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The thermal decomposition of azide polymers containing ferruginous compounds

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Abstract

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), as well as dynamic exothermic deflagration and vacuum stability tests, were employed to investigate the thermal characteristics of azide polymer binder systems in the presence of ferruginous compounds. Various ferruginous compounds in GAP, GAP/BDNPA/F, BAMO and BAMO/BDNPA/F binder systems were examined. The results revealed that *n*-butyl ferrocene, catocene and ferrocenecarboxaldehyde play an important catalysing role in the decomposition of binder systems.

INTRODUCTION

A major goal of current research is to increase the energy content and safety of gun or rocket propellants. Polymers containing the azide group are a particularly important class of energetic material. Of the azide polymers, glycidyl azide polymer (GAP) and poly-bisazidomethyl oxetane (poly-BAMO) energetic binders have been widely studied in recent years [1–9].

Ferruginous compounds, such as Fe_2O_3, catocene (Cat), *n*-butyl ferrocene (nBF), etc., are very popular catalysts for burning-rate modification of composite solid propellants. Although there are many studies related to the performance of propellants containing the azide group, there is so far no report on the effect of ferruginous compounds on GAP or poly-BAMO binder systems.

In this study, the thermal decomposition of GAP and poly-BAMO containing various ferruginous compounds was determined experimentally by both isothermal and non-isothermal methods. Thermal analyses with differential scanning calorimetry (DSC) and thermogravimetry (TG) were carried out at a constant heating rate. In addition, dynamic exothermic deflagration tests were performed to provide a comparison with the DSC results. The vacuum stability test was also carried out.

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EXPERIMENTAL

Materials

The poly-BAMO, GAP pre-polymer and BDNPA/BDNPF nitroplasticizer examined in this study were laboratory synthesized. All the ferruginous compounds were obtained from the manufacturers. The crosslinking agent used, N-100, was a commercially available triisocyanate.

Sample preparation

The specimens were formulated by curing GAP, GAP/BDNPA/F, BAMO and BAMO/BDNPA/F binder systems with an isocyanate curative

TABLE 1

Thermal properties of GAP and GAP/BDNPA/F with and without ferruginous compounds

No.[a]	Formulation						DSC T_m (°C)	Auto ign. Temp. (°C)	Vacuum test (ml g^{-1})
	GAP	BDNPA/F[b]	Cat[c]	nBF[d]	FCHO[e]	Fe_2O_3			
1A	+						251	240	0.968
1B	+						240	219	–
2A	+		+				226	173	–
2B	+			+			235	178	–
2C	+				+		188	168	–
2D	+					+	240	211	–
3A	+	+					239	207	0.507
3B	+	+	+				201	190	2.855
3C	+	+		+			205	189	1.660
3D	+	+			+		196	187	2.580
3E	+	+				+	229	205	1.220

[a] 1A; uncured; 1B; cured. [b] BDNPA/F; bis-2,2-dinitropropyl acetal and formal. [c] Cat, catocene. [d] nBF, *n*-butyl ferrocene. [e] FCHO, ferrocenecarboxaldehyde.

TABLE 2

Thermal properties of BAMO and BAMO/BDNPA/F with and without ferruginous compounds

No.[a]	Formulation						DSC T_m (°C)	Auto ign. temp. (°C)	Vacuum tests (ml g^{-1})
	BAMO	BDNPA/F[b]	Cat[c]	nBF[d]	FCHO[e]	Fe_2O_3			
1A	+						248	239	1.304
1B	+						240	220	–
2A	+		+				190	173	–
2B	+			+			191	168	–
2C	+				+		184	165	–
2D	+					+	227	210	–
3A	+	+					238	207	2.660
3B	+	+	+				193	186	11.25
3C	+	+		+			210	188	1.540
3D	+	+			+		206	185	–
3E	+	+				+	229	208	2.170

[a] 1A, uncured; 1B, cured. [b] BDNPA/F, bis-2,2-dinitropropyl acetal and formal. [c] Cat, catocene. [d] nBF, *n*-butyl ferrocene. [e] FCHO, ferrocenecarboxaldehyde.

