Thermal behavior of propellants containing polycaprolactone as binder

by Chen-Chia Huang*, Tsao-Fa Yeh* and Huey-Cherng Perng**

The thermal characteristics of polycaprolactone(PCL)propellant was determined by thermogravimetry (TGA), differential thermal analysis (DTA), and modified manometric vacuum stability test(MVST). Two sets of PCL-RDX propellants prepared, with or without ammonium nitrate (AN), were examined. It was found from the results of MVST that propellants containing AN evolved much more gas than ones without AN did. The thermal decomposition reactions of both series propellants during dynamic heating were indicated by two major stages of weight losses in the TGA curves. The PCL polymer is rather compatible with RDX. From the DTA measurements, the exothermic peak temperature of AN in the propellant obviously dropped when both AN and RDX were in the present.

1. Introduction

Solid propellants generally comprise particulate solids, including oxidizers and fuel material, dispersed in an elastomeric binder which spatially immobilizes the solids. There have been numerous attempts in the last three decades to synthesize new polymers for use as energetic solid propellant binders. Nowadays, one of the most widely used binders is the hydroxy-terminated polybutadiene (HTPB) polymer. In order to increase energy of propellants, partial substituting more energetic compounds, such as nitramines, to general used oxidizer and developing energetic polymeric binders have been tried. The alternative to enhance the energy value of propellants is to contain nitro-plasticizers in the composition. Bennert et al.[1] reported that polycaprolactone (PCL) polymer is nitrate ester miscible. Shen et al.[2] confirmed that PCL is compatible with a nitrate-plasticizer trimethylolethane trinitrate (TMETN). Obviously, the PCL with suitable nitro-plasticizer has received

considerable attention as a binder in propellants. Ammonium nitrate (AN) is one of the important oxidizers in propellants[3]. The problems of hygroscopicity, phase transitions, and low burning rate limit the use of AN. Oppositely, the characteristics of the low flame temperature and no chlorine containing combustion gases take advantages to some special applications[4]. Lin et al.[5] recently investigated thermal decomposition of mixtures containing PCL and nitramines. They found that PCL is compatible with both RDX and HMX. Yet, there is no study reported on a cured PCL-RDX propellant with or without AN. Therefore, the purpose of this study is to determine the thermal behavior of cured propellants containing PCL, RDX and/or AN in various percentages.

2. Experimental

The cyclo-1, 3, 5 - trimethylene-2, 4, 6 - trinitramine (RDX)employed in this study was manufactured by a domestic arsenal. The ammonium nitrate(AN) employed was an instrument grade(99%), supplied by Ferak Laborat GmbH. The polycaprolactone (PCL)binder was synthesized in the laboratory by the method given in the patent[6]. The number average molecular weight of produced PCL polymer was 6000. Table 1 lists the summary of tested samples' compositions. Two groups of propellants were formulated and

Table 1 Summary of tested samples compositions and vacuum stability testing results

Sample No.	Composition (Weight %)			VST result (ml/g)	
	PCL	RDX	AN	110°C	120°C[*]
A-2	15	70	15	3.5	10.8
A-3	25	25	50	4.6	13.2(21)
A-4	20	40	40	5.3	13.2(27)
A-5	40	20	40	7.4	13.5(16)
A-6	25	50	25	5.7	12.9(21)
B-2	25	75		0.36	---
B-4	50	50		0.52	---

[*]: The numbers in parentheses are the heating time in hours.

tested. The first group propellants (A-series) were prepared by initial melting PCL binder and AN in an oil bath at 175°C. Then adding the surfactant, SPAN 80, the liquid mixture was emulsified with a high speed (1000 rpm) mixer. After emulsification, the mixing speed was slow down to 60 rpm. Batches of RDX particulates were added in liquid solution by several times. To obtain a well-mixed compound, the mixer was continuously operated at least 40 minutes after the last adding of RDX. The curing agent, PN-75, was then added at a NCO/OH ratio of 1.3. The slurry propellants were cured in an oven at 60°C for four days. The second group propellants (B-series) were obtained by simple blending PCL binder and RDX particles at 60°C with a low speed (60 rpm) mixing. The curing process of B-series propellants was the same as that of A-series ones.

