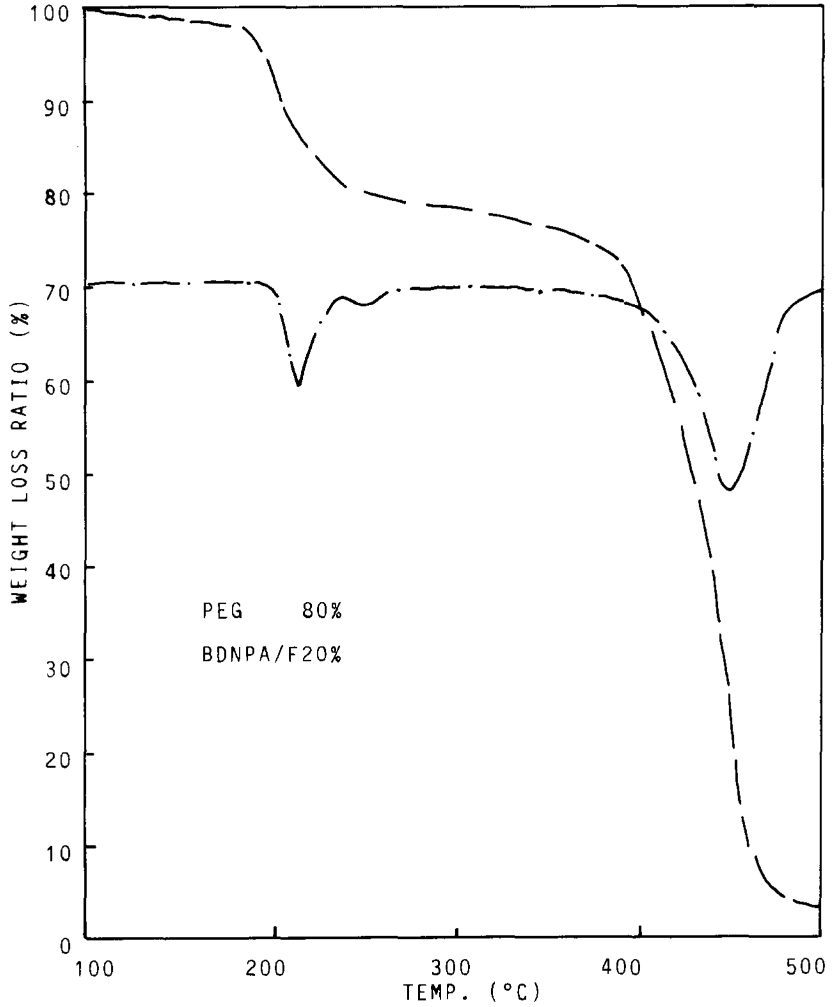

Fig. 8. TG–DTG results of PEG + BDNPA/F.

test results only slightly [14]. For example, it has been found that the reaction of the energetic composite changes from decomposition to violent detonation when the test condition is changed.

The purpose of this study is to understand the thermal decomposition behaviour and sensitivity of the energetic binder materials and energetic composites thereof. For example, in Table 1, the maximum reaction temperature (T_m) and onset reaction temperature (T_o) increased as the heating rate changed from 10 to 30 °C min^{-1}. It was also found that for every formulation, the relative changes were constant even with higher heating rate. Therefore, the discussion below is based on the test results obtained with a heating rate of 10 °C min^{-1}.

