Thermochimica Acta, 181 (1991) 277–288
Elsevier Science Publishers B.V., Amsterdam

THERMAL BEHAVIOUR AND COMPATIBILITY OF POLYURETHANE PCL/BDNPA/F AND PCL/TMETN BLENDS

SHIN-MING SHEN, FANG-MO CHANG, JEN-CHING HU and AN-LU LEU *

Department of Applied Chemistry, Chueg Cheng Institute of Technology, Tachi 33509 (Taiwan)

(Received 18 September 1990)

ABSTRACT

The thermal behaviour of two sets of polymer blends, mixtures of poly(caprolactone) (PCL) of molecular weights 2000, 6000 and 10000 with eutectic mixtures of bis(2,2-dinitropropyl) acetal (BDNPA) and bis(2,2-dinitropropyl) formal (BDNPF), and of PCL with nitrate-plasticizer trimethylolethane trinitrate (TMETN), were examined by thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC). The thermal decomposition reactions of PCL/BDNPA/F or PCL/TMETN blends during dynamic heating are indicated by two major stages of weight loss in the TG–DTG traces. The DSC traces show that there are two major exothermic reactions for each formulation. It was found that the enthalpy change, ΔH, for the first exothermic reaction is proportional to the BDNPA/F or TMETN concentration. The maximum peak temperature (T_m) of the first exothermic reaction shifted to a higher temperature as the BDNPA/F ratio increased. However, for the TMETN system, there was no obvious change. It is concluded that TMETN has a higher thermal compatibility with PCL than has BDNPA/F.

INTRODUCTION

The use of polyurethane polymers as binders has been a cornerstone of solid rocket-propellant technology. Lately, there has been an interest in reducing the signature and in increasing the performance of solid rockets. Several varied programs have been devised to develop and evaluate new ingredient materials [1–4]. Poly(caprolactone) (PCL), the nitrate plasticizer TMETN and BTTN (butylene glycol dinitrate) have received considerable attention as suitable binder systems in propellants [5], and the mechanical properties of the composite system are especially good when using this binder system. Thermal analytical techniques such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG) and derivative thermogravimetry (DTG) have been used extensively for the study of the thermal behaviour and decomposition patterns of

---

* To whom correspondence should be addressed.

0040-6031/91/$03.50

polymers [1–4]. In this work TG–DTG and DSC have been employed to investigate the thermal behaviour of the blends of PCL with eutectic mixtures of BDNPA/F and with TMETN in various percentages.

EXPERIMENTAL AND RESULTS

Materials

PCL prepolymers are difunctional for PCL 2000 (molecular weight 2000) and PCL 6000 (molecular weight 6000) systems, and multifunctional for the PCL 10000 (molecular weight 10000) system. The cross-linking agent N-100 is a commercially available tri-isocyanate made by the Nan-Pao company, Taiwan. General specifications of one nitroplasticizer BDNPA, BDNPF and nitrate plasticizer TMETN are listed in Table 1.

Sample preparation

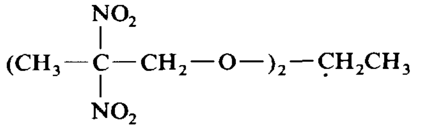
The polymer blends were generally formulated to an NCO/OH ratio of 1:2. All the polymer blends were prepared by a one-step method. The ingredients were dried to a moisture content of less than 0.02 wt.%. The compositions of the four series of polymer blends are listed in Table 2: AB (PCL 6000/BDNPA/F), BB (PCL 10000/BDNPA), CB (PCL 2000/

TABLE 1

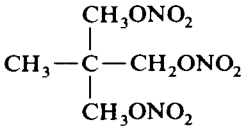
Physical properties of BDNPA, BDNPF, BDNPA/F and TMETN

Compound [a]	Boiling point (°C/mmHg)	Melting point (°C)	Density at 25°C (g ml^{-1})
BDNPA	150/0.01	33 ~ 34	1.366
BDNPF	152/0.01	31	1.411
BDNPA/F	150/0.01	−15	1.397
TMETN	–	−3	1.460