The thermal stability of PCL propellants under vacuum was investigated with a set of automated manometric vacuum stability testing (MVST) apparatus. The apparatus consists a personal computer (Acer 915P) with a data acquisition system, pressure transducers (Sayama Model 10 - 760 M-V-R), and a metal heating block thermostat (Julius Peters) with a temperature control device (West 3000). Before testing, all transducers were well calibrated with a standard pressure gauge. The upper limit and accuracy of the pressure transducer are 760mmHg and ±0.49mmHg, respectively. The temperature of the thermostat is controlled within ±0.1°C. Five grams of samples put in a heating tube were vacuumized with a mechanical pump for more than an hour. The heating tubes were then installed in the thermostat at a desired temperature (110 or 120°C). The heating period usually was 40 hours. Since the transducers

were designed for vacuum use, the experiments were terminated whenever the system pressure was higher than the upper limit of transducers. During experiment, the pressure measurements at every ten second were stored in the computer. By using the ideal gas law, the pressure readings were then simply converted to the volume, under the standard conditions, taken of the gases released. The related description about the MVST is referred to Huang et al.[7].

The dynamic thermal decompositions of PCL-based propellants were determined by a du Pont 2000 thermal analysis system with type 1600 differential thermal analyzer (DTA), 951 thermogravimetric analyzer (TGA). A heating rate of 10 °C/min was employed throughout. The purge gas was nitrogen with a rate of 50 ml/min. The amounts of sample used in all thermal analysis measurements were 3 - 5mg. On all DTA measurements, the samples were placed in an open ceramic cell. The standard material, pure silver, was used to calibrate temperature measurements.

3. Results and Discussion

The MVST experimental results along with compositions of tested samples are listed in Table 1. For 110°C tests, the heating times were 40 hours. For 120°C tests, the gas volume evolved by A-series (except for A-2) propellants increased so much that the heating times were shortened due to the limitation of equipment. From Table 1, the gas volume released by A-2 propellant heated at 120°C for 40 hours was 10.8 ml/g. The amount of gas produced by pure RDX and pure AN heated at 120 °C under vacuum were reported[8,9] to be 0.18 and 0.06ml/g, respectively. Lin et al.[5] determined the vacuum stability test (VST) of pure PCL by the same apparatus as one
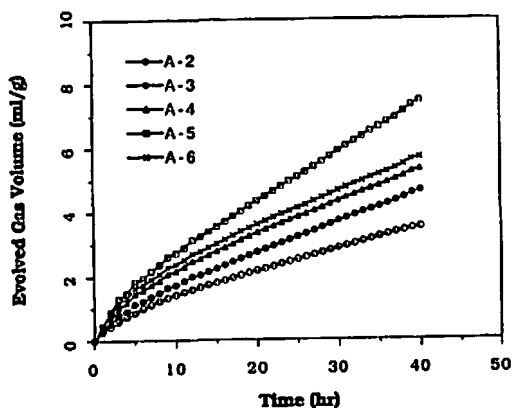
Fig. 1 Vacuum stability testing results of A-series propellants at 110℃

Fig. 3 Comparison of decomposition curves of A-6 (with AN) and B-4 (without AN) propellants at 110℃, testing started in vacuum
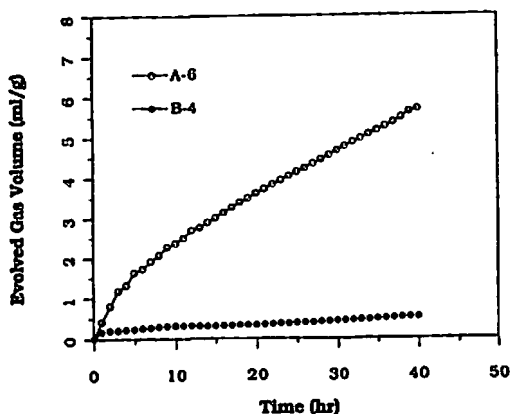

