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SIMULTANEOUS TG/DSC AND TG/MS ANALYSES OF POLYMERIC AND ENERGETIC MATERIALS

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ABSTRACT

The use of simultaneous thermal analysis techniques for characterization of materials has become more widespread, with greater availability of instrumentation for such analysis. Advantages of simultaneous thermal analyses, such as TG/DSC (thermogravimetry/differential scanning calorimetry) and TG/MS (thermogravimetry/mass spectrometry) include the exact correlation of TG decomposition data with enthalpic transitions and with evolved gas analysis. Sample inhomogeneity problems are also eliminated. In this study, a simultaneous Setaram TG/DSC-111 and a Mound-developed TG/MS system were used for the analysis of several polymeric and energetic materials of interest to Mound. In addition, high temperature TG/DTA analyses of pyrotechnic blends were performed at GTE Corp.

Some of the polymeric materials analyzed included: ethylene/vinyl acetate/vinyl alcohol co- or terpolymers, which had endothermic decomposition enthalpies, poly(etheretherketone)(PEEK) and polyetherimide (PEI), which exhibited exothermic decomposition enthalpies, and polytetrafluoroethylene (PTFE). Energetic materials examined by TG/DSC included several scondary explosives and blends of a Sylgard silicone resin with pentaerythritol tetranitrate (PETN), and titanium with boron. The high temperature TG/DTA analyses of the Ti/B blends showed a sharp exothermic transition (and a small weight loss) in the 1200-1400°C region, associated with TiB_2 formation.

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INTRODUCTION

The use of simultaneous thermal analysis techniques for the characterization of materials has become more widespread in recent years, with the greater availability of instrumentation for such analyses. The advantages of simultaneous analyses, such as TG/DSC (thermogravimetry/differential scanning calorimetry) and TG/MS (thermogravimetry/mass spectrometry) include exact correlation of TG weight loss or decomposition data with enthalpic transitions and with evolved gas analysis. In this study, a number of polymeric and energetic materials of interest to MRC-Mound were analyzed by TG/DSC and TG/MS. In addition, high temperature TG/DTA (differential thermal analysis) analyses of Ti/B pyrotechnic blends were performed at GTE Corp., Towanda, PA.

EXPERIMENTAL

For TG/DSC analyses of polymeric and explosive materials, a Setaram TG/DSC-111, with a useful temperature range of ambient to 825°C, was employed.[1] The analysis conditions used were: argon gas flow, 50 mL/min; 10°C/min heating rate, beginning at 30°C and continuing through the decomposition of the material being analyzed. Sample weights were about 1-2 mg for explosives

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and 20-30 mg for polymers. Indium and zinc were employed as calibration standards. For the high temperature TG/DTA analysis of Ti/B blends with a Netzsch STA 429,[2] heating rates were 50°C/min up to 500°C and then 30°C/min up to 2100°C. All runs were made in vacuum (10^{-5} mbar), after initial purging with an inert gas, and sample weights were about 15-25 mg. Tungsten crucibles with graphite inserts were used, and gold and nickel were the calibration standards. The Mound-developed TG/MS instrumentation has been described previously.[3] For this study, the Stanton-Redcroft TG-761 TG analyzer was employed (upper temperature limit, 1000°C).

The explosives analyzed were generally "standard reference materials," used without further purification. The Ti/B blends used an amorphous boron (nominally 1 μm diameter) and either a very fine Ti powder (nominally 2 μm diameter) or a "coarser" Ti (nominally 8 μm diameter). Blends were a 2:1 molar ratio of B to Ti. Polymeric materials included some used in Mound production or experimental work and some obtained from Scientific Polymer Products, Inc.

RESULTS AND DISCUSSION

Energetic Materials

Analyses of the Mound prepared Ti/B blends were performed to determine if differences in the blends would affect the reaction of $Ti + 2B \rightarrow TiB_2$ and be detectable by thermal analysis. It has been shown that both Ti and B are coated with surface oxides, and that volatilization of B_2O_3 from the B surface may be required for initiation of the Ti-B reaction.[4] Typical results obtained in TG/DTA analysis of these blends are shown in Fig. 1. Both TB-5A (a "coarse" Ti blend) and TB-6 (a fine" Ti blend) exhibit sharp exotherms in the 1200-1400°C region, and possibly other, broader exotherms above 1800°C. The fine particle Ti blends consistently exhibited the initial exotherm at a lower temperature than did the "coarse" Ti blends.

