Thermochimica Acta, 176 (1991) 75–87
Elsevier Science Publishers B.V., Amsterdam

THERMAL CHARACTERISTICS OF POLYURETHANE PEG AND BDNPA/F BLENDS

SHIN-MING SHEN *, AN-LU LEU ** and HSI-CHENG YEH

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

(Received 2 May 1990)

ABSTRACT

Thermal behaviours of polymer blends, mixtures of polyurethane PEG (PEG, mol.wt. = 2000 or 3000) and eutectic mixtures of bis-2,2-dinitropropyl acetal (BDNPA) and bis-2,2-dinitropropyl formal (BDNPF), were examined by thermogravimetry, differential thermogravimetry and differential scanning calorimetry. The thermal decomposition reaction of a PEG/BDNPA/BDNPF blend at a dynamic heating rate is indicated by two major stages of weight loss in the TG-DTG traces. The DSC trace indicates that two major exothermic reactions exist for each formulation. It is found that the enthalpy change (ΔH) is proportional to the BDNPA/F concentration for the first stage exothermic reaction. The maximum peak temperature (T_m) of the first exothermic reaction shifts to higher temperature as the BDNPA/F ratio is increased.

INTRODUCTION

The polyurethane polymeric system has been widely used as an adhesive sealing fiber, a foam elastomer, and as an excellant base for solid composite propellants [1–3]. Polyurethane polymer binders have been a cornerstone of solid rocket propellant technology. Lately, there has been interest in reducing the signature and in increasing the performance of solid rockets. Several programs have been conducted in different ways to develop and evaluate new energetic ingredients. Polyurethane plasticized with nitroplasticizer, a mixture of polyethylene glycol (PEG) and a eutectic composition of bis(2,2-dinitropropyl) acetal (BDNPA) and bis(2,2-dinitropropyl) formal (BDNPF), has received considerable attention as a good energetic binder system to be used in minimum smoke propellant and plastic bonded explosives [3–5]. Furthermore, this binder system has received particular attention in the low vulnerability ordnance program [6,7] for a gun propellant. Thermoanalytical techniques such as differential thermal analysis (DTA), differential scanning

---

* School of Defence Sciences.

** Author to whom correspondence should be addressed.

0040-6031/91/$03.50

calorimetry (DSC), thermogravimetry (TG) and differential thermogravimetry (DTG), have been used extensively for the study of the thermal behavior and decomposition patterns of polymers [3–5]. In this work TG-DTG and DSC have been employed to investigate the thermal behavior of polymer blends, a mixture of PEG and a eutectic mixture of BDNPA/F, in various percentages.

EXPERIMENTAL AND RESULTS

Materials

All PEG prepolymers are difunctional, PEG 4000 (mol.wt. 3000) and PEG 2000 (mol. wt. 2000); both were supplied by the Wako Company. Crosslinking agent N-100 is a commercially available triisocyanate. General specifications of nitroplasticizer BDNPA and BDNPF are listed in Table 1.

Sample preparation

The polymer blends were generally formulated to an NCO/OH ratio of 1.1. All the polymer blends were prepared by a one-step method. Ingredients were dried to a moisture content of less than 0.02%. The compositions of series A and B samples are listed in Table 2. The mixtures of PEG prepolymer, crosslinking agent N-100 and BDNPA/F were cured in an oven at 65 °C for 7 days.

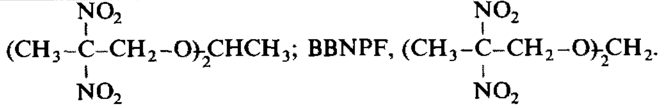
TG-DTG measurements

TG-DTG measurements were carried out using a Perkin–Elmer thermal analyzer. In the TG-DTG measurements, samples weighing 6–8 mg were heated at a rate of 20 °C min^{-1} from 25 °C to 700 °C under a static

TABLE 1

Physical properties of BDNPA, BDNPF and BDNPA/F

Compound [a]	Boiling point [b] (°C)	Melting point (°C)	Density at 25 °C (g ml^{-1})
BDNPA	150	33–34	1.366
BDNPF	152	31	1.411
BDNPA/F	150	−15	1.383, 1.397

[a] Formulae: BDNPA,  $(CH_3-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-O)_2CHCH_3$; BBNPF, $(CH_3-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-O)_2CH_2$.

[b] At 0.01 mm Hg.

TABLE 2

Composition and weight loss at various TG-DTG measurement stages

Sample no.	Composition			Weight loss (%)		
	PEG (wt.%)		BDNPA/F	1st stage	2nd stage	3rd stage
	3000 [a]	2000 [a]				
A-0	100		0	17	79	
A-1	80		20	16	4	78
A-2	70		30	28	2	67
A-3	60		40	40	57	
A-4	50		50	50	47	
A-5	40		60	60	37	
A-6	30		70	59	39	
A-7	20		80	79	19	
B-0		100	0	24	70	
B-1		80	20	16	4	77
B-2		70	30	28	2	68
B-3		60	40	35	5	57
B-4		50	50	50	48	
B-5		40	60	55	42	
B-6		30	70	67	30	

[a] Mol. wt.