Fig. 2 Comparison of decomposition curves of A-2 propellant at various temperatures

used by this research and noted 0.155ml/g of gas evolved. Apparently, the evolved gas volume of A-2 propellant (mixture of PCL, RDX and AN) was much larger than that of any pure components. Though the pure constituents are stable, the mixed PCL-RDX-AN propellants might be thermal unstable. The VST of an uncured mixture of PCL and RDX with the same composition as B-4 propellant was also determined by Lin et al.[5] to be 0.133ml/g at 110℃. From Table 1, the VST result of B-4 propellant was 0.52ml/g. Therefore, it is noted that the evolved gas volume of cured propellant is larger than that of uncured slurries with the same composition. It is also found from Table 1 that the gas amounts released by A-series propellants are much larger than those by B-series propellants. For the same content of RDX, the VST result of A-6 propellant was much larger than that of
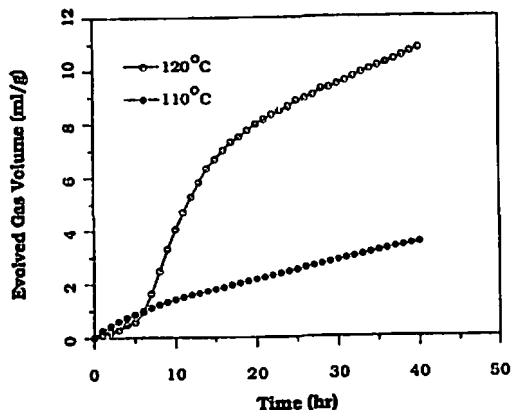
B-4 propellant. This indicates those PCL-based propellants containing AN cause to less thermal stable.

Figure 1 demonstrates the histories of MVST results of A-series propellants. The evolved gas volume increased along with the heating time. Comparing the decomposition curves of A-4 and A-5 propellants, it is found that the evolved gas increases as PCL content increases. The effect of heating temperature on the stability of propellants is illustrated in Figure 2. Initially, the decomposition curve of A-2 propellant at 120℃ was similar to that at 110℃. After 5 hours of the induction period, the curve at 120℃ became steeper. The final MVST result at 120℃ was about three times of that at 110℃. It implies that the stability of A-series propellants is obviously affected by the heating temperature. Figure 3 compares the decomposition curves of propellants with and without AN. Obviously, the decomposition curve of A-6 propellant contained AN is much sharper than that of B-4 propellant without AN.

Table 2 lists the results of thermal analyses by TGA and DTA. There were two stages weight losses observed in the TGA curves of both A and B series propellants. The percentage of weight loss in first stage was closed to the weight percentage of oxidizer (RDX and AN) of composition. This implies that PCL binder is compatible with both RDX and AN. The onset temperatures of the first stage weight loss in TGA curves of pure RDX and AN were 226.3℃ and 230.8℃, respectively. The onset temperatures of

Table 2 The TGA and DTA results

Sample No.	TGA			DTA						
	First stage weight lost		2nd stage weight lost	endothermic temp. (°C)					exothermic temp. (°C)	
	T_0(°C)	wt %	wt %	1st	2nd	3rd	4th	5th	1st T_m	2nd T_m
A-2	212.0	81.3	12.3	48.2	—	125.3	166.4	200.0	241.4	--
A-3	208.9	76.1	18.8	47.7	87.5	127.5	167.2	--	238.9	247.6
A-4	213.9	80.0	18.1	50.6	88.2	128.7	167.6	195.8	233.8	242.5
A-5	211.7	59.9	34.3	50.5	—	125.0	165.6	--	233.9	251.8
A-6	216.2	73.9	21.1	50.1	89.3	127.3	166.5	195.8	236.1	--
B-2	216.8	76.7	20.6	49.5	—	--	--	202.1	238.5	--
B-4	223.9	52.1	41.6	47.6	—	--	--	--	239.1	--
PCL	272.0	95.9	--	50.5	--	--	--	--	--	--
RDX	226.3	93.0	--	--	--	--	--	204.3	241.1	--
AN	230.8	95.3	--	--	87.3	128.9	169.8	--	277.1	--