Table 1 indicates that the onset temperature, T_o, was unchanged whether

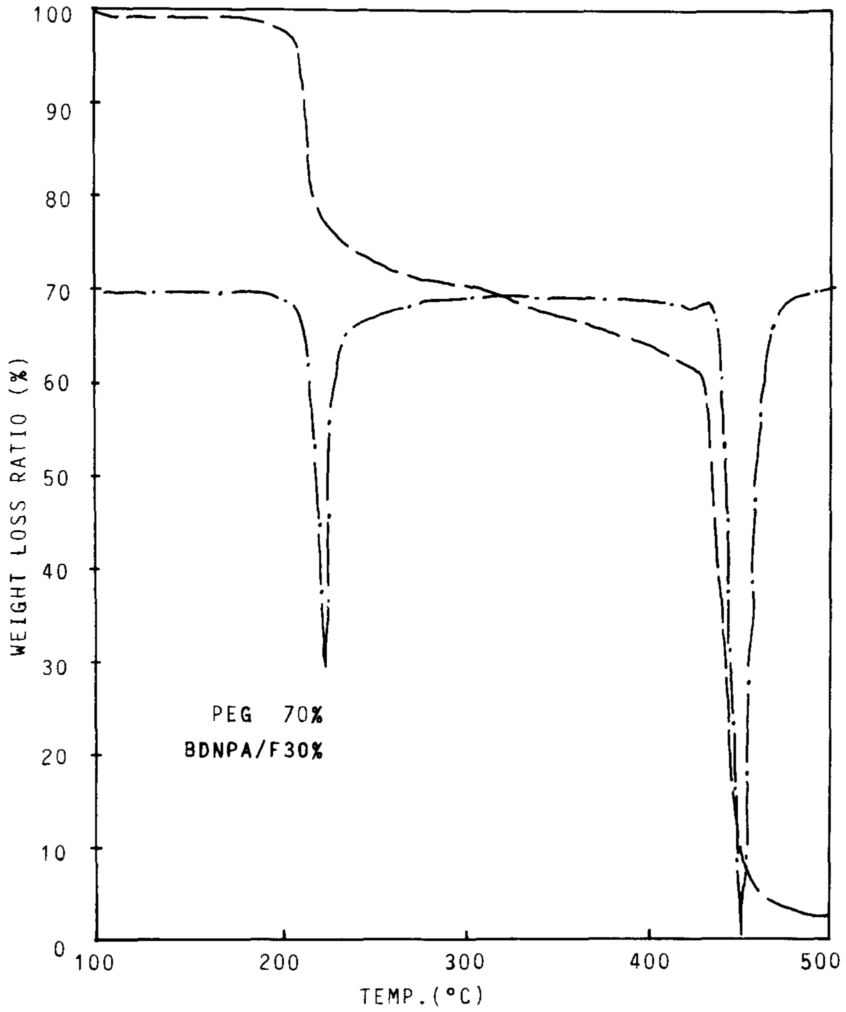

Fig. 9. TG–DTG results of PEG+BDNPA/F.

the GAP polymer was cured or uncured, but that the maximum reaction temperature, T_m, is 240 °C for cured GAP and 251° C for uncured GAP. For the formulations GAP-1 (25% BDNPA/F), GAP-2 (30% BDNPA/F), and GAP-3 (50% BDNPA/F), T_o was 232, 233 and 231° C, and T_m was 239, 239 and 237 °C, respectively. For the cured system, it can be seen that the reaction temperature is not affected by the addition of BDNPA/F plasticiser.

Thermal analysis techniques have been widely used by many investigators in the evaluation of the compatibility of explosive ingredients [7–13]. Beach and Canfield [8] have suggested that a system be regarded as compatible if the change of peak maximum temperature, T_m, is less than 2 °C. Therefore