TABLE 3

DSC results for BDNPA/F with various ferruginous compounds

No.	Formulation					DSC T_m (°C)		Auto ign. temp. (°C)	Weight loss (%)	
	BDNPA/F[a]	Cat[b]	nBF[c]	FCHO[d]	Fe_2O_3	1st	2nd		1st	2nd
1	+					–	265	204	82	–
2	+	+				179	231	183	55	27
3	+		+			189	245	195	21	66
4	+			+		206	255	192	34	57
5	+				+	–	260	222	80	–

[a] BDNPA/F, bis-2,2-dinitropropyl acetal and formal. [b] Cat, catocene. [c] nBF, *n*-butyl ferrocene. [d] FCHO, ferrocenecarboxaldehyde.

in a NCO:OH ratio of 1:1. The ingredients were dried to a moisture content of less than 0.02%. Tables 1–3 show the binder with added ferruginous compound mixtures. The mixtures were blended well, and then the slurries were cured in an oven at 65°C for four days.

DSC and TG measurements

DSC and TG measurements were carried out using a Setaram thermal analyser. For these measurements, samples weighing about 2–4 mg were heated from 30 to 450°C at a constant heating rate of 5°C min^{-1} under a static atmosphere of nitrogen with a gas flow rate of 50 ml min^{-1}.

Dynamic exothermicity test

The dynamic exothermicity test apparatus consists of a metal heating device with a temperature controller and temperature recording system. In this study, the minimum temperature at which a substance can undergo exothermic decomposition is defined as the auto-ignition temperature. The test samples weighed about 300 mg. The temperatures recorded during the experiments are shown in Tables 1–3.

Vacuum stability test

The vacuum stability test was designed to determine the thermal stability of explosives and propellants under vacuum conditions. This test can be made at any desired temperature: 100 or 120°C is generally employed. The test sample is placed in a glass tube and then heated under a vacuum; the gas liberated is measured. In our test, each sample weighing 50 mg was heated for 40 h under vacuum at 100°C. The results are shown in Tables 1 and 2.

RESULTS AND DISCUSSION

The DSC traces of GAP, BAMO, GAP/DBNPA/F and BAMO/BDNPA/F binder systems with different ferruginous compounds are shown in Figs. 1–4, respectively. Figure 5 shows the DSC patterns of BDNPA/F plasticizer with various ferruginous compounds.

Comparing Figs. 1 and 3, it is clear that different thermal decomposition mechanisms are observed for pure GAP binder and GAP, GAP/BDNPA/F two-binder systems with various ferruginous compounds. The maximum exothermic peak temperatures T_m of the GAP/ferruginous compound and GAP/BDNPA/F ferruginous compound systems are apparently lower than that of pure GAP. Table 1 shows the T_m results for each system: the T_m values of the systems GAP/Ferr and GAP/BDNPA/F/Ferr are lower by about 20–60°C than that of pure GAP. Comparing Figs. 2 and 4, similar effects are observed for BAMO/Ferr and BAMO/BDNPA/F/Ferr two-binder systems. Table 2 shows that the decomposition temperatures T_m of the BAMO/Ferr and BAMO/BDNPA/F/Ferr systems are lower than that of pure BAMO by about 30–60°C.

Comparing the T_m results of the four binder systems, it was found that the four ferruginous compounds have different effects. The Fe_2O_3 powder has little effect on the GAP, GAP/BDNPA/F, BAMO and BAMO/

