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A study on the thermal decomposition of mixtures containing an energetic binder and a nitramine

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Abstract

In this paper, a differential thermal analyzer (DTA) and a thermogravimetric analyzer (TGA) were both employed to study the thermal decomposition of mixtures containing an energetic binder and a nitramine compound. The energetic binders investigated were polyethylene glycol (PEG) and glycidyl azide polymer (GAP). Both cyclotriethylene trinitramine (RDX) and cyclotetraethylene tetranitramine (HMX) were studied. The heating rate was set at 10°C min^{-1}. The purge gas was nitrogen or oxygen. It was found that the thermal decompositions of the mixtures were affected by the sample composition and the atmosphere employed. The decomposition reaction rates of PEG and GAP increased when they were heated under oxygen. Because the polymer binders are energetic, both RDX and HMX nitramine compounds in the mixtures decomposed earlier and the reaction rate was increased.

INTRODUCTION

At present, two of the major topics in propellant research are the achievement of high performance and an increase in safety. Performance increases can be expected when employing energetic materials. For instance, the commonly used oxidizer, ammonium perchlorate, is partially replaced by a highly energetic nitramine, and/or the conventional non-energetic polymeric binder is substituted by an energetic polymer. Energetic polymers containing azide groups have recently received much attention as potential candidates for energetic propellant binders. Glycidyl azide polymer (GAP) is a typical energetic azide represented by two –N3 bonds in its molecular structure. In addition, the two terminal hydroxyl groups can be cured with the –NCO group of isocyanates to form a

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solidified polymer with good mechanical properties. Recently, the characteristics of thermal decomposition and combustion of GAP have been extensively studied. Kubota et al. [1] studied the burning rate characteristics of GAP propellants in energetic mixtures of GAP binder with three different oxidizers (AP, HMX or TAGN). Nakashita and Kubota [2] examined the burning rate characteristics and combustion wave structure of a double-base propellant, the so-called "nitro/azide propellant", which consists of NG/NC and GAP. Shen et al. [3] investigated the decomposition of GAP-AP propellants in the presence of catocene as a burning rate modifier. Chen and Brill [4] applied simultaneous mass and temperature change technique (SMATCH/FTIR) to study the thermal decomposition kinetics and combustion products with both low (1°C min^{-1}) and high heating rates (150°C s^{-1}).

The addition of energetic plasticizers, such as bis(2,2-dinitropropyl)-acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF), to polyethylene glycol (PEG) could increase the performance of PEG-based propellants. PEG has been reported for use as an energetic binder in minimum-smoke propellants and in plastic-bonded explosives (PBX) [5]. Recently, it has also been reported [6] that PEG could be used as the binder for formulating low-vulnerability ammunition (LOVA). Thermal analysis investigations of composites containing PEG and BDNPA/F were reported by Shen et al. [7].

Although GAP and PEG offer a great potential for producing a new generation of advanced propellants, there has been little research on the thermochemical properties of mixtures containing energetic binder (GAP or PEG) and nitramine (RDX or HMX). In this study, thermal analysis techniques were employed to study the decomposition behaviors of these mixtures.

EXPERIMENTAL

The energetic materials investigated in this study were cyclotriethylene trinitramine (RDX), cyclotetraethylene tetranitramine (HMX), polyethylene glycol (PEG) and glycidyl azide polymer (GAP). Among these materials, HMX and RDX were manufactured by a domestic arsenal; the PEG (MW, 3000) was a product of Wako Co. and GAP (MW, 4000) was laboratory synthesized.

Thermal analysis measurements were made using a Du Pont Instruments 9900 thermal analyzer with 951 TGA and 1600 DTA modules. For these measurements, samples weighing about 2.4–5.6 mg were heated from room temperatures to 500°C. A heating rate of 10°C min^{-1} was employed throughout, with a 50 ml min^{-1} flow of either nitrogen or oxygen gas. The standard materials, pure silver and calcium oxalate, were used to calibrate the DTA and TGA, respectively.