No TG data is shown for TB-6, as some of the sample was lost at the point of the initial exotherm. A small weight loss from TB-5A was noted at this point, however, which fits the postulated reaction ignition mechanism. The measured calorific output of the initial reaction exotherm does not account for all of the expected theoretical output (962 cal/g) for the Ti-B reaction.[5] The remainder may be accounted for by the additional exotherms observed at or above

1800°C. X-ray diffraction analyses at Mound showed the reaction products from the TG/DTA analyses to be TiB_2.

Several secondary explosive materials were examined by TG/DSC to determine any weight losses on melting, prior to decomposition. Table 1 lists these explosives and the results obtained by TG/DSC. HNAB and HNS both exhibit small weight losses on melting and a "double" enthalpic transition on decomposition. Other secondary explosives which exhibited a small weight loss on melting were RDX, PETN, and LX-13 (see Table 1 for the chemical identification of these compounds). HMX exhibits only a polymorphic transition (no melting) prior to its decomposition.[6]

Polymeric Materials

TG/MS data on poly(etheretherketone) (PEEK), an engineering thermoplastic used at Mound, has been presented previously.[3] The decomposition of PEEK (in an inert atmosphere) is exothermic, as shown in Table 2 (which includes TG/DSC results for several thermoplastic polymers). The decomposition of polyetherimide (PEI) is also exothermic. In both cases the decomposition in an inert atmosphere is only partial. Complete decomposition of PEEK in air has previously been demonstrated.[7]

The decomposition of poly(tetrafluoroethylene) (PTFE) is initially exothermic, then endothermic, as it proceeds to completion. The decomposition of polystyrene (PS) and a series of ethylene vinyl acetate (EVA) co- and terpolymers is entirely endothermic. The decomposition of an ethylene vinyl acetate copolymer, shown graphically in Fig. 2, proceeds in two steps, each having a distinct endothermic transition. The initial decomposition step is known to correspond to the vinyl acetate (VA) decomposition (with release of acetic acid) in EVA copolymers.[8] Table 2 shows a lower initial TG weight loss (and hence lower vinyl acetate content) for a series of E/VA/VOH terpolymers prepared from a 40% VA content EVA copolymer (DuPont's Elvax 40). These E/VA/VOH terpolymers are useful in microencapsulation applications.[9]

TG/MS data obtained on the PS sample listed in Table 2 showed that at the decomposition point of the TG experiment, the primary MS products were, as expected, mass 103 and 104, styrene, along with lesser amounts of mass 78(benzene) and mass 52($C_4H_4^+$).

TG/MS data were also obtained on the EVA copolymer, Elvax 40. The total ion current trace of the EVA TG/MS run shows two peaks corresponding to the two TG decomposition temperature maxima. The first peak consists of ions of m/e 44(CO_2) and 59($C_2H_3O_2^+$), characteristic of the acetate fraction of EVA. The second peak is largely made up of the ions m/e 27($C_2H_3^+$), 41($C_3H_5^+$), 43($C_3H_7^+$), 55($C_4H_7^+$), and 67($C_5H_7^+$), from ethylene fragments of the EVA copolymer.

CONCLUSIONS

The utility of simultaneous thermal analysis techniques, such as TG/DSC and TG/MS, has been demonstrated for both energetic and polymeric materials. TG/DSC can assist in elucidating reaction mechanisms and determining weight losses for endothermic transitions which precede decomposition of energetic materials. The endothermic and exothermic nature of decomposition processes can be defined by TG/DSC and the decomposition products identified by TG/MS.