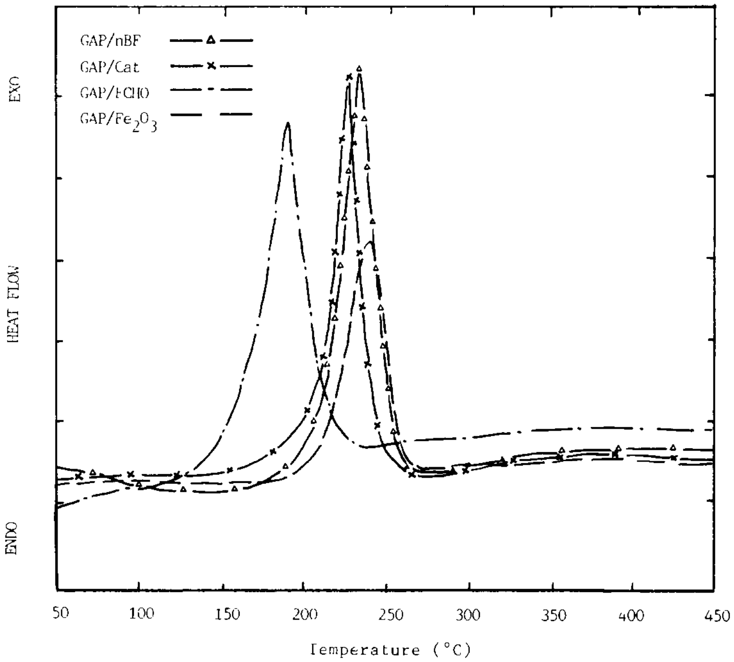

Fig. 1. DSC curves of GAP binder containing ferruginous compounds.

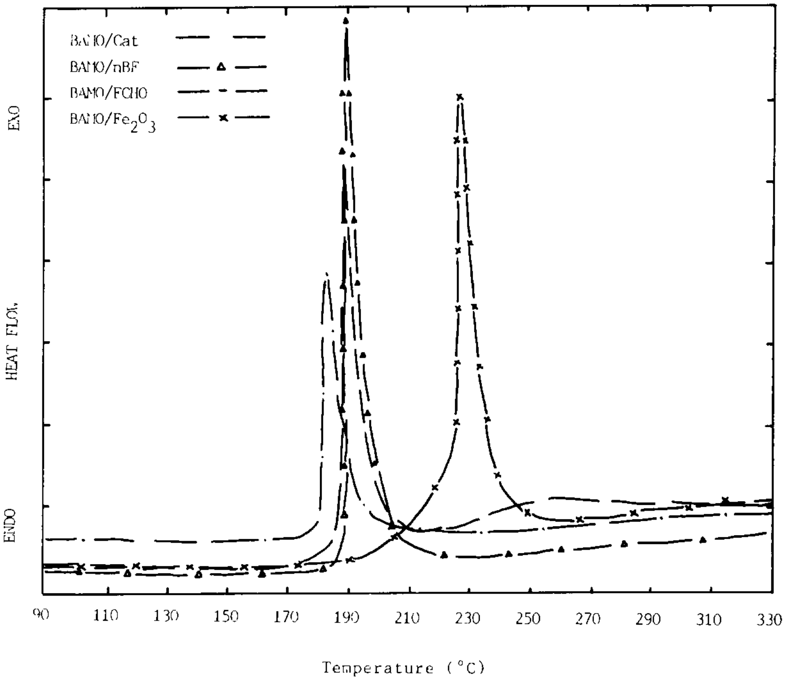

Fig. 2. DSC curves of BAMO binder containing ferruginous compounds.

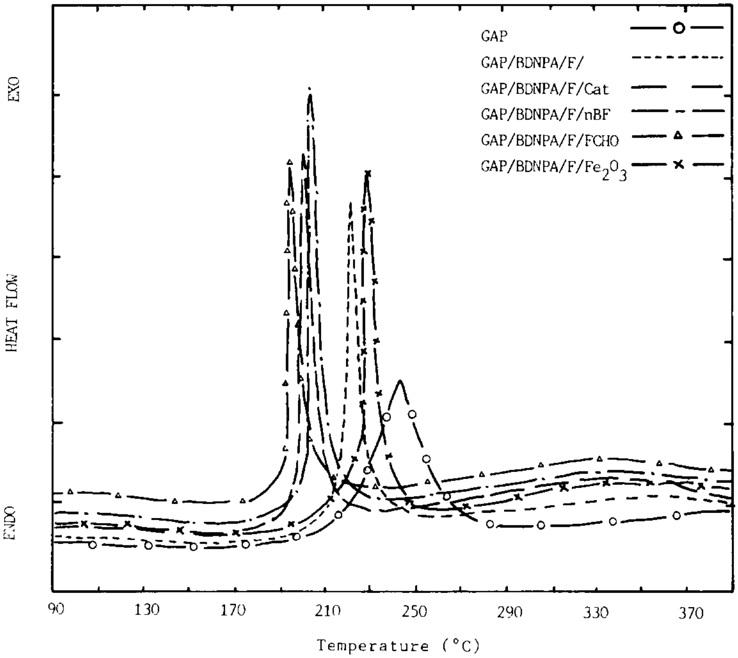

Fig. 3. DSC curves of GA/BDNPA/F binder containing ferruginous compounds.