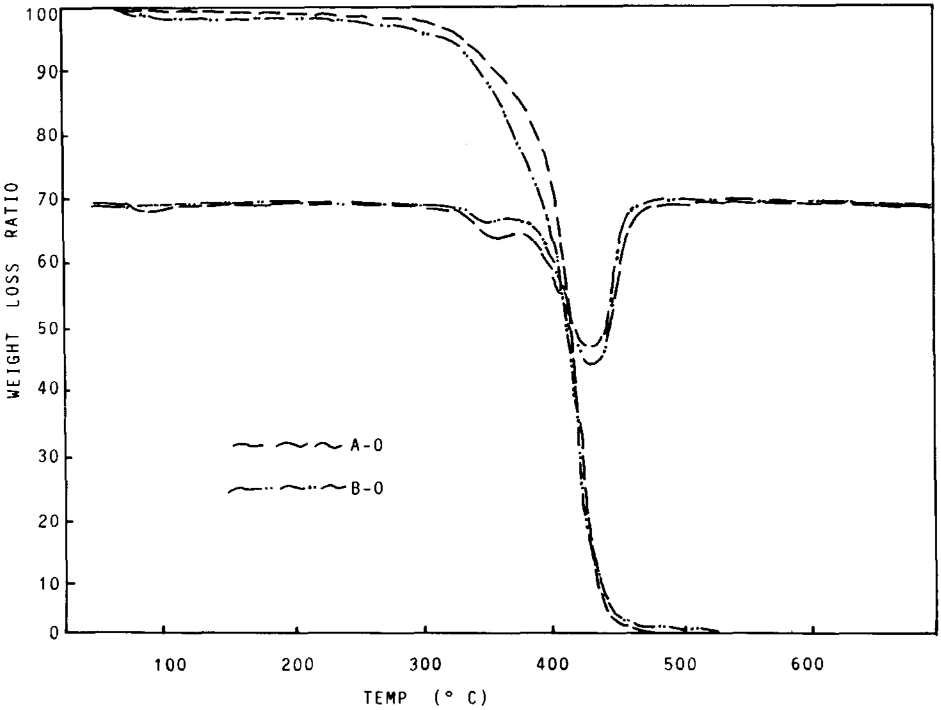


Fig. 1. TG-DTG results for formulations A-0 and B-0.

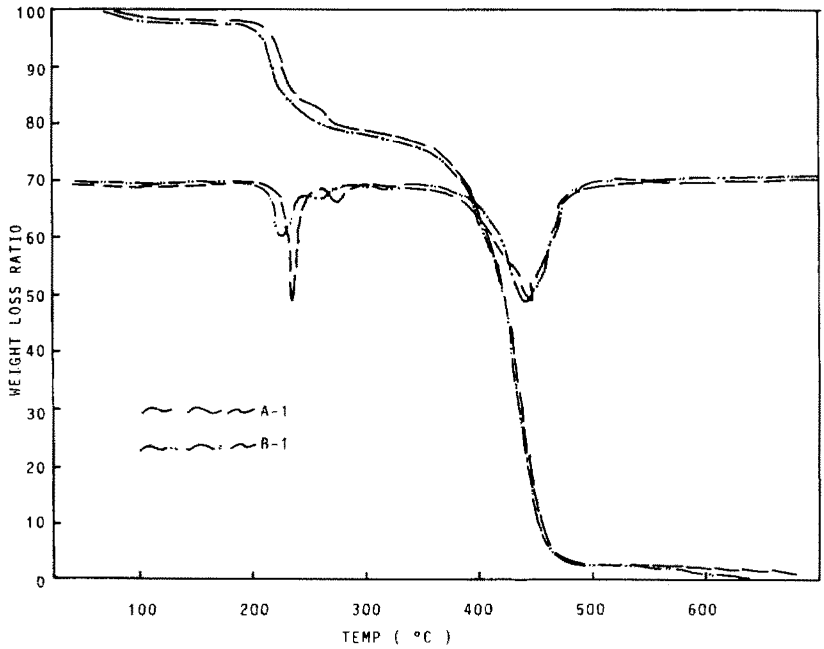


Fig. 2. TG-DTG results for formulations A-1 and B-1.