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REFERENCES

1. SETARAM, 7, rue de l'Oratoire - B.P. 34 - 69641 Caluire Cedex - France
2. Netzsch, Inc., Pickering Creek Industrial Park, Exton, Pa. 19341
3. R.O. Yelton, T.L. Shell, and R.B. Whitaker, "Characterization of Poly(etheretherketone) and Diallylphthalate-Fiberglass Composites by Combined Thermogravimetry Mass Spectrometry and Ancillary Techniques", MLM-3331, Jan. 24, 1986; presented at the 14th NATAS Conf., San Francisco, Cal., Sept. 1985.
4. A.R. Burke et al, "Thermal and XPS Studies Elucidating the Ignition Mechanism of a Ti/B Pyrotechnic Blend", 9th Symposium of Applied Surface Analysis, June 3-5, 1987, Dayton, O.
5. Merzhanov, A.G., "Symposium on Chemical Problems Connected with the Stability of Explosives," (Proceedings), _4_, 381-401, 1977.
6. T.R. Brill and R. J. Karpowicz, J. Phys. Chem., _86_, 4260 (1982).
7. W.R. Moddeman et al, Polymer Engr. & Sci., _26_, 1469 (1986).

8. J. Chiu, S.G. Fischer and D.E. Robson, Thermochimica Acta, <u>84</u>, 83 (1985); S.G. Fischer and J. Chiu, Thermocimica Acta, <u>65</u>, 9 (1983).
9. R.G. Bayless et al, U.S. Patent 3,674,704, July 4, 1972.

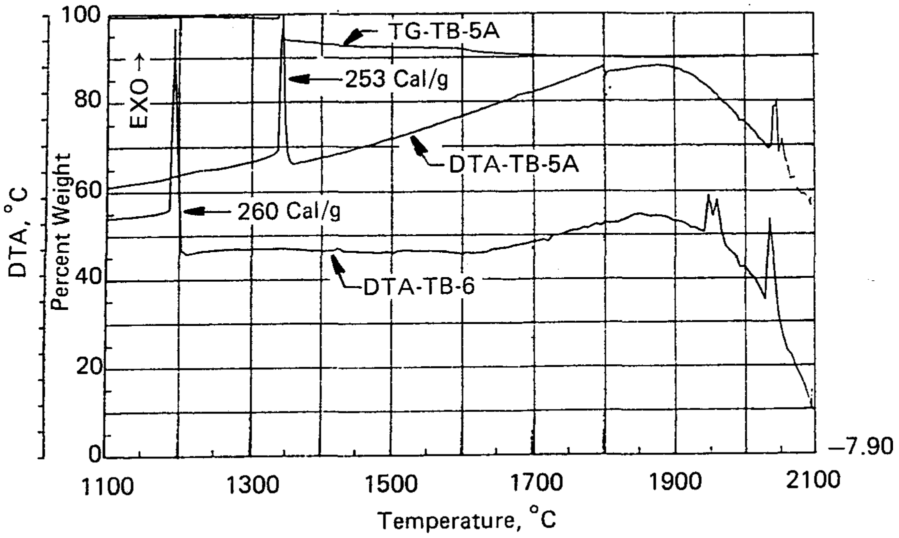

Figure 1 - High temperature TG/DTA of Ti/B blends: TB-5A - "Coarse" Ti; TB-6 - "Fine Particle" Ti.