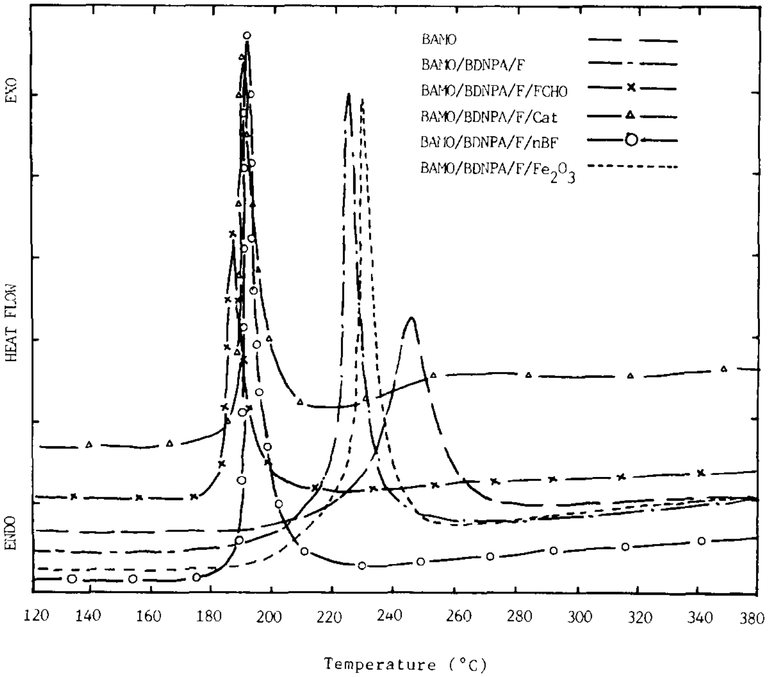

Fig. 4. DSC curves of BAMO/BDNPA/F binder containing ferruginous compounds.

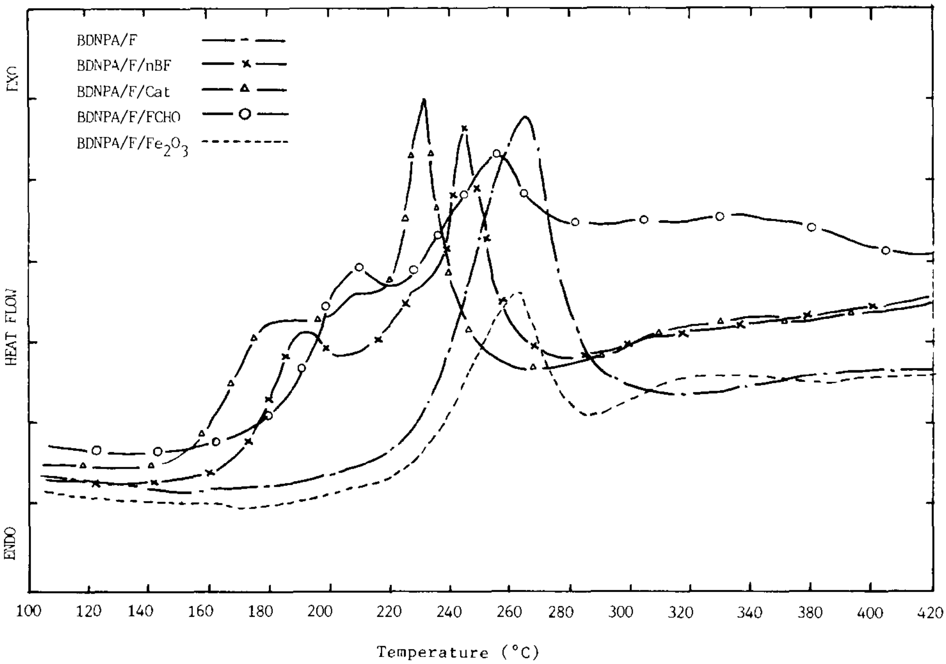

Fig. 5. DSC curves of BDNPA/F plasticizer containing ferruginous compounds.