RESULTS AND DISCUSSION

Typical DTA thermograms of PEG, RDX and their mixtures are displayed in Fig. 1. It can be seen from the figure that the DTA curve of pure PEG shows two distinct peaks: an endotherm at 58.6°C and an exotherm at 264.9°C. These two peaks are ascribed to the melting point and the maximum exothermic peak temperature (T_m), respectively. The presence of this exotherm, which has a peak height similar to that obtained from RDX, means that PEG can be described as an energetic material. The DTA curve of pure RDX shows a melting point at 204°C and the temperature at maximum decomposition rate is 241.1°C. These experimental results are close to the literature data [8, 9]. The DTA curves of mixtures PER1 and PER2, whose compositions are listed in Table 1, are also illustrated in Fig. 1. There is an endothermic valley around 58°C on the DTA curves of both mixtures, indicating the melting point of PEG. This melting endotherm decreases with decreasing PEG concentration. It is also observed that the exotherm on the DTA curves of the mixtures shifts to a lower T_m value as the PEG content in the mixture increases. Furthermore, the maximum exothermic peak temperatures of the mixtures are several degrees below those of pure PEG and pure RDX. Because the onset temperature of decomposition of PEG is at 175°C, it is believed that the presence of PEG causes RDX to decompose earlier. Because RDX is affected by the heat released by the decomposition of PEG, its melting endotherm on the DTA curve of the mixtures (at around 204°C) is absent. In other words, the heat absorbed by the melting of RDX is balanced by the partial heat released by the decomposition of PEG.

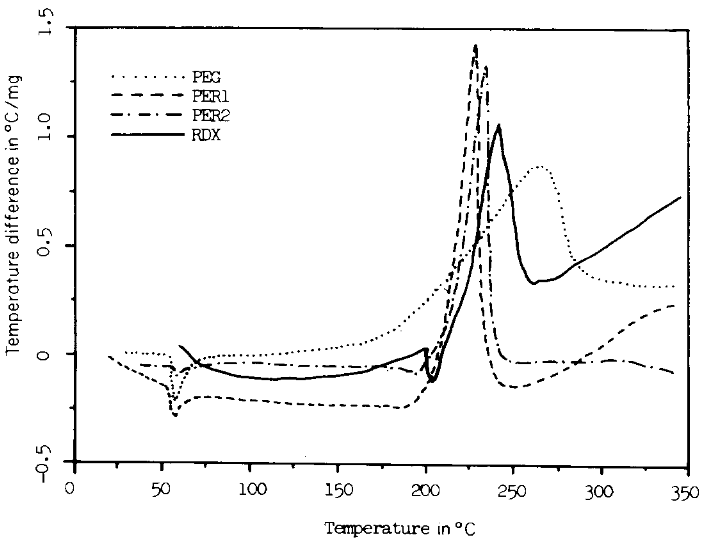

Fig. 1. DTA thermograms of PEG, RDX and their mixtures under nitrogen atmosphere.

TABLE 1

DTA and TGA measurements of PEG, RDX, HMX and their mixtures under nitrogen flow

Sample	Composition/%			DTA			TGA			
	PEG	RDX	HMX	Sample weight/mg	T_m/°C	E_a/ (kcal mol^{-1})	Sample weight/mg	1st stage		2nd stage
								T_0/°C	Weight loss/%	Weight loss/%
PEG	100			3.10	264.9	21.6	4.003	272.0	95.91	–
PER1	50	50		4.40	230.0	46.9	4.987	213.0	47.50	47.03
PER2	25	75		4.00	234.7	42.0	6.505	207.5	74.56	21.90
RDX		100		3.00	241.1	44.8	4.121	226.3	93.02	–
PEH1	50		50	3.60	257.4	47.4	6.059	251.3	63.54	30.07
PEH2	25		75	4.00	260.9	49.0	5.221	252.7	76.19	14.17
HMX			100	2.40	288.1	51.0	3.218	282.2	99.23	–