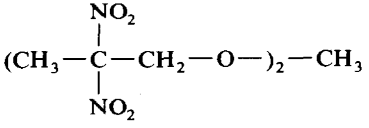
[a] Structure formulae

BDNPA: 

$(CH_3-\overset{NO_2}{\underset{NO_2}{C}}-CH_2-O-)_2-CH_2CH_3$

TMETN: 

$CH_3-\overset{CH_3ONO_2}{\underset{CH_3ONO_2}{C}}-CH_2ONO_2$

BDNPF: 

$(CH_3-\overset{NO_2}{\underset{NO_2}{C}}-CH_2-O-)_2-CH_3$

TABLE 2

Composition and weight loss at various TG–DTG measurement stages of PCL with various concentrations of BDNPA/F and TMETN

Sample no.	Composition (wt.%)					Weight loss (%)	
	PCL6000	PCL10000	PCL2000	BDNPA/F	TMETN	1st stage	2nd stage
AB-1	100	–	–	–	–	97	3
AB-2	80	–	–	20	–	26	71
AB-3	70	–	–	30	–	37	59
AB-4	60	–	–	40	–	45	53
AB-5	50	–	–	50	–	57	41
AB-6	40	–	–	60	–	66	33
AB-7	30	–	–	70	–	73	25
BB-1	–	100	–	–	–	97	2
BB-2	–	80	–	20	–	30	65
BB-3	–	70	–	30	–	37	58
BB-4	–	60	–	40	–	45	51
BB-5	–	50	–	50	–	53	42
BB-6	–	40	–	60	–	63	32
B8-7	–	30	–	70	–	72	24
CB-1	–	–	100	–	–	97	0
CB-2	–	–	80	20	–	27	70
CB-3	–	–	70	30	–	34	63
CB-4	–	–	60	40	–	45	52
CB-5	–	–	50	50	–	56	41
CB-6	–	–	40	60	–	65	32
CB-7	–	–	30	70	–	74	24
CT-1	–	–	100	–	–	99	1
CT-2	–	–	80	–	20	20	78
CT-3	–	–	70	–	30	30	68
CT-4	–	–	60	–	40	39	58
CT-5	–	–	50	–	50	50	48
CT-6	–	–	40	–	60	55	43
CT-7	–	–	30	–	70	70	29

BDNPA/F) and CT (PCL 2000/TMETN). The mixtures of PCL prepolymer, cross-linking agent N-100 and plasticizer BDNPA/F or TMETN were cured in an oven at 65°C for 7 days.

TG–DTG measurements

TG–DTG measurements were carried out on a Perkin–Elmer thermal analyser. In the TG–DTG measurements, samples weighing 6–8 mg were heated at the rate of 20°C min^{-1} from 30 to 700°C under a static