BDNPA/F systems and the catalytic action of catocene and *n*-butyl ferrocene on the four binder systems are all enhanced. The orders of catalytic effectiveness of the ferruginous compounds for the four binder systems are: ferrocenecarboxaldehyde (FCHO) > catocene (Cat) ≈ *n*-butyl ferrocene (nBF) > Fe_2O_3.

It is well known that the ferruginous compound is the burning-rate modifier of AP composite propellants [10–13]: the burning rate of the propellant is increased when a ferruginous compound is added. In our test, it was found that the decomposition mechanisms of polymer binders containing azide groups would be affected by ferruginous compounds.

Moreover, we added the ferruginous compound to each formulation by weight percent. The percentage of Fe in Fe_2O_3 is much higher than in the other ferruginous compounds, but the effect of Fe_2O_3 is much less than for the other compounds. Shadman-Yazdi and Petersen [14] have investigated the effect of metal oxides on the combustion of ammonium perchlorate (AP). They found that smaller particle sizes of metal oxide had more effect on the decomposition of AP than larger particle sizes.

In our test, the physical properties of the organic compounds Cat, FCHO and nBF are different from that of Fe_2O_3 powder. Although the combustion products of Cat, FCHO and nBF are Fe_2O_3 powder, the particle sizes (Fe_2O_3) of the former compounds are much smaller than when Fe_2O_3 powder is added. In addition, the distributions of Cat, FCHO and nBF in each binder system are much better than that of Fe_2O_3 powder. Therefore, it is clear that the decompositions of GAP, GAP/BDNPA/F, BAMO and BAMO/BDNPA/F are much affected by Cat, FCHO and nBF. However, the effect of the metal oxide on the solid propellant is unclear in detail, even today. A description of the exact reaction mechanisms between azide polymer and ferruginous compounds would make an interesting, timely article.

In addition, a comparison was made of the DSC results and the auto-ignition reaction temperature (T_{ar}), obtained in the dynamic exothermicity test. The results of the dynamic exothermicity test shown in Tables 1 and 2 were obtained using large sample masses: the trends obtained are similar to the DSC test results. Comparing the values of T_m from DSC and T_{ar} from the dynamic exothermicity test, the reaction temperatures of T_{ar} are lower than T_m for each system. The sample mass used in the dynamic exothermicity test is a hundred times that of the DSC measurement; therefore, the decomposition data from the dynamic exothermicity tests have more relevance to practical applications. In the vacuum stability test, it was found that the gases are liberated from binder systems with ferruginous compounds to the same extent as from the pure binder systems.

Table 3 and Fig. 5 show the DSC test results for BDNPA/F plasticizer with and without ferruginous compound. In Fig. 5, it is clear that different thermal decomposition mechanisms are observed for each system. The one-step exothermic decomposition reaction of BDNPA/F becomes three exothermic decomposition reactions when Cat, FCHO or nBF is added to the BDNPA/F system. The first reaction temperature (T_m) of BDNPA/F/Cat, BDNPA/F/FCHO or BDNPA/F/nBF is about 80°C lower than that of pure BDNPA/F. The reaction weight-loss ratio of each system is given in Table 3. In the TG measurement, it was found that two weight-loss reactions take place for the BDNPA/F/Cat, BDNPA/F/FCHO and BDNPA/F/nBF systems. For the BDNPA/F and BDNPA/F/Fe_2O_3 systems, only one weight-loss reaction took place. Comparing the DSC and TG measurements, it is demonstrated that the decomposition reaction of BDNPA/F is changed when Cat, FCHO or nBF ferruginous compound is added.

Although it is well known that ferruginous compounds affect the decomposition characteristics of ammonium perchlorate (AP) composite propellant, the exact mechanism of its effect is by no means clear. Further investigation of the effects of ferruginous compounds on the ingredients of composites, such as polymer and oxidizer, is recommended.

CONCLUSIONS

The decomposition reaction temperatures of GAP and BAMO polymers, which contain azide groups, are shifted to lower temperatures when Cat, FCHO or nBF ferruginous compounds are added. The catalytic effectiveness of Fe_2O_3 on the decomposition of GAP or BAMO is much smaller than those of Cat, FCHO and nBF. The decomposition mechanism of the nitroplasticizer BDNPA/F is changed and the decomposition temperature is lowered when the organometallic compounds Cat, FCHO or nBF are added.

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