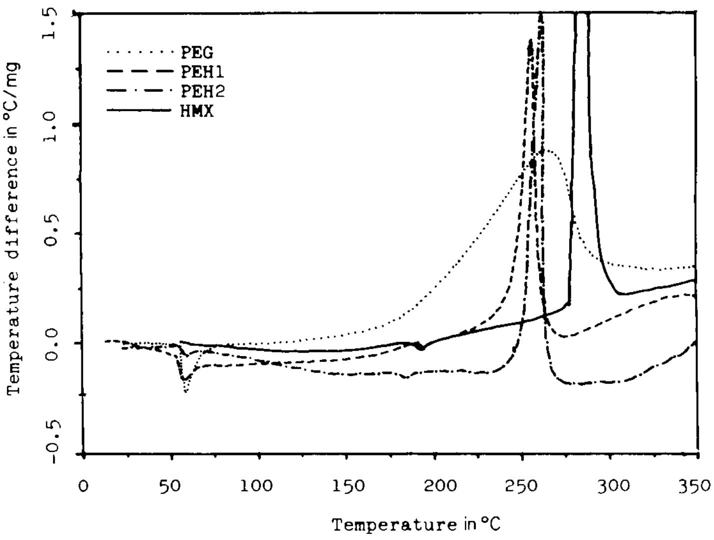

Fig. 2. DTA thermograms of PEG, HMX and their mixtures under nitrogen atmosphere.

Figure 2 shows DTA thermograms of pure PEG, pure HMX and their mixtures. The DTA curve of pure HMX shows a small endotherm at around 196°C, assigned to transformation of the crystal structure, and an obscured endotherm at around 275°C which is followed immediately by a strong exothermic peak. The last two peaks are ascribed to the melting point and the maximum exothermic decomposition temperature of HMX, respectively. This indicates that HMX decomposes in a condensed phase, which is in agreement with literature reports [8, 9]. Comparing the DTA curves of RDX and HMX, it is clear that HMX is more energetic and has a higher decomposition temperature than that of RDX. As seen in the PEG–HMX systems, the maximum decomposition rate peak temperature of mixtures PEH1 and PEH2 are apparently lower and closer to that of pure PEG. This again suggests that the heat liberated by PEG decomposition causes HMX to decompose earlier.

Figures 3 and 4 illustrate TGA thermograms for PEG–RDX and PEG–HMX mixtures, respectively. The thermograms of pure PEG, pure HMX and pure RDX are also illustrated in these two figures. The onset temperature of weight loss for RDX is 226.3°C, and that for HMX is 282.2°C. It can be seen that the TGA curves for the nitramine compounds drop sharply after weight loss starts, indicating their rapid pyrolysis processes. The corresponding weight loss of PEG binder starts at about 210°C and progresses slowly. The decomposition of PEG starts at a temperature far below its onset temperature (T_0) of the TGA curve, i.e. 272°C. As shown in these figures, the thermal decompositions of PEG–RDX and PEG–HMX mixtures consist of a two-stage weight loss process. The first stage of weight loss is owing to the decomposition of the nitramine

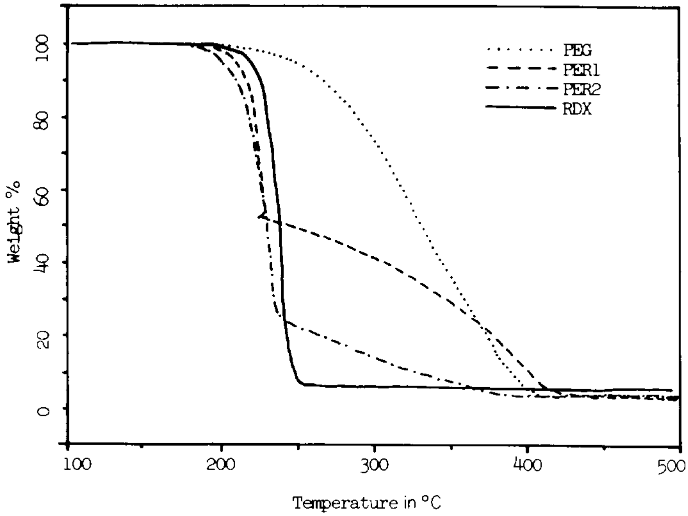

Fig. 3. TGA thermograms of PEG, RDX and their mixtures under nitrogen atmosphere.

compound, RDX or HMX. The decomposition of PEG binder causes the second stage of weight loss. The percentage of weight loss is close to the composition of mixture. However, the weight loss curve shifts to the left for all mixtures and the first-stage weight loss curves of the mixtures are similar to that of the ingredient with the lower T_0. In other words, the first-stage weight loss curve of PEG–RDX mixtures is analogous to that of RDX and the first-stage weight loss curve of PEG–HMX mixtures, however, is similar to that of PEG. It should be noted that the T_0 of the TGA curve of