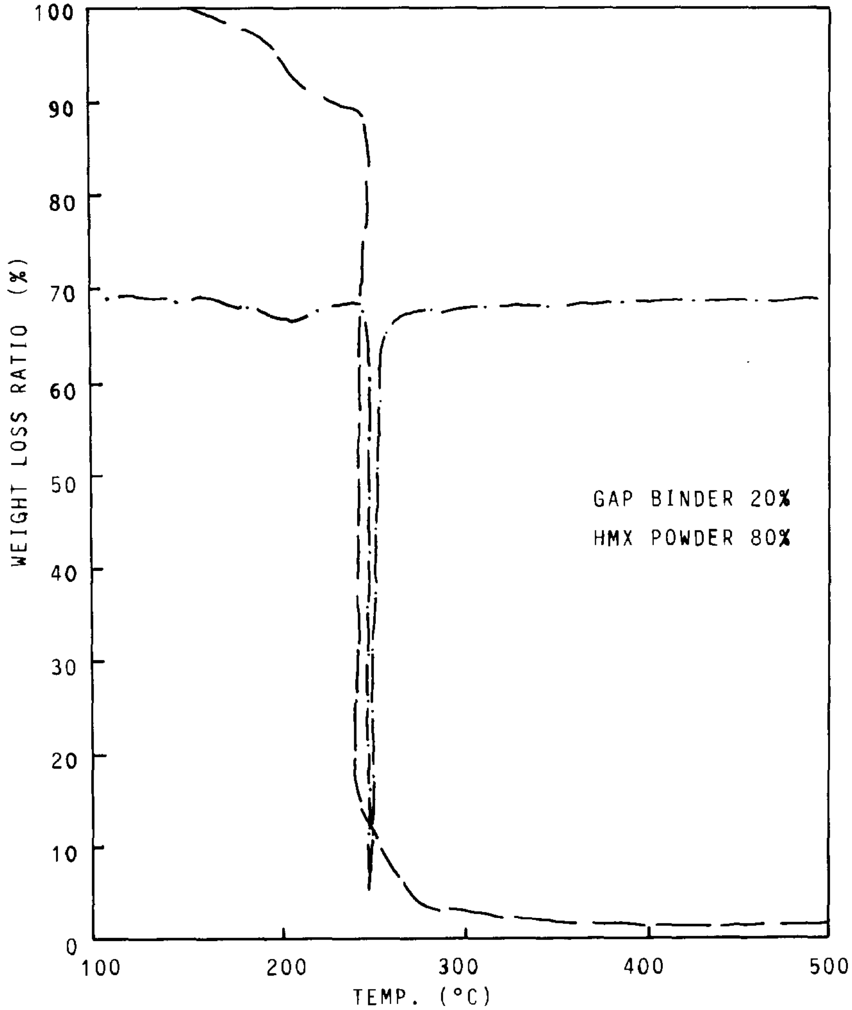

Fig. 10. TG–DTG results of GAP+HMX composite.

in this study, GAP and BDNPA/F can be considered compatible according to this criterion.

Table 3 shows that the glass transition temperature (T_g) of the energetic binder was not affected by the addition of BDNPA/F nitroplasticiser.

Figure 1 shows the DSC pattern of GAP binders with and without BDNPA/F. There is one exothermic reaction peak for pure GAP binder. But for GAP binder systems containing BDNPA/F, there are one or two overlapping exothermic reaction peaks. In the TG–DTG measurement, it was found that two weight-loss reactions take place at 240 and 260–500 °C for pure GAP system, with weight-loss ratios of 42 and 33%, respectively. For formulation GAP-1 (25% BDNPA/F), there were three weight-loss reactions, with weight-loss ratios 30, 22 and 33% at 225, 240 and 270–500 °C,