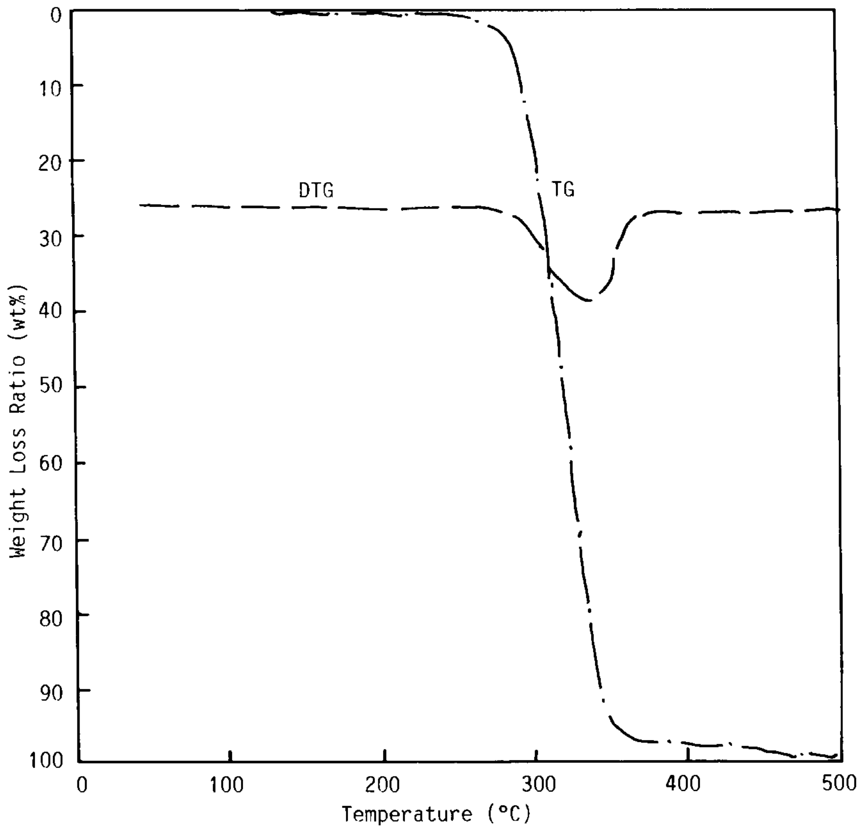


Fig. 1. TG–DTG results for pure PCL binder.

atmosphere of nitrogen gas. The results of the TG–DTG measurements are shown in Figs. 1 and 2, and are also listed in Table 2.

DSC measurements

DSC measurements were performed on a Dupont 1090 thermal analyser. In the DSC measurements, samples weighing 1–2 mg were heated at the rate of 20 °C min^{-1} in an aluminium crucible from 30 to 700 °C under a static atmosphere of nitrogen gas. The results of the DSC measurement are shown in Table 3 and in Figs. 3 and 4.

DISCUSSION

Typical features of TG–DTG curves for PCL binder (without plasticizer) and PCL binder with various percentages of plasticizer are shown in Figs. 1 and 2. The percentage weight losses for each binder are listed in Table 2.

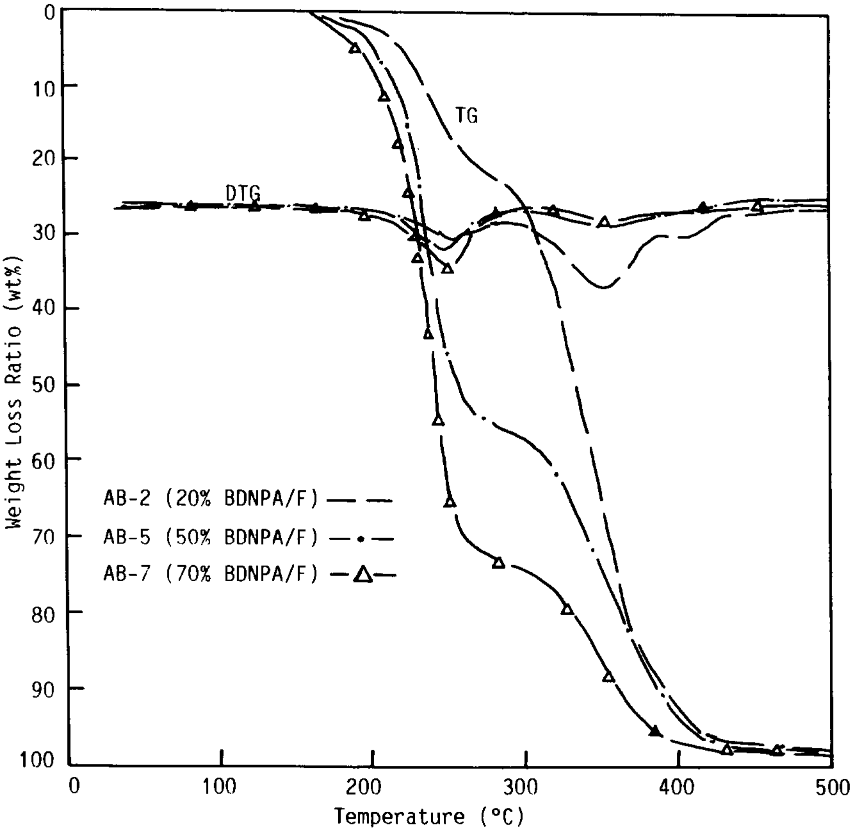


Fig. 2. TG–DTG results for PCL with nitroplasticizer BDNPA/F in various concentrations.