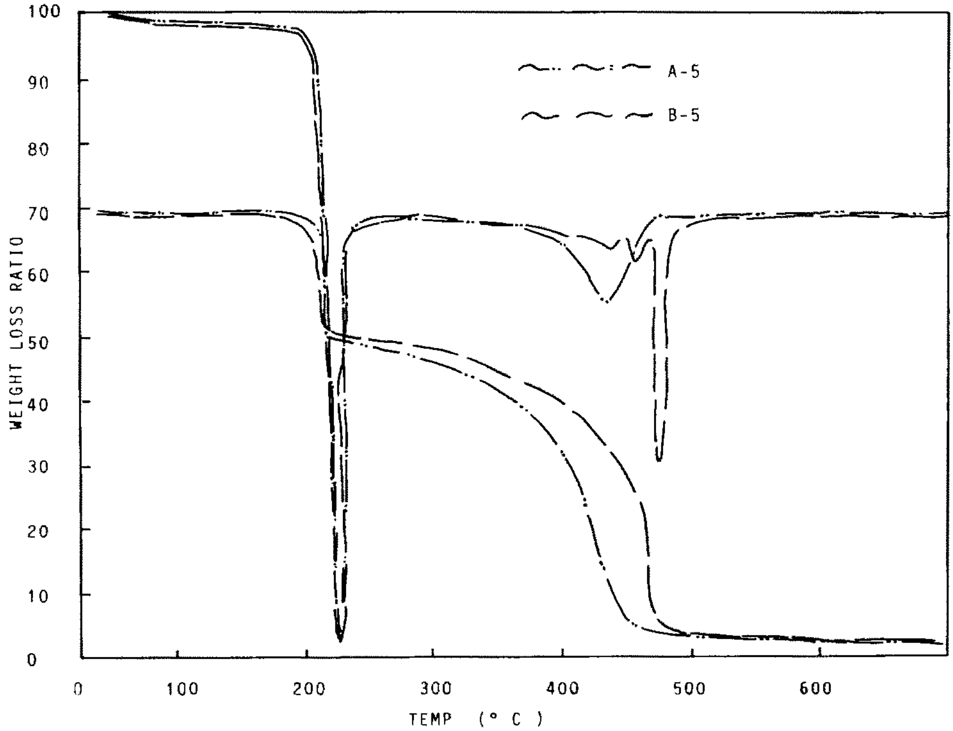


Fig. 3. TG-DTG results for formulations A-5 and B-5.

TABLE 3

Maximum reaction temperature (T_m), on set temperature (T_o), and enthalpy change for various samples in DSC measurements

Sample No.	ΔH (cal g^{-1})	T_m (°C)	T_o (°C)	ΔH/(BDNPA/F)% (cal g^{-1})
A-1	−99	222	208	−49.4
A-2	−157	222	203	−52.4
A-3	−210	226	209	−52.5
A-4	−240	230	206	−48
A-5	−301	233	205	−50.1
A-6	−337	239	209	−48.1
A-7	−369	243	209	−46
B-1	−107	228	207	−53.2
B-2	−159	222	206	−52.8
B-3	−192	226	207	−47.8
B-4	−232	223	208	−46.3
B-5	−262	232	208	−43.6
B-6	−321	238	210	−45.8

atmosphere of nitrogen. Results of TG-DTG measurements are shown in Figs. 1–3 and in Table 2.

DSC measurements

DSC measurements were performed using a Dupont 1090 thermal analyzer. In the DSC measurements, samples weighing 1–2 mg were heated at a rate of 20°C $\min^{-1}$ in an aluminum crucible from 25°C to 700°C under a static atmosphere of nitrogen. The results of DSC measurements are shown in Table 3 and Figs. 4–9.

DISCUSSION

Three typical features of TG-DTG curves for series A and B samples are shown in Figs. 1–3. The percentage weight loss for each binder is displayed in Table 2. According to Table 2, and referring to the concentration of BDNPA/F of each binder, the percentages of the first-stage weight loss of each formulation are equal to the nitroplasticizer concentration of the corresponding binder. Table 3 shows the DSC measurements of each sample. It is shown that the maximum reaction temperature (T_m) increases as the concentration of BDNPA/F increases and the onset temperature (T_o) changes slightly as the BDNPA/F concentration increases. The enthalpy change of each sample increases as the concentration of BDNPA/F increases.