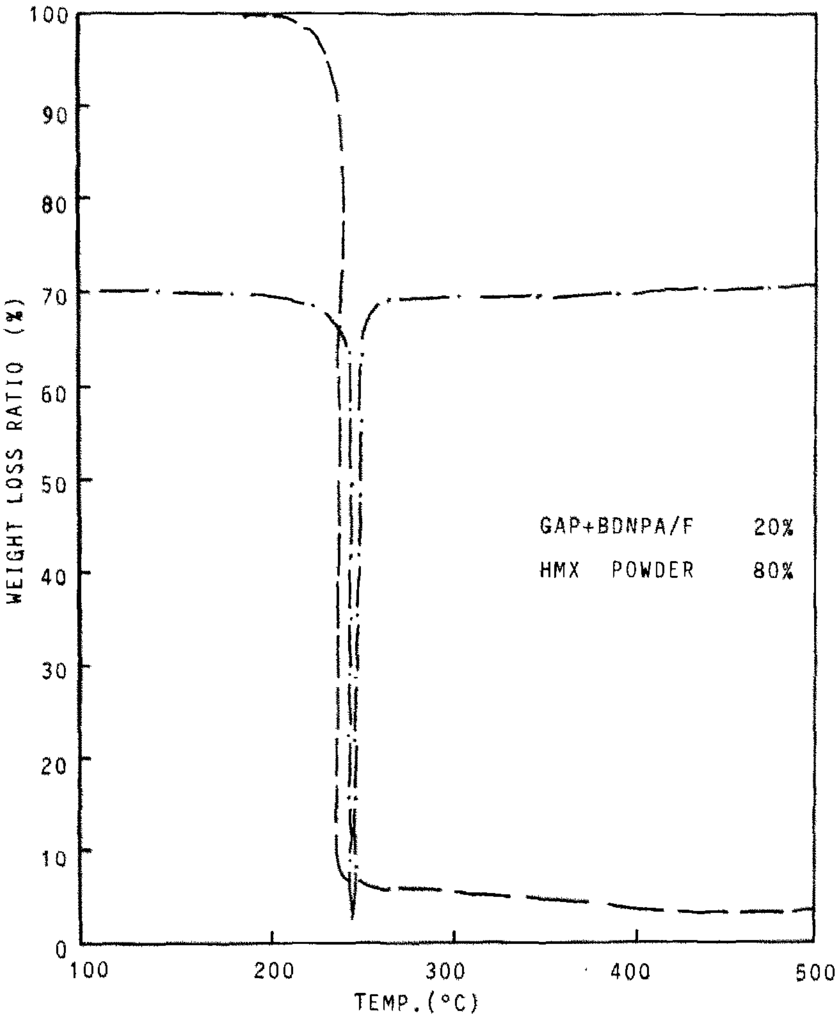

Fig. 11. TG–DTG results of GAP+BDNPA/F composite.

respectively. For formulation GAP-2 (30% BDNPA/F), three weight-loss reactions with weight-loss ratios of 35, 20 and 30% occurred at 210, 245 and 260–500 °C, respectively. For the GAP-3 system, the weight-loss ratios were 55, 15 and 20% at 220, 245 and 270–500 °C, respectively.

DSC and TG measurement results showed that there are two weight-loss stages for pure GAP binder. The first stage corresponds to an exothermic reaction. At the second stage, a slow weight-loss reaction occurred without heat production. These results agree with those reported earlier [6].

For GAP + BDNPA/F systems, a three-stage weight-loss process was found. Comparing the weight-loss ratio with the percentage of ingredients for each formulation and the combined DSC and TG–DTG pattern in Fig. 2, it can be seen that BDNPA/F decomposes before GAP. There are two