both series propellants were less than those of either oxidizers. A similar result was reported by Lin et al. [5] There were several endothermic peaks in DTA curves, though some of them were dim. Comparing the obtained DTA results of propellants to those of pure constituent, the reasons caused to temperature differences could be rationally guessed. The first endotherm around 50 ℃ is believed to be the melting of PCL polymer. The second and third endotherms might be the phase transitions of AN crystalline. According to literature[10], the g-form (orthorhombic) of AN transits to d-form (tetragonal) at 84.2 ℃, and then transfers to e-form (cubic) at 125.2 ℃. The forth endotherm might be due to melting of AN. Urbanski[10] reported the melting point of AN is 169.6 ℃. The fifth endothermic temperature is believed to be the melting of RDX. There were two exotherms on DTA curves of A-series propellants, but only one on those of B-series propellants. Those two exotherms were rather closed each other. The exothermic peak temperatures attained in the DTA curves of pure RDX and AN were 241.1 ℃ and 277.1 ℃, respectively. From the comparison of DTA curves of A-series propellants to those of each pure constituent, it is believed that the first exotherm is due to decomposition of RDX and the second one is caused by AN decomposition. It is found that the first exothermic peak temperature was lower than that of RDX. The second exothermic peak temperature dropped more than 25 ℃ from that of AN. The energy released by decomposed reaction of RDX caused the earlier decomposition of AN.

Figure 4 illustrates the TGA decomposition curves of B-series propellants, pure PCL and RDX. Apparently, there was only one stage weight loss shown
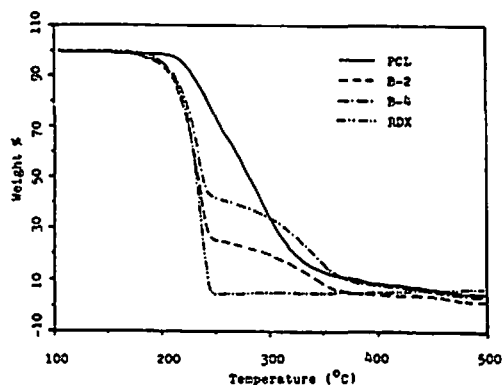

Fig. 4 Typical TGA thermograms of PCL, RDX, and their mixtures

in the TGA curves of pure components, but two stages shown in those of propellants. The TGA curve of RDX descended sharply indicating a fast decomposition reaction. The TGA curve of PCL declined gradually intimating a slow decomposition. The shape of the first stage weight loss of decomposition curves of B-series propellant was rather similar to that of RDX. The second part of TGA curves was related to PCL decomposition curve. In this regard, it might imply that PCL is compatible with RDX.

Figure 5 shows the typical TGA weight loss curves of A-series propellants. There were two stages weight losses in both curves. The A-4 propellant comprised 80 weight percents of energetic compounds (40 wt% of RDX and 40 wt% of AN). There were 20 weight percents of RDX replaced by PCL in A-5 propellant. As expected, the first stage weight loss of A-4 curve was sharper than that of A-5 one. The related DTA curves of A-4 and A-5 propellants are shown in Figure 6. For the same reason, the height of exotherm of A-5 propellant was lower than that of A-4
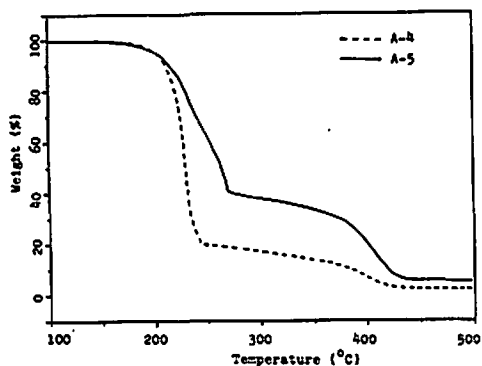
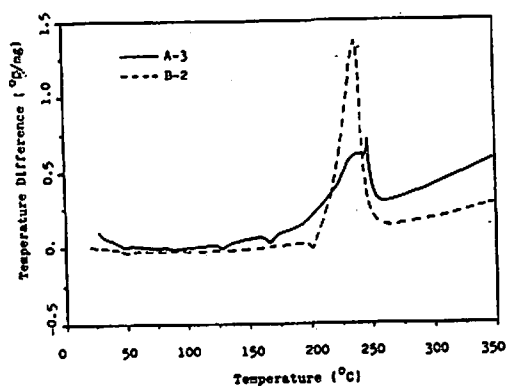Fig. 5 Comparison of TGA curves of A-4 and A-5 propellants