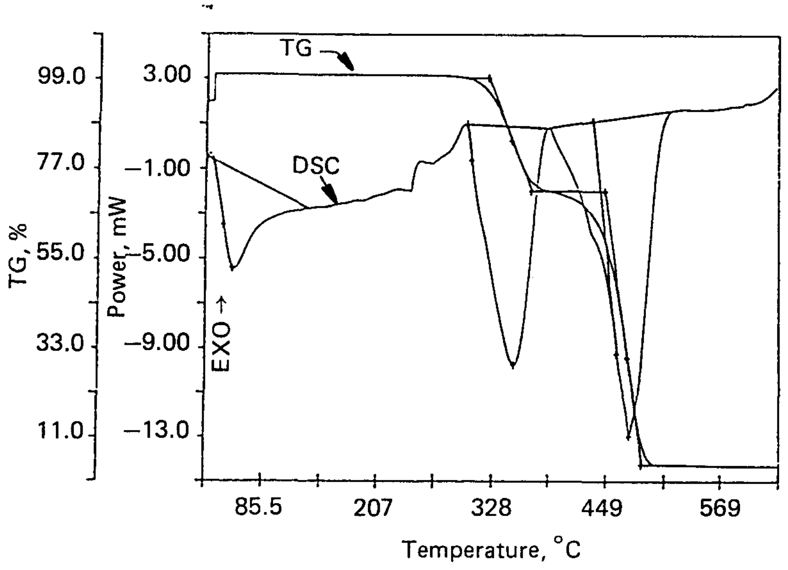

Figure 2 - Simultaneous TG/DSC of poly-(ethylene/ vinyl acetate) - 40% vinyl acetate.

Table 1 - SIMULTANEOUS TG/DS RESULTS ON SELECTED SECONDARY EXPLOSIVES

	Melting - Endotherm				Decomposition - Exotherm			
Explosive	M.P. (°C)	ΔH (j/g)	Weight Loss (%)	Max. At. (°C)	Peak Max. (°C)	ΔH (j/g)	Weight Loss (%)	Max. At. (°C)
HNAB	226	- 60	1.3	224	(1) 324 (2)∿366	3830	(1)45 (2)27	319 355
RDX	205	-152	7.4	209	246	2193	88	238
HNS	322	-141	∿13[a]	326	(1) 340 (2)∿410	5268	65	332
HMX	198 (Polymorphic transition)	89	None	-	278	2349	96	273
TATB	None observed		-	-	382	1538	76	378
PETN	146	-158	1.9	164	205	1996	92	196
LX-13 (Cured)	150	-112	3.7	175	203	1007	72	196

Identification of Explosives:

HNAB = Bis(2,4,6-trinitrophenyl)-diazine; RDX = Hexahydro-1,3,5-trinitro-s-triazine;
HNS = Hexanitrostilbene; HMX = Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine;
TATB = 1,3,5-triamino-2,4,6-trinitrobenzene; PETN = Pentaerythritol tetranitrate;
LX-13 = 80% PETN, 20% Sylgard 182 resin.

[a] Considerable overlap of melting and decomposition.

Table 2 - SIMULTANEOUS TG/DSC RESULTS ON SELECTED THERMOPLASTIC POLYMERS

		Melting Endotherm		Decomposition				
Polymer	Form and/or Source	M.P. (°C)	ΔH (j/g)	Type of Transition	Peak (°C)	ΔH (j/g)	Weight Loss (%)	Max. At. (°C)
PEEK	ICI Gr450 (Powder)	345	- 62	Exothermic	588	266	40.2	579
PS	Powder	Tg 110	-	Endothermic	425	-722	95	420
PTFE	Sci. Polymer Products, Inc. (Powder)	347	- 55	(1) Exothermic (2) Endothermic	522 604	401 -291 }	98	598
PEI	GE-Ultem 1000 (Molded)	Tg 221	-	Exothermic	542	143	41	536
EVA (40% VA)	Sci. Polymer Products, Inc. (Pellets)	55	- 93	(1) Endothermic (2) Endothermic	351 474	-268 -375	28 68	349 471
EVA (40% VA)	Elvax 40 Dupont (Pellets)	65	- 95	(1) Endothermic (2) Endothermic	356 486	-269 -268	31 73	355 483
E/VA/VOH	PB7802 Dupont (Pellets)	77	-165	(1) Endothermic (2) Endothermic	354 472	-232 -247	25 69	351 469
E/VA/VOH	MRC 4.4 OH (Pellets)	74	-121	(1) Endothermic (2) Endothermic	358 478	-220 -281	21 71	353 474
E/VA/VOH	MRC Acetylated (Pellets)	58	-108	(1) Endothermic (2) Endothermic	355 476	-277 -279	19 72	351 474

Identification of Polymers: PEEK = Poly(etheretherketone); PS = Polystyrene; PTFE = Poly(tetrafluoroethylene); PEI = Polyetherimide; EVA = Poly(ethylene co-vinyl acetate); E/VA/VOH = Ethylene/vinyl acetate/vinyl alcohol terpolymer.