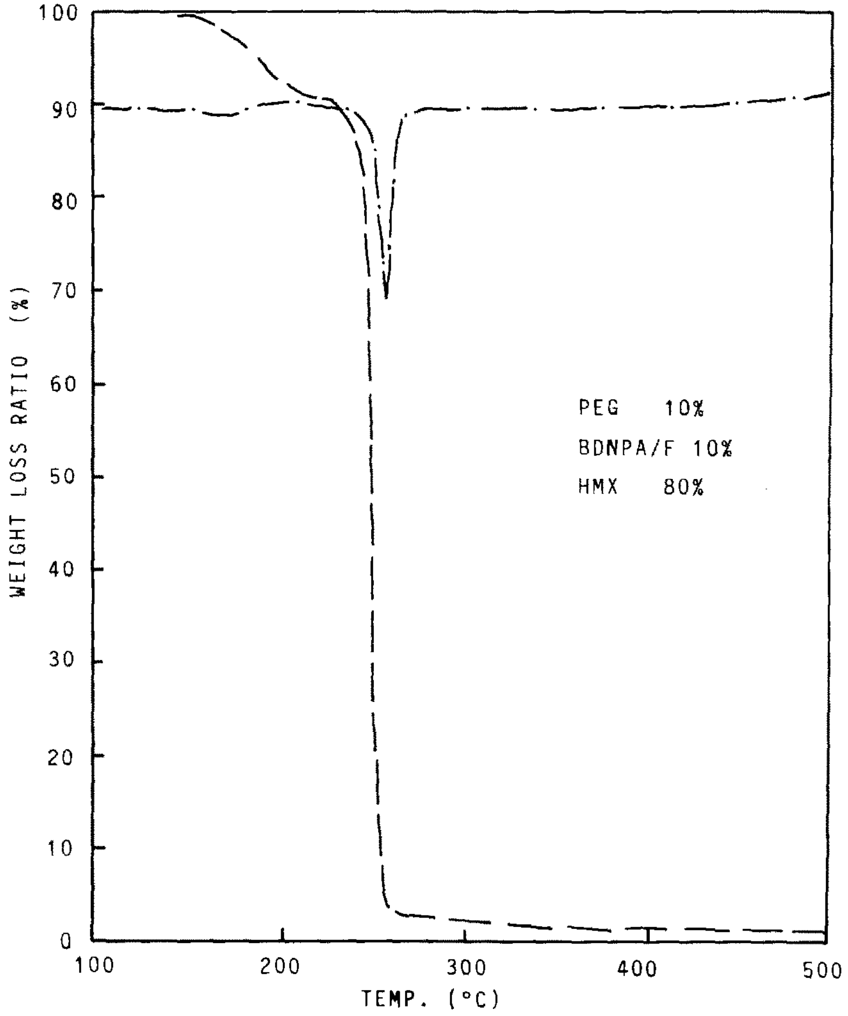

Fig. 12. TG–DTG results of PEG + HMX composite.

overlapping reaction peaks because of the close decomposition reaction temperatures (T_0) of BDNPA/F (220 °C) and GAP (233 °C).

From DSC measurement, the ΔH values were 474 cal g^{-1} for pure GAP binder and 443 (25% BDNPA/F), 455 (30% BDNPA/F) and 483 cal g^{-1} (50% BDNPA/F) for the GAP + BDNPA/F systems. Thus, compared with pure GAP binder, the ΔH of GAP and BDNPA/F mixtures decreased, but increased with increasing concentration of BDNPA/F. According to the results of the Parr bomb calorimeter measurement on a large mass of test sample, the changing trend of heats of explosion for GAP-1, GAP-2, GAP-3 are the same as with the DSC results. The ΔH values of pure BDNPA/F (500 cal g^{-1}) and GAP (474 cal g^{-1}) are larger than those of the GAP-1,