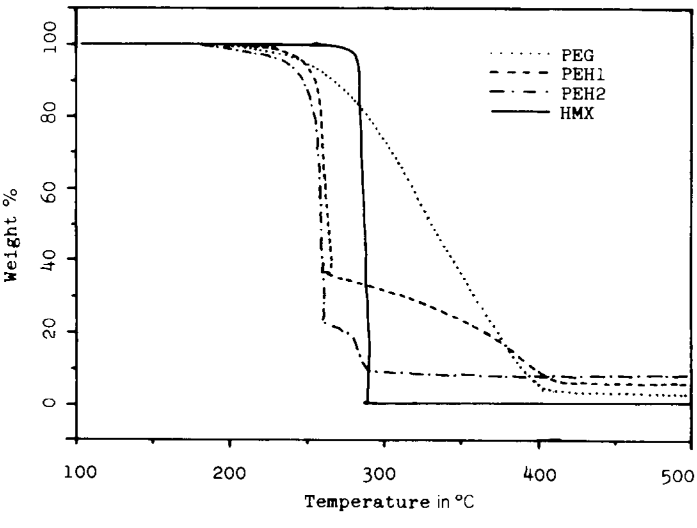

Fig. 4. TGA thermograms of PEG, HMX and their mixtures under nitrogen atmosphere.

PEG-HMX mixtures, as seen for T_m in the DTA determination, drops dramatically. This could be ascribed to the decomposition of PEG. Because the initial decomposition temperature of PEG is much lower than that of HMX, the heat liberated by the PEG decomposition might supply enough energy to induce the decomposition of HMX. Accordingly, the exothermic peak temperatures and the initial temperatures of the first-stage decomposition of PEH1 and PEH2 would be lowered.

The results of thermal analysis measurements for PEG–RDX and PEG–HMX mixtures with various compositions are given in Table 1. From the DTA and TGA data listed in Table 1, it is found that mixtures have lower values of T_m and T_0, indicating the existence of some kind of interaction between the binder and nitramine compounds. Based on the model proposed by Huang et al. [10], the kinetic parameters were determined from a single DTA curve and are also listed on Table 1. The calculated activation energies (E_a) of RDX and HMX were 44.8 and 51.0 kcal mol^{-1}, respectively, in fair agreement with literature values [8]. However, in comparison with the E_a values of RDX and HMX, the corresponding E_a values of the mixtures change only slightly.

Figures 5 and 6 are the DTA and TGA thermograms for PEG–RDX mixtures obtained under identical experimental conditions, except that oxygen rather than nitrogen was used as the purge gas. From DTA curves, it was found that the pure PEG exotherm in an oxygen atmosphere is 234.8°C, which is 30.1°C below that obtained in a nitrogen atmosphere; the exotherms of the mixtures are close to that of PEG. Compared to that obtained in a nitrogen atmosphere, however, the exothermic peak temperature of pure RDX remains unchanged in oxygen. Similarly, the

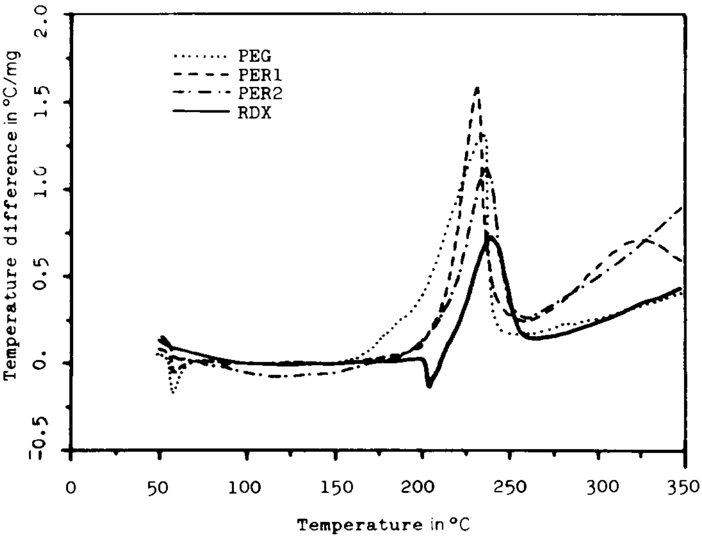

Fig. 5. DTA thermograms of PEG, RDX and their mixtures under oxygen atmosphere.