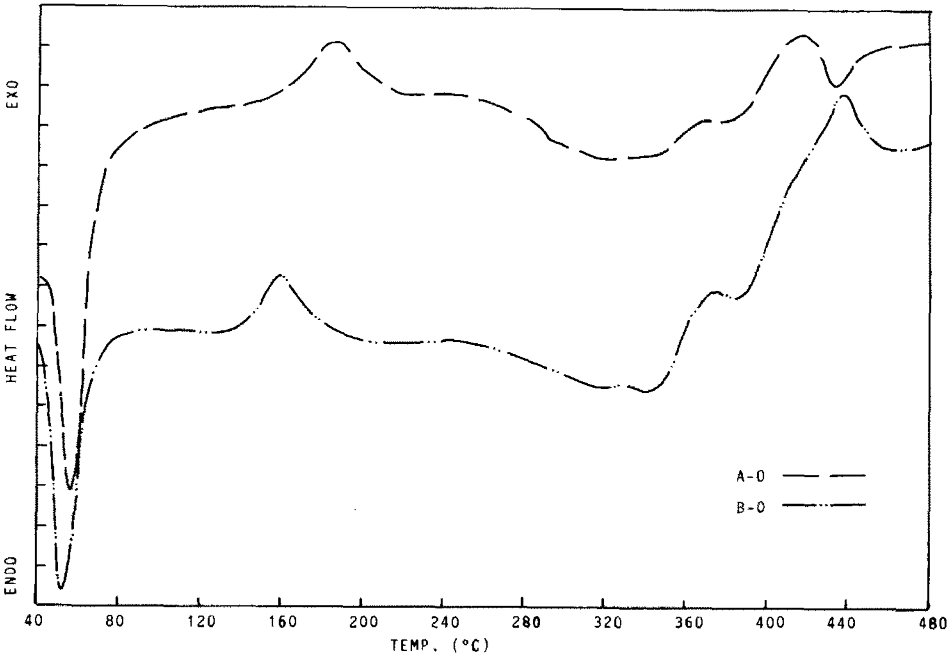


Fig. 4. DSC scans for formulations A-0 and B-0.

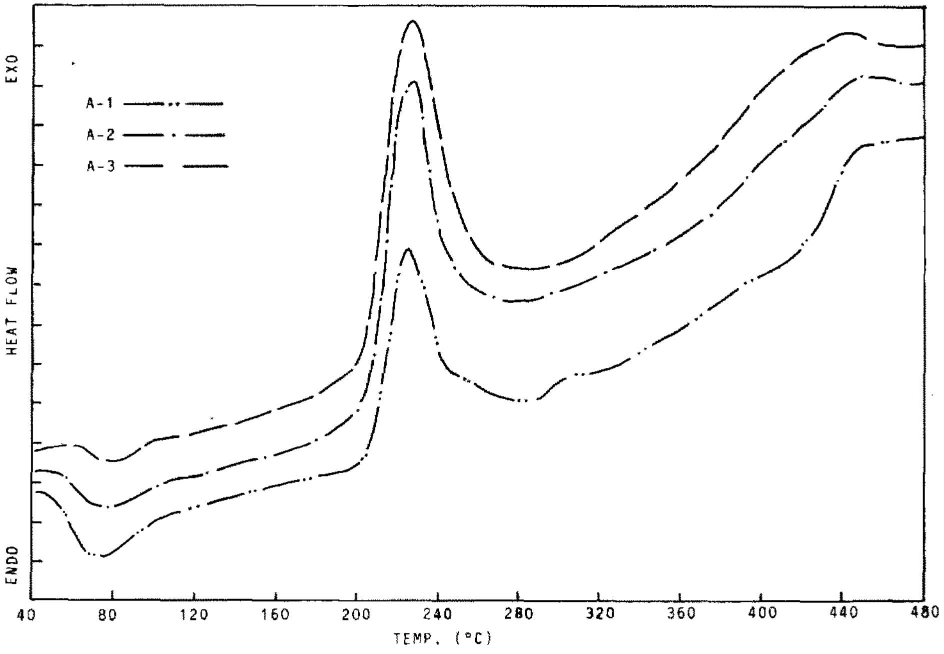


Fig. 5. DSC scans for formulations A-1, A-2 and A-3.

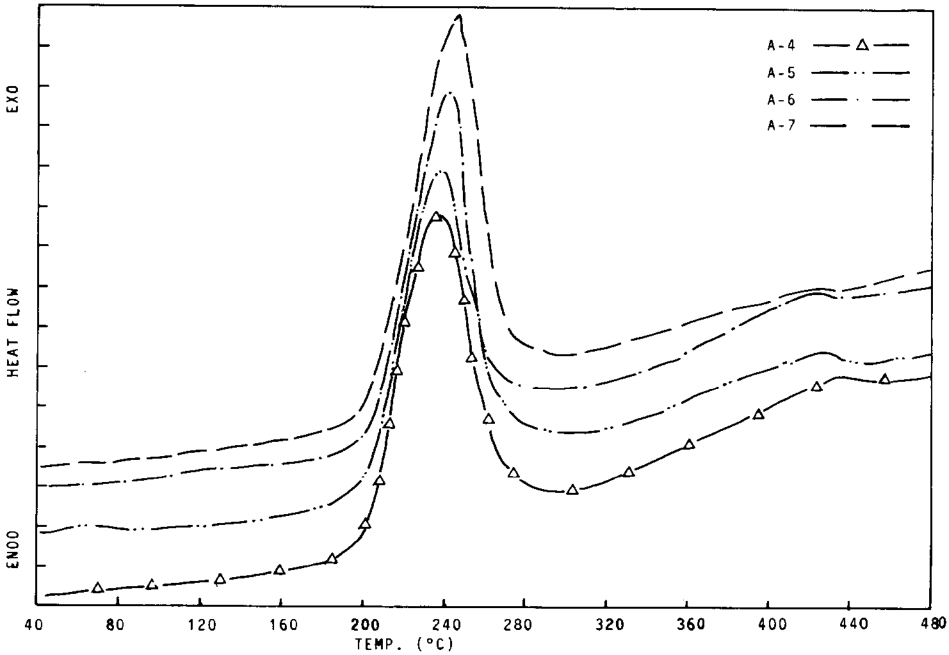


Fig. 6. DSC scans for formulations A-4, A-5, A-6 and A-7.