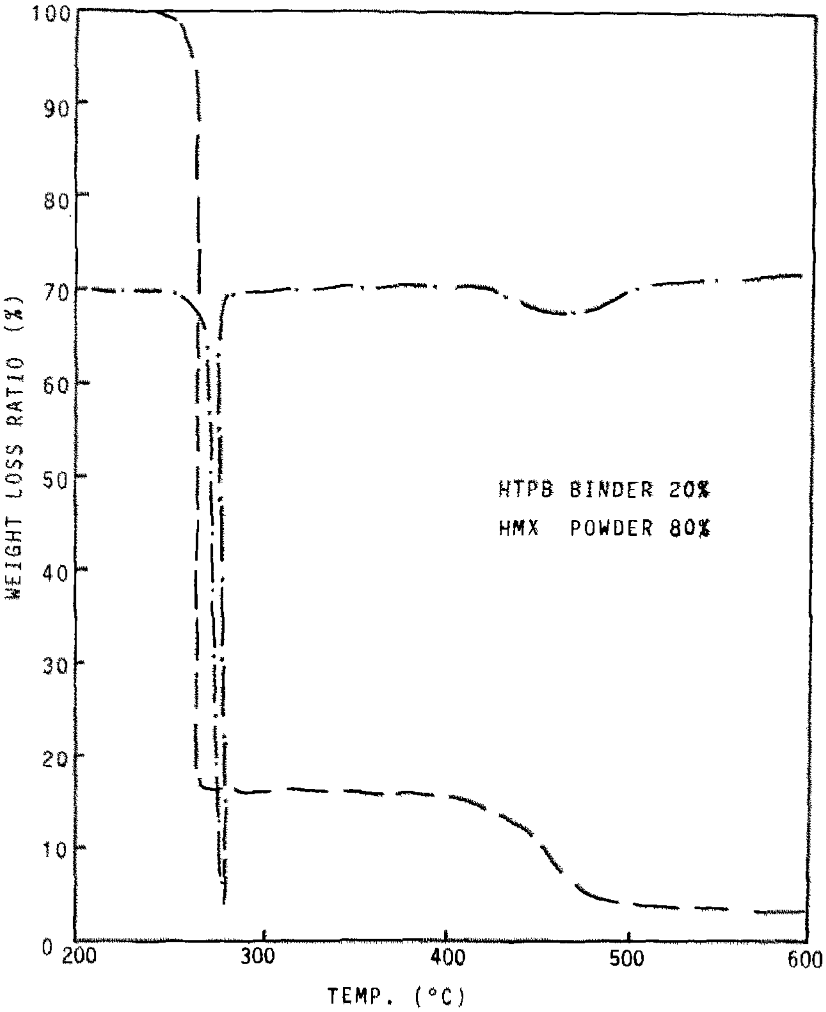

Fig. 13. TG–DTG results of HTPB + HMX composite.

GAP-2 and less than GAP-3 systems; further investigation into the variation of ΔH values of mixtures of GAP and BDNPA/F is required.

The DSC measurement of the PEG + BDNPA/F systems are shown in Figs. 3–7 and the weight losses of each formation are shown in Table 4. Comparing the concentration of BDNPA/F in the P2 and P3 formulations with the weight-loss ratio of each formulation, it is found that the first exothermic reaction peak on the DSC pattern can be attributed to the decomposition of BDNPA/F. The following large exothermic reaction peak is due to the decomposition of residual polyurethane of the PEG molecule. Table 4 shows small weight-losses for P3-1, P2-1 and P2-2 systems (2, 1 and 2%, respectively) below 100 °C, caused by the vaporisation of moisture. Figures 3 and 5 show that the T_m of the first reaction peak of the mixture