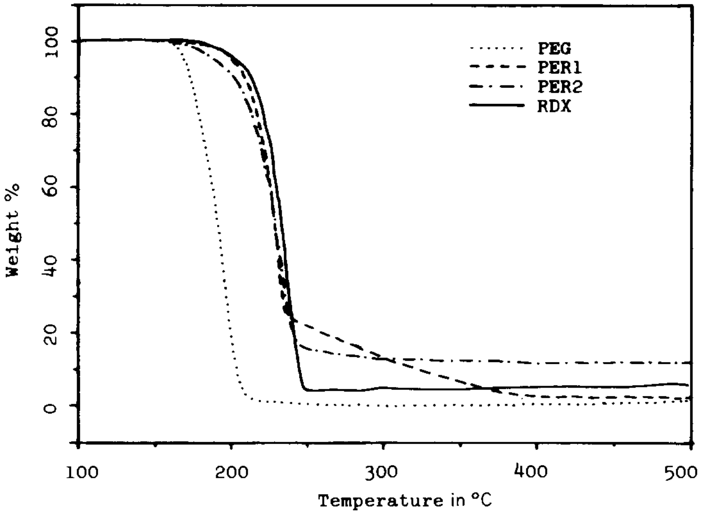

Fig. 6. TGA thermograms of PEG, RDX and their mixtures under oxygen atmosphere.

TGA thermogram of pure PEG shows that the T_0 of pure PEG also decreases to 175.8°C in oxygen, and the rate of weight loss increases to an extent which is close to that of RDX. For the mixture PER2, however, only a one-stage weight loss process is observed on the TGA curve. Although mixture PER1 still shows a two-stage weight loss process, there is much more than 50% of total weight loss in the first-stage decomposition. The difference between the thermal decompositions of the mixtures under oxygen and under nitrogen atmospheres is quite remarkable. The difference could be explained as being due to the occurence of an oxidative degradation reaction of PEG in an oxygen environment.

Figure 7 displays the DTA thermograms for GAP–RDX mixtures. A distinct exothermic peak located at 246°C is seen on the DTA curve of GAP. Like PEG, the peak height of this exotherm is quite close to that obtained for pure RDX. Thus, GAP could also be considered as an energetic material. Nakashita and Kubota [2] reported that GAP is an energetic polymer. As can be seen in Fig. 7, the characteristic melting endotherm at around 204°C is not found on DTA curves of the mixtures GAR1 and GAR2. The same results are found by DTA measurements of PEG-containing mixtures as shown in Fig. 1. The RDX endotherm is overlapped by the exothermic decomposition of GAP. Furthermore, after an exothermic peak temperature is attained, a decline is observed on the DTA curves of the mixtures. This decline could be attributed to the effect of excess heat release generated by our using an over-large sample. The figure also shows that the peak height of the mixtures is much higher than that of either RDX or GAP alone. This implies that there is a strong interaction between RDX and GAP. The interaction between the

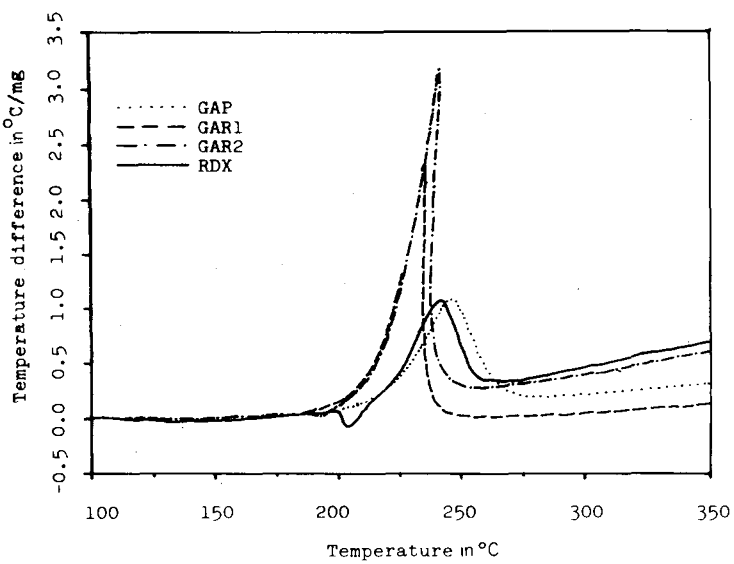

Fig. 7. DTA thermograms of GAP, RDX and their mixtures under nitrogen atmosphere.

compounds causes more heat release and, consequently, a lowering of the exothermic peak temperature.