Figure 1 illustrates the TG-DTG trace for A-0 and B-0 systems. It is shown that there are two distinct weight loss stages. This phenomenon could be explained as PEG of different molecular weights reacting at different decomposition temperatures [8]. Figure 2 shows some typical TG-DTG traces selected either from formulation series A-1, A-2, A-3 or from series B-1, B-2, B-3. Figure 3 shows typical TG-DTG traces selected either from formulation series A-4, A-5, A-6, A-7 or from series B-4, B-5, B-6. Referring to Figs. 2 and 3 and Table 2, it is found that both series have two major stages of weight loss. However, for the A-1, A-2, A-3 (or B-1, B-2, B-3) system, the first stage weight loss curve indicates two distinct peaks and the total weight losses are about 20%, 30% and 40%, respectively. For the A-4 to A-7 (or B-4 to B-6) system, the first stage weight loss curve indicates only one peak and the weight losses are about 50%, 60%, 70% and 80%, respectively.

The DSC curves of polyurethane A-0 and B-0 (without BDNPA/F) are shown in Fig. 4 and the typical DSC traces of formulation A-1 to A-7 and B-1 to B-6 are shown in Figs. 5–8. A-0 and B-0 systems have similar DSC patterns. Both have one endothermic peak at about 60 °C and three exothermic peaks at about 170, 350 and 429 °C. However, some differences exist between formulations A-0 and B-0 which may be explained as follows:

From Fig. 4, the curve shows that there is one endothermic peak at 59.6 °C for system A-0 (prepolymer mol. wt. 3000) and at 58.2 °C for system

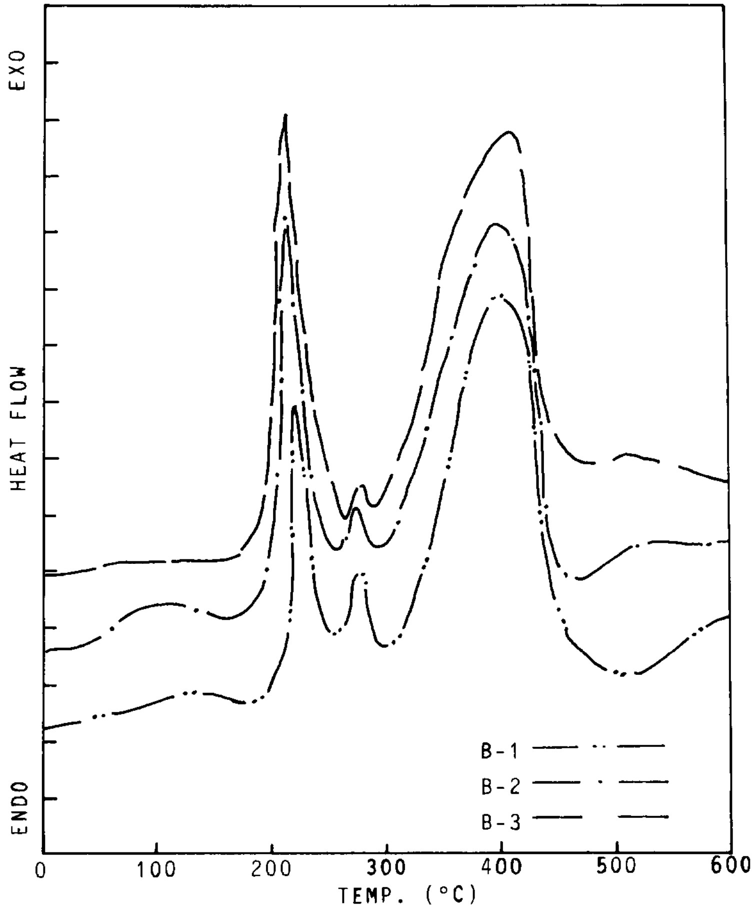


Fig. 7. DSC scans for formulations B-1, B-2 and B-3.

B-0 (prepolymer mol. wt. 2000). The difference was attributed mainly to the different bonding forces of the soft segment of each polymer [11]. The soft segment of PEG 4000 is longer than that of PEG 2000 and the bonding force (van der Waals forces) of PEG 4000 is larger than that of PEG 2000. Therefore the endothermic temperature of PEG 4000 is higher than that of PEG 2000. From Fig. 4, it is shown that exothermic reaction occurred at 184 ° C for system A-0 and at 161 ° C for system B-0; this is attributed to the partial oxidative degradation, curing or crosslinking reaction of the polymer [11]. According to TG-DTG results there is no weight change for formulations A-0 and B-0 at 180 ° C. Therefore, the exothermic reaction for systems A-0 and B-0 at 180 ° C or 164 ° C could be explained as being due to a crosslinkage reaction. From 280 ° C to 340 ° C there is a broad endothermic peak for both PEG 4000 and PEG 2000 systems. All these observations might be attributed to the breaking of the crosslinked form of the polymer [11]. At temperatures above 340 ° C two exothermic peaks were recorded for