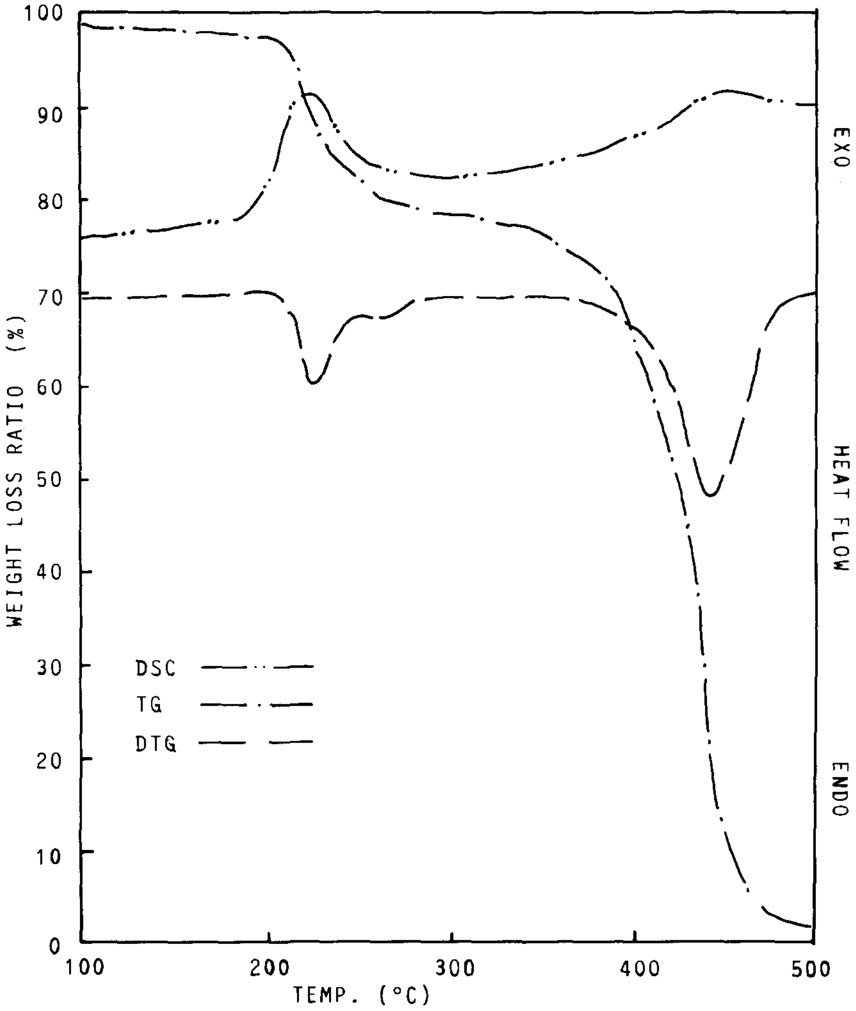

Fig. 14. TG–DTG and DSC results for P3-1 binder.

increased as the BDNPA/F concentration increased, finally approaching the T_m of pure BDNPA/F, 240°C.

Figure 7 shows the DSC pattern of pure PEG binder: an exothermic reaction occurs at 180°C ($\Delta H = 9$ cal g^{-1}). For PEG + BDNPA/F systems, the decomposition of BDNPA/F is affected by the heat of reaction as the PEG molecules predominate in the mixture, which causes the decomposition temperature, T_m, to shift to lower temperatures, and vice versa.

Figure 3 shows that the T_m values of the residual PEG molecules shift to lower temperatures as the BDNPA/F concentration increased. Therefore, it is proposed that the decomposition behaviour of mixtures of BDNPA/F and PEG is affected by the interaction of the components.

TABLE 4

TG results of test samples

Formulation	Binder (wt.%) [a]				Solid (wt.%)	Weight-loss ratio (wt.%)		
	A	B	C	D	HMX	1st	2nd	3rd
GAP	100	–	–	–	–	42	33	–
GAP-1	75	–	–	25	–	30	22	33
GAP-2	70	–	–	30	–	35	20	30
GAP-3	50	–	–	50	–	55	15	20
P3-1 [b]	–	80	–	20	–	2	20	75
P3-2	–	60	–	40	–	40	57	–
P3-3	–	40	–	60	–	60	37	–
P3-4	–	20	–	80	–	80	19	–
P2-1	–	80	–	20	–	1	20	75
P2-2	–	70	–	30	–	2	23	68
P2-3	–	40	–	60	–	55	42	–
P2-4	–	30	–	70	–	67	30	–
A-1	20	–	–	–	80	15	82	–
A-2	20	–	–	–	80	10	87	–
A-3	20	–	–	–	80	10	85	–
B-1	10	–	–	10	80	15	80	–
B-2	10	–	–	10	80	95	–	–
B-3	10	–	–	10	80	94	–	–
C-1	–	–	20	–	80	75	22	–
C-2	–	–	20	–	80	84	13	–
C-3	–	–	20	–	80	87	5	–
D-1	–	10	–	10	80	10	88	–
D-2	–	10	–	10	80	10	87	–
D-3	–	10	–	10	80	10	87	–

[a] A, GAP binder; B, PEG binder; C, HTPB binder; D, BDNPA/F plasticiser.

[b] P2, PEG (mw = 2000); P3, PEG (mw = 3000).

Figure 4 shows that there is a linear relationship between ΔH and BDNPA/F described by

$$\Delta H = \Delta H_{\mathrm{PEG}} + C\,\Delta H_{\mathrm{BDNPA/F}} \tag{1}$$

where ΔH is the overall heat of reaction of the binder system, ΔH_{PEG} is the heat of reaction of pure PEG binder, C is the concentration of BDNPA/F and $\Delta H_{\mathrm{BDNPA/F}}$ is the heat of reaction of pure BDNPA/F.

Table 1 shows that the exothermic reaction heats of the GAP systems are higher than those of the PEG + BDNPA/F system. For the GAP systems, because the reaction heats of GAP and BDNPA/F are close, the heat of reaction remains unchanged as BDNPA/F is added to GAP binder. But for the PEG systems, addition of BDNPA/F causes an increase in the reaction heat as the concentration of BDNPA/F increases.