According to Table 2 and referring to the concentration of BDNPA/F or TMETN in each binder system, it can be seen that the first-stage weight-loss of each system is almost the same as the corresponding plasticizer concentration. Table 3 shows the DSC measurement results: the maximum reaction temperature (T_m) increases proportionally with the concentration of BDNPA/F. However, blends containing TMETN show no notable change in T_m values as the concentration of TMETN changes. The enthalpy change of each sample is proportional to the concentration of BDNPA/F or TMETN. Figure 2 illustrates TG–DTG traces for samples of PCL with various percentages of BDNPA/F. Referring to Fig. 2, it can be seen that both formulations have two major stages of weight loss. The first-stage weight-loss is about 20%, 50% and 70% for formulations with 20%, 50% and 70% BDNPA/F respectively. The second-stage weight-loss is about 80%, 50% and 30% for formulations with 20%, 50% and 70% BDNPA/F respectively. The DSC curves of polyurethane PCL without plasticizer BDNPA/F or TMETN are shown in Fig. 3. Some typical DSC traces for formulations with plasticizer are shown in Fig. 4. Figure 3 shows that two endothermic

TABLE 3

Maximum reaction temperature (T_m) and enthalpy change (ΔH) in DSC measurements of PCL with various concentrations of BDNPA/F or TMETN

Sample no.	T_m (°C)	$-\Delta H$	$-\Delta H$/(BDNPA/F)%	$-\Delta H$/(TMETN)%
		(cal g^{-1})		
AB-2	245	72	36	–
AB-3	250	106	35	–
AB-4	251	137	34	–
AB-5	253	163	33	–
AB-6	254	165	28	–
AB-7	257	195	28	–
BB-2	253	90	45	–
BB-3	251	117	39	–
BB-4	252	135	34	–
BB-5	252	156	31	–
BB-6	257	184	31	–
BB-7	260	192	27	–
CB-2	240	97	48	–
CB-3	242	134	45	–
CB-4	247	168	42	–
CB-5	248	170	34	–
CB-6	250	210	35	–
CB-7	252	231	33	–
CT-2	201	100	–	50
CT-3	202	144	–	48
CT-4	202	161	–	40
CT-5	203	169	–	34
CT-6	201	174	–	29
CT-7	203	224	–	32

reactions take place at 58 and 337 °C; an exothermic reaction peak then appears at 430 °C. The first endothermic reaction is attributed to the breaking of the aggregated soft segment, and the second may be attributed to the breaking of the cross-linked form of the polymer [6]. At temperatures above 430 °C, exothermic reaction peaks were recorded for the PCL binder (without plasticizer) system. This is attributed to the overwhelming oxidative reaction of the polymer. The TG–DTG results of Fig. 1 support the above explanation.

Figure 4 shows the DSC curves of systems of PCL with different ratios of BDNPA/F. An endothermic reaction peak appears at around 55 °C for PCL systems with 20% BDNPA/F and 50% BDNPA/F. This behaviour is attributed to the breaking of the aggregated soft segment. However, for the PCL system with 70% BDNPA/F, there is no endothermic reaction peak at around 55 °C. This discrepancy may be explained by the lower density of