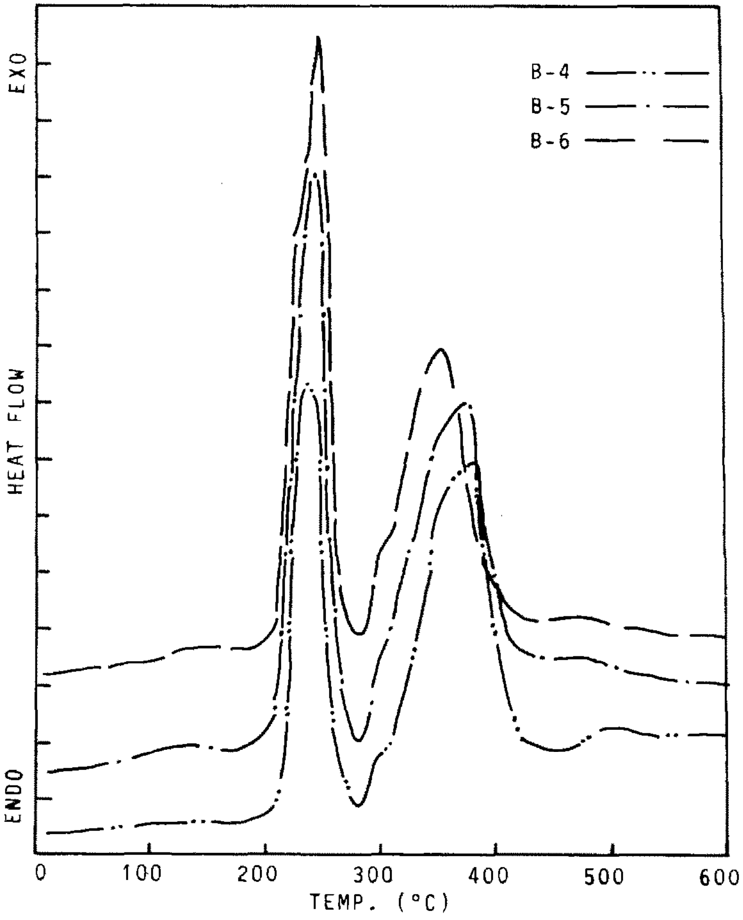


Fig. 8. DSC scans for formulations B-4, B-5 and B-6.

each system; these are attributed to the overwhelming oxidative reaction of the polymer. The TG-DTG results support the above explanation.

Figure 5 shows the DSC curves of systems A-1, A-2 and A-3. An endothermic peak appears at 75 °C for each system. These observations are attributed to the requirement of breakage of the aggregated soft segment. However, for the DSC curves of A-4, A-5, A-6 and A-7, there is no endothermic peak at 75 °C. This difference might be explained by the lower density of polyurethane PEG in the A-4 to A-7 binder systems than that of the A-1 to A-3 systems. Therefore, the endothermic reaction peak vanishes gradually. From 200 to 280 °C, formulations A-1 and A-2 show two indistinct peaks, the first of which shows only a shoulder. From 200 to 280 °C, formulations A-3 to A-7 show only one peak. Table 3 and Fig. 10 illustrate that the values of ΔH for each binder increase as BDNPA/F concentration increases. Table 3 and Fig. 11 illustrate that T_m shifts to higher temperature as BDNPA/F increases. Referring to the weight loss results of each binder

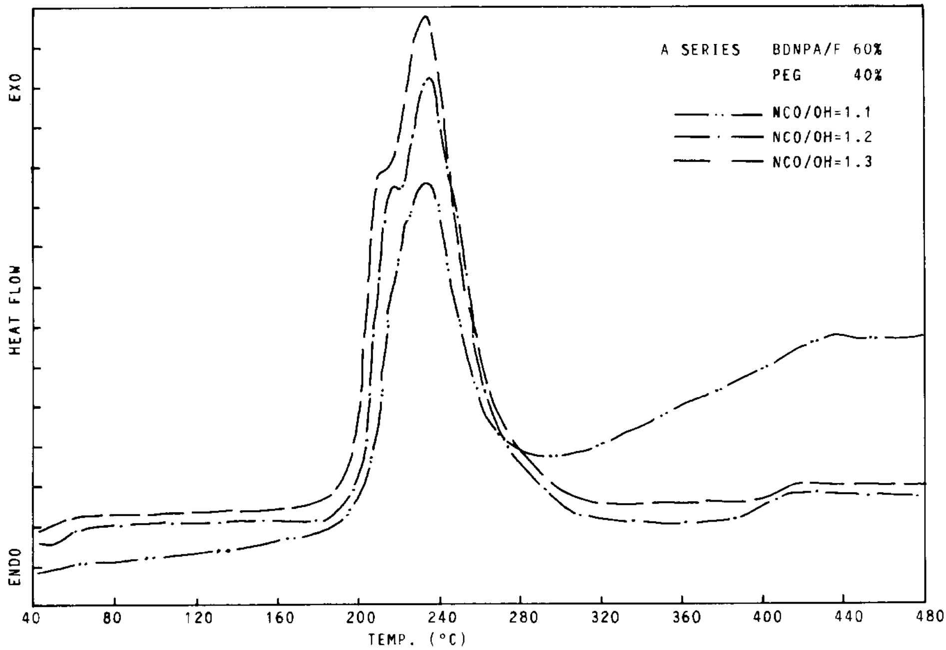


Fig. 9. DSC scans for formulation A-5 with various NCO/OH ratios.