Figure 8 shows the DTA curves of GAP–HMX mixtures. As shown in this figure, the exothermic peak temperatures of the mixtures GAH1 and GAH2 are close to that of GAP. However, the shape of the DTA curves of mixtures matches that of HMX, both displaying sharp, high peaks. A

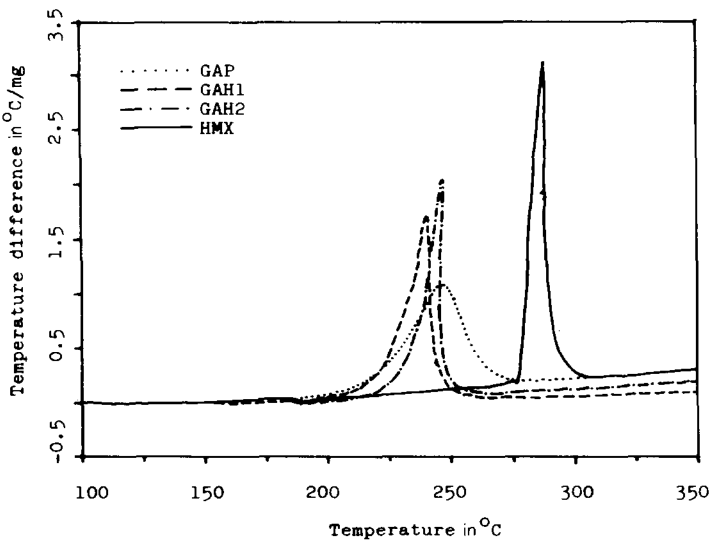

Fig. 8. DTA thermograms of GAP, HMX and their mixtures under nitrogen atmosphere.

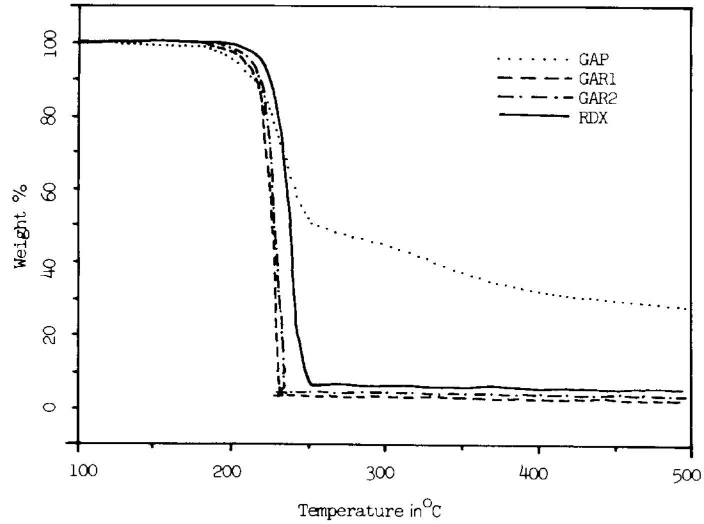

Fig. 9. TGA thermograms of GAP, RDX and their mixtures under nitrogen atmosphere.

similar result is found on DTA scans of PEG-HMX mixtures. It is obvious that these exotherms in the mixtures represent an earlier decomposition of HMX, as a result of the heat liberated by the decomposition of GAP. The results of our study on a series of PEG-HMX and GAP-HMX mixtures indicate that when both constituents of the mixture undergo an exothermic decomposition reaction, the exothermic peak on the DTA curve of the mixture matches that of the constituent with a lower peak temperature.