Fig. 7 Comparison of DTA curves of A-3 (with AN) and B-2 (without AN) propellants
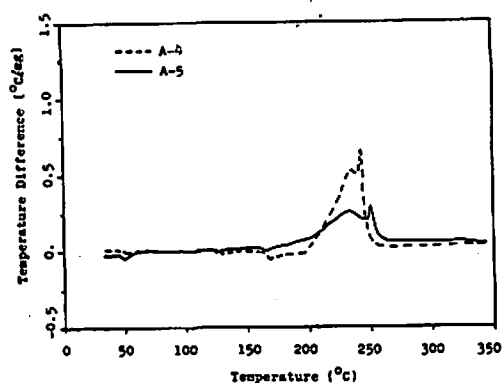

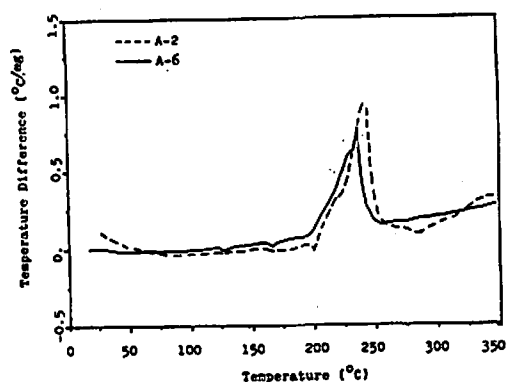Fig. 6 Comparison of DTA curves of A-4 and A-5 propellants

Fig. 8 Comparison of DTA curves of A-2 and A-6 propellants

propellant. As aforementioned, there are several small endotherms on DTA thermograms of A-series propellants. From Figure 6, the melting endotherm of RDX virtually disappeared on the DTA curve of A-5 propellant. It should be remarked that two exotherms by decomposition of RDX and AN are partially overlapped. Both exothermic peak temperatures of propellants apparently dropped comparing to those of pure RDX and pure AN.

Figure 7 compares the DTA curves of propellants with (A-3) and without (B-2) AN. These two propellants contained the same amount of PCL binder. Only a single exothermic peak could be seen in the DTA curve of B-2 propellant. Two split exothermic peaks were observed for A-3 propellant. The exothermic peak of B-2 propellant is much higher than that of A-3 one. This is expected because the heat of decomposition of RDX is larger than that of AN[b]. It is noted that there are no endotherms on the DTA curve of B-2 pro-

pellant observed due to phase transition of AN.

Both A-2 and A-6 propellants contained the same weight fraction of PCL binder and AN oxidizer. The A-2 propellant contained much more RDX than the A-6 propellant did. The DTA thermograms of A-2 and A-6 propellants are compared in Figure 8. The exotherms caused by thermal decompositions of RDX and AN were seemingly merged in a singlepeak. This is a little difference from the results shown in Figure 6. By comparing the DTA curve of A-6 to that of A-3 (in Figure 7), the difference could be explained by the large content of RDX. It is noted that the exothermic peak of A-2 propellant is higher than that of A-6 propellant owing to a higher content of energetic compounds.

4. Conclusions

The thermal decomposition of PCL-based propellants was investigated by a manometric stability testing (MVST) apparatus under vacuum, by a dif-

ferential thermal analyzer (DTA) and by a thermogravimetric analyzer (TGA). From results of the MVST experiments, the evolved gas volumes of mixtures containing AN were much larger than those of ones without AN. There were two stages weight losses observed in the TGA curves of propellants. The percentage of weight loss during the first stage was closed to the weight percentage of oxidizer contained. The PCL polymer was confirmed to be compatible with RDX. From the DTA measurements, the exothermic peak temperature of AN obviously dropped when both AN and RDX were simultaneously presented in the propellant.

5. References

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バインダーとして Polycaprolactone を含有する推進薬の熱的挙動

黄　振家*，葉　早發*，彭　匯成**

Polycaprolactone(PCL)とRDXを含む推進薬の熱的性質を熱重量分析（TGA），示差熱分析（DTA）および改良真空安定度試験（MVST）を用いて測定した。その結果硝酸アンモニウムを含むPCL-RDX推進薬は硝酸アンモニウムを含まないものよりも多量のガスを発生することが確認された。また，硝酸アンモニウムの発熱温度は，RDXの存在により低下することがわかった。

（*中正理工学院　応用化学系，大渓　桃園　台湾　中華民国
　　**中山科学研究院　第4研究所，龍潭　桃園　台湾　中華民国）