system given in Table 2, it is concluded that the first exothermic reaction corresponds to the BDNPA/F decomposition reaction, and there is a linear relationship between BDNPA/F concentration and ΔH. At temperatures higher than 300 ° C, a broad exothermic reaction peak due to the decomposition of residual polyurethane PEG is observed. The DSC scan patterns of B-1 to B-6 binder systems are shown in Figs. 7 and 8. There is no remarkable change between the PEG 4000 and PEG 2000 systems. From Figs. 7 and 8, and the TG-DTG results in Table 2, it is concluded that the first exothermic peak in Figs. 7 and 8 may be attributed to the decomposition of BDNPA/F. The sequential large exothermic peak is due to the decomposition of residual polyurethane of the PEG molecule. In addition, the DSC pattern shows that the PEG molecule affects the decomposition temperature of BDNPA/F. From Figs. 5–8 and Table 3 it is found that T_m shifts to a lower temperature as PEG concentration increases. In other words, the decomposition temperature of the PEG molecule shifts to a lower temperature as the concentration of BDNPA/F increases. The PEG molecule and the BDNPA/F molecule interact with each other.

In order to understand whether or not the NCO/OH ratio affects the decomposition reaction of PEG/BDNPA/F blends, various ratios of NCO/OH were examined by DSC and the results are shown in Fig. 9. It is found that the decomposition of BDNPA/F is not affected by the NCO/OH ratio, but for the polyurethane of PEG the decomposition reaction is

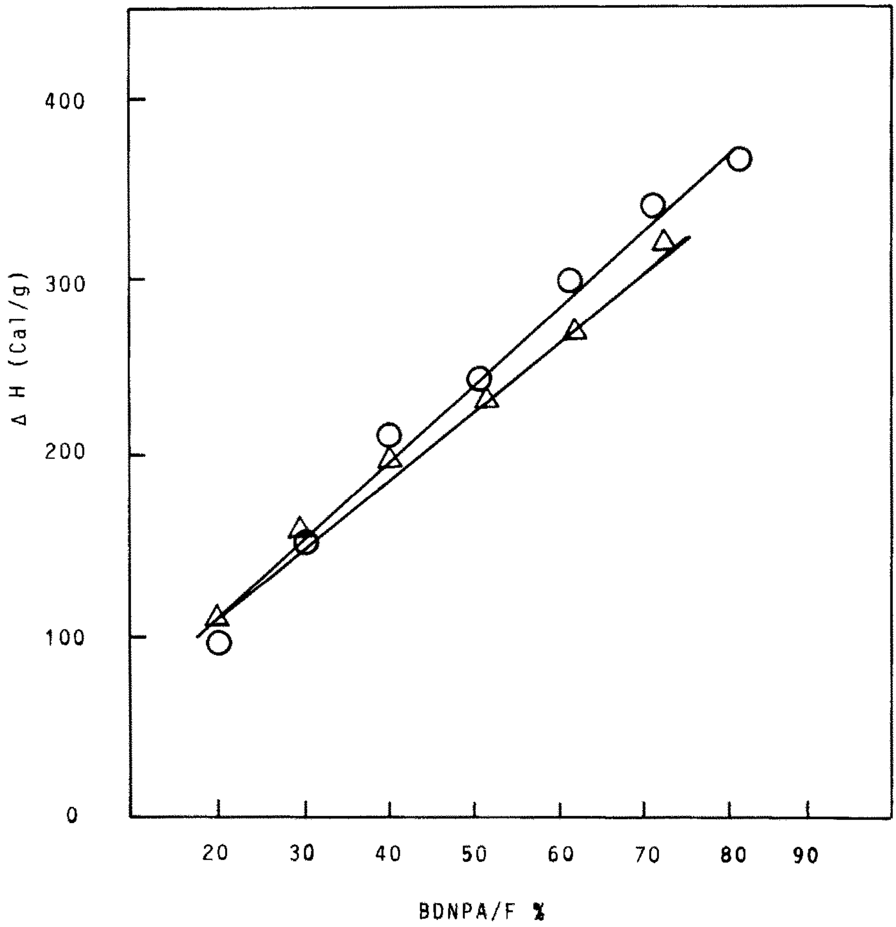


Fig. 10. Dependence of ΔH on BDNPA/F concentration.

changed. It is shown that there is a broad exothermic reaction peak for the system with an NCO/OH ratio of 1.1 at 410 °C. However, for the system with an NCO/OH ratio of 1.2 or 1.3 there is no marked change. These phenomena could be attributed to the increase in the NCO/OH ratio and the amount of the crosslinked form. Therefore, more energy is needed for the decomposition taking place.