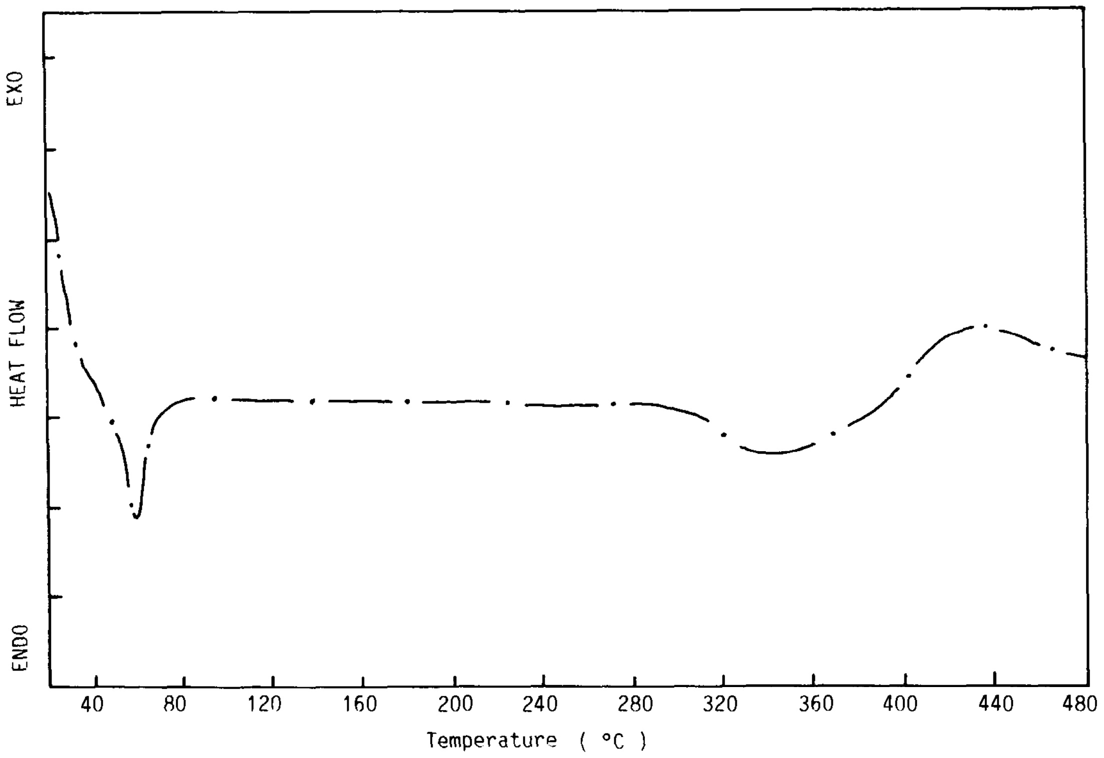


Fig. 3. DSC scans for pure PCL binder.