Figures 9 and 10 illustrate the TGA thermograms of GAP-RDX and

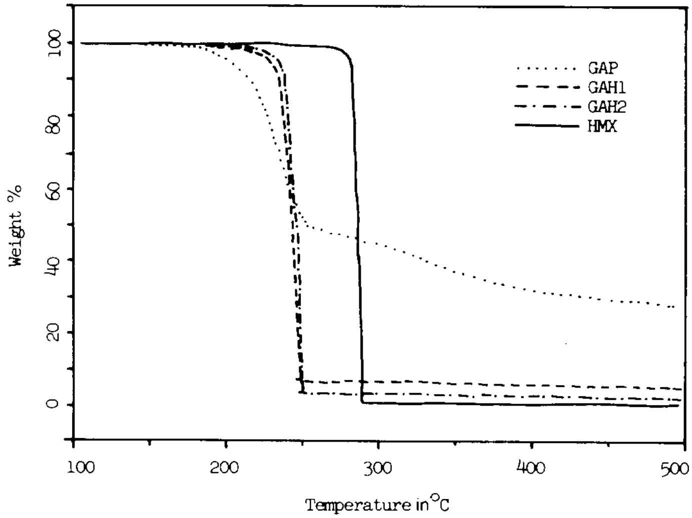

Fig. 10. TGA thermograms of GAP, HMX and their mixtures under nitrogen atmosphere.

GAP–HMX mixtures, respectively. A decreasing trend is observed on the TGA thermograms of GAP, and of GAP–RDX and GAP–HMX mixtures. As mentioned above, this is also caused by the high sample weight used which could liberate excess heat. As can be seen in these two figures, only the thermal decomposition of GAP displays a two-stage weight loss process. The first stage of the decomposition starts at a temperature below that of HMX and is close to that of RDX. The second-stage weight loss proceeds slowly. For GAP–RDX and GAP–HMX mixtures, however, there is only one stage of weight loss, as shown in their TGA curves. The starting temperature of weight loss for the mixtures is lower than that of either RDX or HMX alone. This implies that the large amount of heat released by the decomposition of GAP results in a strong interaction between GAP and nitramine compounds. The TGA results are in good agreement with the DTA results and indicate the influence of this interaction on the decomposition behavior of RDX or HMX with the addition of GAP.

The results of the thermal analyses of GAP–RDX and GAP–HMX mixtures of various compositions are listed in Table 2. The differences in T_m between the mixtures GAH1 and GAH_2 and HMX were 47.6°C and 41.3°C, respectively. This indicates that the thermal decomposition of HMX is enhanced with the GAP concentration in the mixtures. From the TGA data, the first-stage decomposition of pure GAP involves only a 60.5% weight loss. For mixture samples, however, there is only a one-stage weight loss and the residue is less than 10 wt.% of the samples, despite different composition. Our results suggest that the thermal decomposition of RDX and HMX is accelerated in the presence of GAP due to its heat liberation. However, the heat released by the decomposition of RDX or HMX is so high that a nearly complete decomposition of GAP could result. This decomposition behavior is different from that of PEG-containing mixtures.

DTA curves for GAP–RDX mixtures heated at $10°C\,min^{-1}$ in oxygen atmosphere are shown in Fig. 11. From the figure, it can be seen that the DTA curve of GAP becomes narrower and steeper, indicating that GAP might have a faster decomposition rate in oxygen atmosphere. Furthermore, the DTA curve of GAP shows that there is a shoulder on the decomposition exothermic peak. Figure 12 displays the typical TGA/DTG thermograms of GAP under nitrogen and oxygen atmospheres, respectively. Apparently, GAP has a faster rate of weight loss and a higher weight loss percentage under oxygen atmosphere than under nitrogen atmosphere. However, the TGA curve of GAP still consists of two stages of weight loss. There are two differential peaks on the DTG curve of GAP in an environment of oxygen. The data obtained by DTG and DTA are consistent. Thus, it can be concluded that a faster, more complete decomposition of GAP can be accomplished by the oxidation reaction of GAP with oxygen.

TABLE 2

DTA and TGA measurements of GAP, RDX, HMX and their mixtures under nigrogen flow

Sample	Composition/%			DTA			TGA			
	GAP	RDX	HMX	Sample weight/mg	T_m/°C	E_a/ (kcal mol^{-1})	Sample weight/mg	1st stage		2nd stage
								T_0/°C	Weight loss/%	Weight loss/%
GAP	100			3.70	246.6	52.1	7.539	227.2	60.50	38.45
GAR1	50	50		4.40	235.4	49.7	8.204	216.2	95.52	–
GAR2	25	75		5.60	242.9	51.4	8.197	217.0	96.03	–
RDX		100		3.00	241.1	44.8	4.121	226.3	93.02	–
GAH1	50		50	4.50	240.5	53.7	6.473	233.0	93.21	–
GAH2	25		75	5.20	246.8	45.5	7.846	225.7	96.13	–
HMX			100	2.40	288.1	51.0	3.218	282.2	99.23	–