CONCLUSION

According to the above discussions, the thermal decomposition of polyurethane PEG and BDNPA/F blends indicates a two-stage reaction. The first stage corresponds to the BDNPA/F decomposition, and the second decomposition stage corresponds to that of the PEG molecule. PEG and

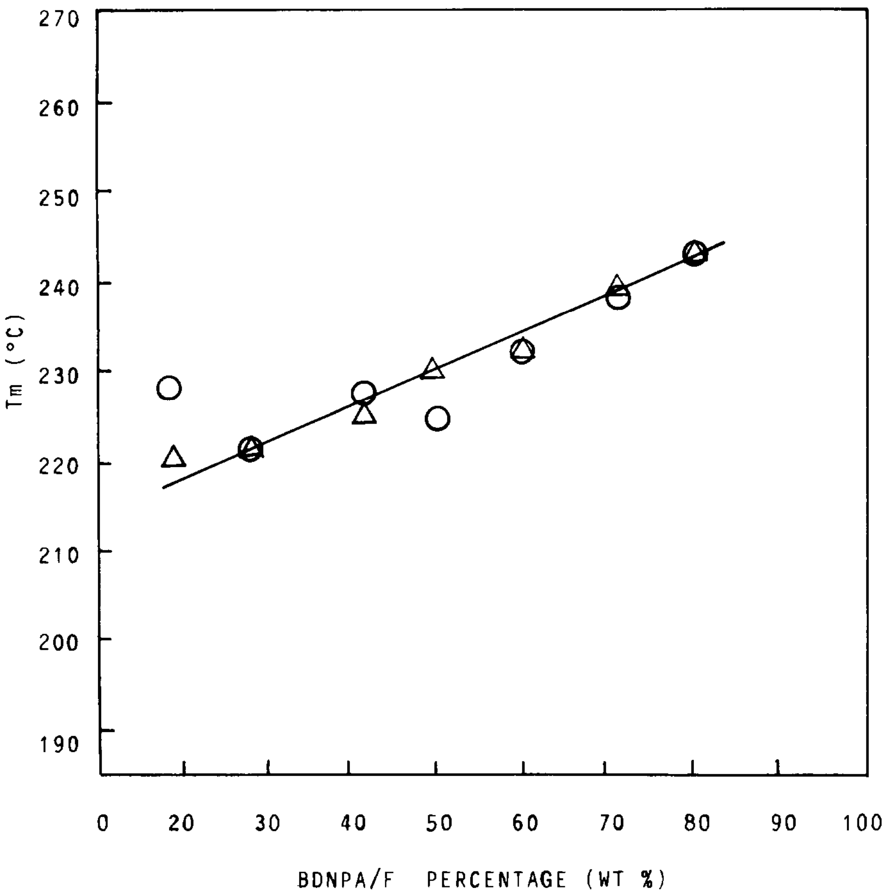


Fig. 11. Relationship between T_m and BDNPA/F concentration.

BDNPA/F molecules interact with each other and then their decomposition temperatures change. The values of ΔH and T_m of the first decomposition stage are proportional to BDNPA/F concentration. A linear relationship exists between ΔH and BDNPA/F concentration.

REFERENCES

1 K. Klager, History of binder development in composite propellants, ICT Symp. Ser., 1982 p. 11.
2 K. Klager, Polyurethane: the most versatile binder for solid composite propellants, AIAA paper AIAA-84-1239, 1984.
3 R. Reed, A review of liquid curable pyrotechnic binder, Proc. 13th Int. Pyrotechnic Seminar, 1988, p. 661.
4 A.M. Helmy, Investigation of new energetic ingredients for minimum signature propellant, AIAA paper AIAA-84-1434, 1984.

5 S. Wise and J.J. Rocchio, Binder requirements for low vulnerability propellants, 1981 JANAF Combustion Meeting, October 1981.
6 J.J. Rocchio, The low vulnerability ammunition (LOVA) program: A progress report, Proc. 1981 JANAF propulsion meeting, CPIA Publ. 340, May 1981.
7 H.J. Reves, Vulnerability testing of candidate LOVA propellants, Proc. 1980 JANAF Propulsion Systems Hazards Subcommittee Meeting, CPIA Publ. 330, Dec. 1980.
8 D. Al-Sammerrai and N. Nidawy, Thermochim. Acta, 132 (1988) 245.
9 D. Al-Sammerrai, J. Appl. Polym. Sci., 31 (1986) 1.
10 D. Tingfa, Thermochim. Acta, 138 (1989) 189.
11 C. Hepburn, Polyurethane Elastomers, Elsevier Applied Science , London, 1982. Chap. 3.