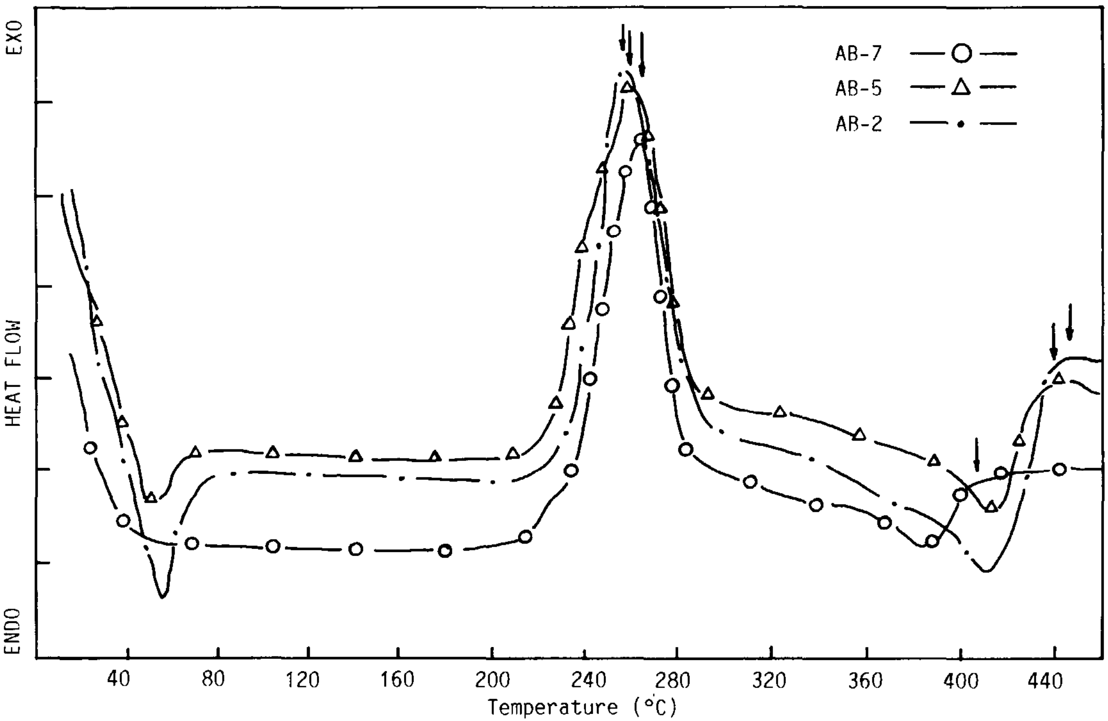


Fig. 4. DSC scans for PCL with nitroplasticizer BDNPA/F in various concentrations.

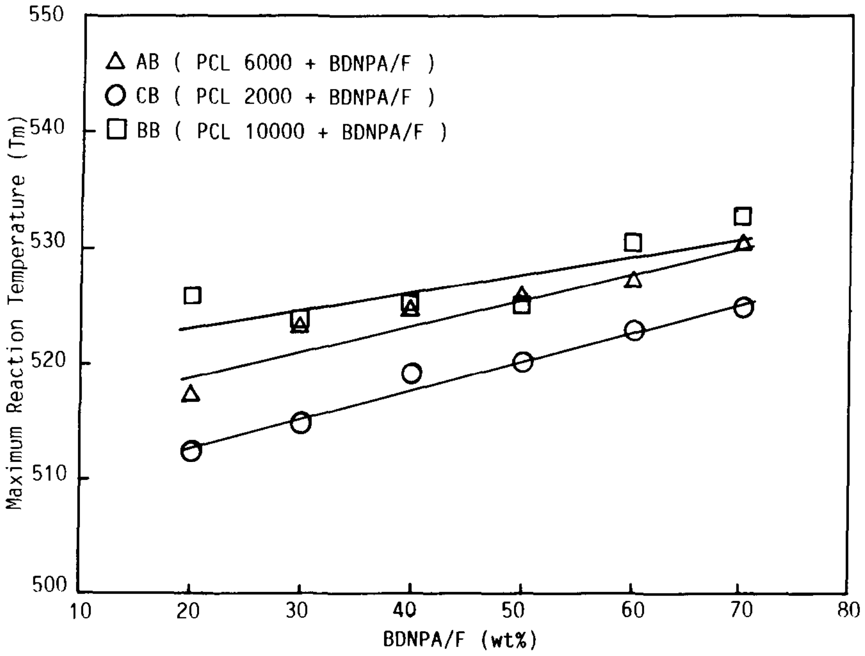


Fig. 5. Dependence of T_m on the BDNPA/F contents for samples of PCL/BDNPA/F.