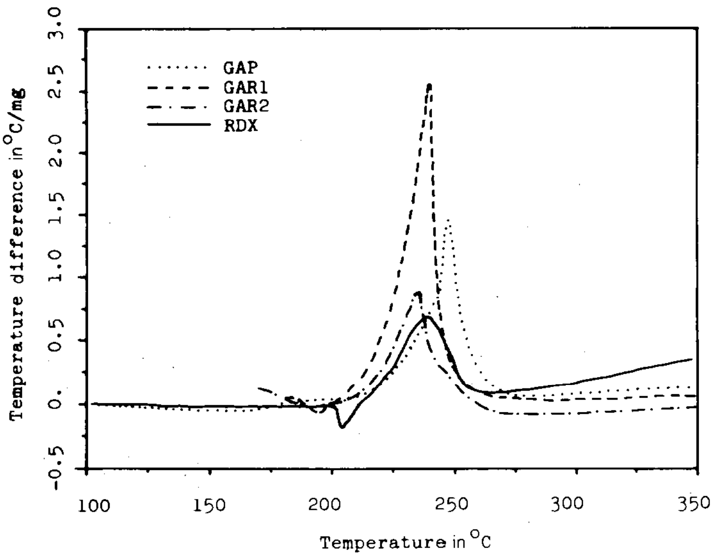

Fig. 11. DTA thermograms of GAP, RDX and their mixtures under oxygen atmosphere.

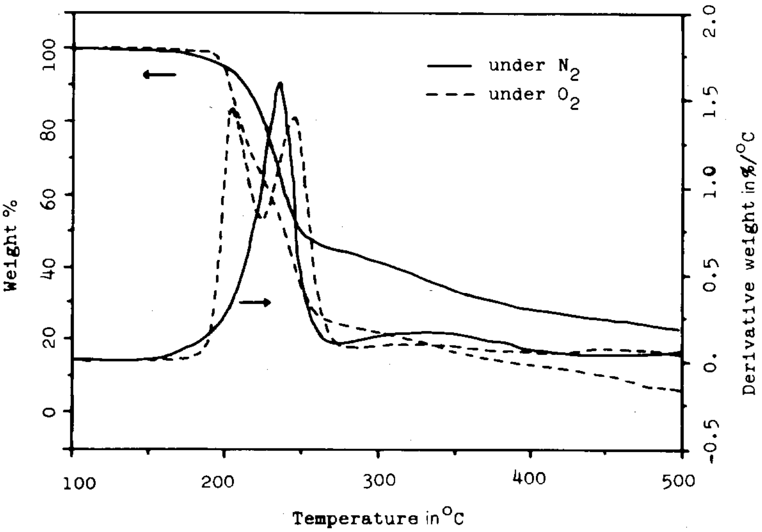

Fig. 12. DTA/DTG thermograms of GAP under nitrogen and oxygen atmospheres.

CONCLUSIONS

The thermal decompositions of mixtures containing a nitramine compound (RDX or HMX) and an energetic binder (PEG or GAP) were studied with a thermogravimetric analyzer (TGA) and a differential thermal analyzer (DTA). Experimental results showed that the thermal decompositions of the mixtures were affected by the sample composition and the atmosphere (purge gas). The decomposition reaction rates of PEG and GAP increase markedly when oxygen is used as the purge gas. These results are mainly attributed to the oxidation reaction of PEG and GAP in an environment of oxygen.

Furthermore, the obtained activation energies of decomposition for pure RDX as well as for pure HMX were in quite good agreement with the literature data. The activation energy difference between the mixture and that of its corresponding pure nitramine is only slight. However, the interaction between constituents has a synergistic effect on the decomposition of the mixtures. All the mixtures, particularly the HMX-containing mixtures, have lower T_0 and T_m values than those of the pure ingredients. The DTA curves of all mixtures, of which each constituent along has an exothermic decomposition reaction, show a similar trend in which the shape of the exothermic peak of the mixture is similar to that of the constituent have a lower T_m.

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