The results of DSC and TG–DTG measurements for the energetic composites of GAP, GAP + BDNPA/F, PEG + BDNPA/F, HTPB and various particle sizes of HMX powder are shown in Figs. 10–13 and in Tables 2 and 4. Table 2 shows that the T_m value of the energetic composite made of coarse HMX is larger than that of the composite which includes medium or fine HMX powder for the same binder system. In the GAP and GAP + BDNPA/F binder systems, the reaction temperatures, T_o and T_m, for systems with medium or fine HMX are the same. In PEG + BDNPA/F binder systems, the reaction temperatures, T_o and T_m, are the same with various HMX particles sizes. In HTPB binder systems, the T_o and T_m are the same for systems with coarse and medium particles of HMX, but are smaller with fine HMX particles. Table 4 shows that there are two types of weight-loss reactions for the energetic composites. For GAP, GAP + BDNPA/F and PEG + BDNPA/F binder systems, there are two distinct weight-loss reactions for each energetic composite. The decomposition of the binder takes place before that of the HMX particles. For HTPB systems, the HMX particles decompose before the HTPB binder.

In PEG + BDNPA/F systems, there are two weight-loss reaction stages. In the first stage, the weight-loss ratio is about 10% around 210 ° C and, for the second stage, the weight-loss ratio is about 87% near to 265 ° C. The decomposition temperature of HMX powder and PEG + BDNPA/F is about 270 and 200/210 ° C, respectively. As mentioned above, BDNPA/F decomposes first in a PEG + BDNPA/F binder system. Comparing the weight-loss ratios and reaction temperatures, it seems probable that BDNPA/F decomposes before the HMX (80%) and PEG (10%) in the energetic composite HMX + PEG + BDNPA/F.

In the HTPB systems, there are two weight-loss stages. For example, formulation C-1 undergoes a weight-loss reaction at 275 ° C with a weight-loss ratio of about 75% and a second-stage weight loss at 350–500 ° C with a ratio of about 22%. The weight-loss ratios are in correspondence with the ingredient ratio of the energetic composites, i.e. 80/20. The decomposition temperature of pure HTPB binder ($T_m = 360$ ° C) is higher than that of pure HMX ($T_m = 270$ ° C); therefore, it is concluded that the HMX decomposes before the HTPB binder. In HTPB systems, the decomposition of HMX is not affected by the HTPB binder. But in GAP, GAP + BDNPA/F and PEG + BDNPA/F systems, the binder affects the decomposition of HMX and shifts the decomposition temperature of HMX to lower temperatures. In addition, it is found that the decomposition temperatures, T_o and T_m, are affected by the heating rate and the particle size of HMX. Therefore, in the measurement of T_o and T_m, low heating rates are recommended for safety considerations. From Table 2, it is found that the heats of explosion of composites of the A, B and D series, made using GAP, GAP + BDNPA/F or PEG + BDNPA/F as binder, are higher than those with HTPB binder by about 200–300 cal g^{-1}; therefore, GAP, GAP + BDNPA/F or PEG +

BDNPA/F binder could obviously increase the energy content of energetic composites.

CONCLUSION

The following conclusions are drawn from the above results and discussion. The nitroplasticiser BDNPA/F is more compatible with GAP polymer than with PEG polymer. The thermal decomposition parameters are unchanged when BDNPA/F is used in GAP binder systems; but for PEG binder systems, the maximum reaction temperature shifts to higher temperatures as the concentration of BDNPA/F is increased.

The heats of explosion of GAP/HMX, GAP/BDNPA/F/HMX and PEG/BDNPA/F/HMX energetic composites are proportional to the size of the HMX particles. The energy contents of GAP, GAP + BDNPA/F and PEG + BDNPA/F binders are higher than that of HTPB. Therefore, the energy of energetic composite systems is promoted by using GAP, GAP + BDNPA/F or PEG + BDNPA/F.

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