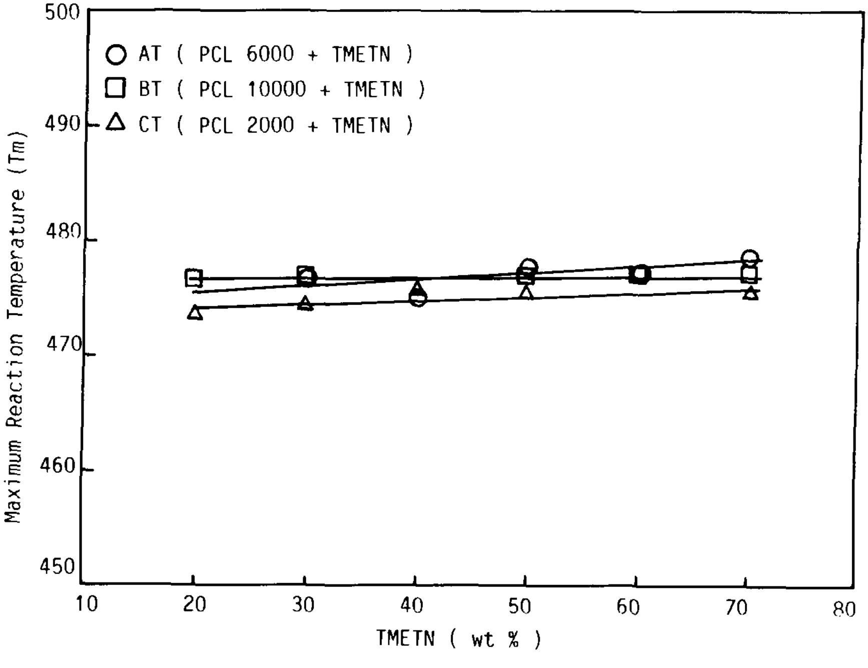


Fig. 6. Dependence of T_m on the TMETN contents for samples of PCL/TMETN.

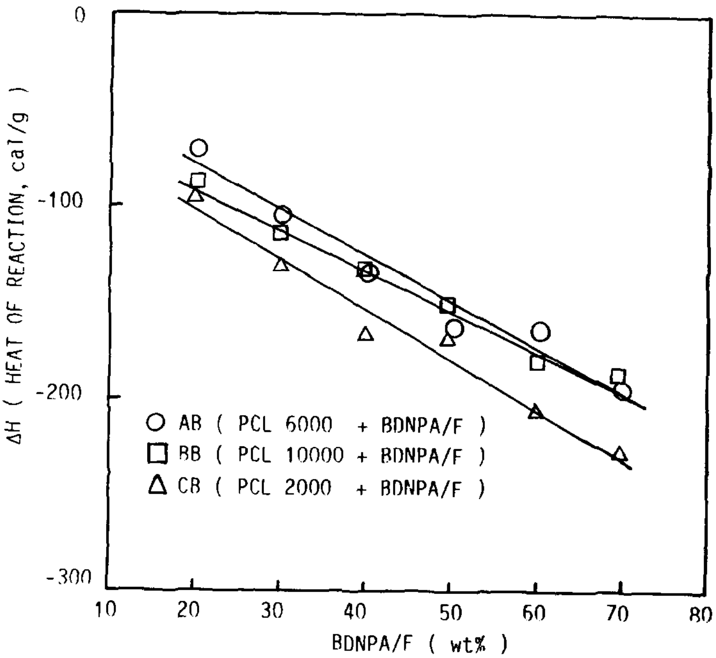


Fig. 7. Dependence of enthalpy change (ΔH) as a function of BDNPA/F concentration.

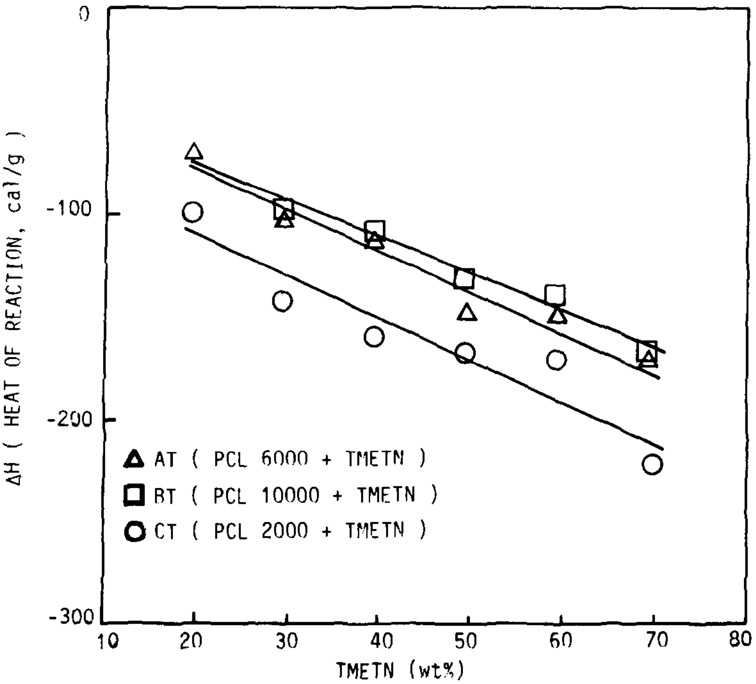


Fig. 8. Dependence of enthalpy change (ΔH) as a function of TMETN concentration.

the PCL polyurethane in the 70% BDNPA/F system. Thus, the endothermic reaction peak gradually vanishes. From 220 to 280 ° C, the AB series (PCL 6000/BDNPA/F) shows only one exothermic peak; and from 400 to 460 ° C, one exothermic reaction takes place. Table 3 and Figs. 7 and 8 illustrate that the value of ΔH for the first exothermic reaction of each system increases with increasing BDNPA/F or TMETN concentration in the test samples; there is a linear relationship between the BDNPA/F or TMETN concentration and the ΔH values. Figure 5 shows that the maximum reaction temperature (T_m) of the first exothermic peak shifts to higher temperatures as BDNPA/F concentration increases. But for the TMETN system, there is no change in T_m values as the concentration of TMETN changes, as shown in Fig. 6.

Thermal analysis techniques have been widely used in the evaluation of the compatibility of explosive ingredients by many investigators [7–11]. Beach and Canfield [8] have suggested that a system be regarded as compatible if the change in maximum temperature (T_m) is less than 2 ° C; thus, in the present study, PCL and TMETN might be considered as compatible with each other according to their criterion.

Referring to the weight loss results of the binder systems listed in Table 2, it is concluded that the first exothermic reaction corresponds to the BDNPA/F or TMETN decomposition reaction. At temperatures higher than 380 ° C, a broad exothermic reaction peak is observed due to the decomposition of residual polyurethane, PCL, molecules. It is found that the decomposition reaction temperature of residual polyurethane shifts to lower temperatures as the concentration of BDNPA/F increases. Therefore it is concluded that the PCL and BDNPA/F molecules interact with each other. The same results were also found for the polyurethane PEG and BDNPA/F blend decomposition reaction [12]. For the TMETN systems, the decomposition reaction temperature of residual PCL molecules shifts to lower temperatures as the concentration of TMETN increases. Further investigation of the decreasing reaction temperature of PCL in mixtures of PCL with BDNPA/F or TMETN is needed.

CONCLUSION

The thermal decomposition of polymer blends, and mixtures of polyurethane PCL and BDNPA/F (or TMETN) indicate a two-stage reaction. The first stage corresponds to the BDNPA/F or TMETN decomposition, and the second stage corresponds to decomposition of the PCL molecule. PCL and BDNPA/F molecules interact with each other and PCL is more compatible with TMETN than with BDNPA/F. The values of ΔH and T_m of the first decomposition stage are proportional to BDNPA/F concentration in the PCL and BDNPA/F system. For the TMETN system, ΔH is proportional to TMETN concentration, but with no significant change in T_m as TMETN concentration increases. There is a linear relationship between ΔH and the concentration of BDNPA/F (or TMETN).

REFERENCES

1 R. Reed, Proc. 13th Int. Pyrotechnic Seminar, Grand Junction, CO, July, 1988, p. 678.
2 A.M. Helmy, AIAA paper no. 84-1434, 1984.
3 S. Wise and J.J. Rocchio, 18th JANNAF Combustion Meeting, Pasadena, CA, October 1981, pp. 539–544.
4 K. Klager, AIAA paper no. 84-1239, 1984.
5 J. Kenneth, U.S. Patent 475432, October 4, 1988.
6 C. Hepburn, Polyurethane Elastomers, Applied Science Publishers, Ltd., London and New York, 1982, Chapter 3.
7 Z.R. Liu, C.M. Yin, C.Y. Wu and M.N. Chang, Propellants, Explosives, Pyrotechnics, 11 (1986) 10.
8 N.E. Beach and V.K. Canfield, Compatibility of Explosives with Polymer, Picatinny Arsenal, Dover, AD-721004, 1971.
9 L. Reich, Thermochim. Acta, 5 (1973) 433.
10 L. Reich, Thermochim. Acta, 8 (1974) 399.
11 A.S. Tompa, Thermochim. Acta, 63 (1983) 9.
12 S.M. Shen and A.L. Leu, Thermochim. Acta, (1990), in press.