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THERMAL ANALYSES FOR QUALITY CONTROL OF PLASTICS, CERAMICS, AND EXPLOSIVES

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INTRODUCTION

Thermal analyses are performed for production quality control (q.c.) and for surveillance at Mound on plastic, ceramic, explosive and pyrotechnic materials. For the weapons surveillance program, weapon components are disassembled after varying times in the field; thermal and other analyses are then performed on the component materials. The types of thermal analyses done include: differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TG), thermomechanical analysis (TMA), and high temperature TG/DTA.

EXPERIMENTAL

Instrumentation

Instrumentation employed in thermal analysis q.c. and surveillance work at Mound includes DuPont 1090 or 9900 thermal analyzers with DuPont 910 DSC/DTA, 951 TGA, and 943 TMA modules, and a DuPont 912 Dual Sample DSC with a 920 DSC Autosampler (for plastics); a Netzsch STA 429 TG/DTA (to 2400°C); and a Setaram TG/DSC-111 (to 825°C). Also, a DuPont 2100 Thermal Analyzer with 2910 DSC and 2950 TGA modules are being obtained to replace some of the older DuPont thermal analysis instrumentation.

Methods and Materials

For each type of thermal analysis for production or surveillance, and/or material to be analyzed, a specific procedure, called a "Standard Analytical Procedure" (SAP) is followed. SAPs were developed at Mound from research on the individual materials. The SAP "Differential Scanning Calorimetry of Energetic Materials" is a method for determining the thermal characteristics of explosive and pyrotechnic materials by DSC. It has exact DSC experimental conditions for 40 different energetic materials in it. Similarly, a SAP on "DSC of Polymeric Materials" includes a procedure for a DSC degree of cure test for poly(diallyl phthalate) (DAP) components molded at Mound, along with DSC conditions for other polymers commonly analyzed.

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In these SAPs the instrument calibration procedures are also given, along with the limits, where required, for acceptance of the calibration runs. For DSC calibration with an indium standard, the melting point onset must be within 156.6 ± 0.5°C, and the calibration must be repeated after 10 runs, or on a daily basis. Also, the indium enthalpy values must not vary by more than ±4% in that period, in order to accept the sample run results. Measurement control charts are kept for each DSC cell and different instrument conditions used.

RESULTS

Only a limited number of examples of the production q.c. or surveillance thermal analyses performed at Mound can be given here. These include DSC degree of cure testing of molded DAP plastics; DTA of glass ceramics and TG/DTA of pyrotechnics; DSC of secondary explosives; and TMA determination of Tg of adhesives.

DSC Degree of Cure Test

The application of DSC degree of cure testing for acceptance of molded DAP components at Mound has been reported. (1,2,3) Chloroform extraction of molded parts was the q.c. test used previously. The procedure was a time-consuming, dimensional measurement of the parts before and after extraction, and gave only a "pass" or "fail" result. The DSC degree of cure test, however, gives rapid, quantitative results, by comparison of the residual curing ΔH_R (if any) of the DAP molded part to the curing ΔH_R of the DAP compound used for molding the parts. (ΔH_R is determined by DSC from the area under the exothermic DAP curing reaction peak.) In this test representative pieces of the small DAP molded parts (selected by the Production Mold Shop from parts molded in a given time frame) are used to make up 15-25 mg DSC samples. These are run, in argon gas, at 20°C/min from 80°C to 240°C. The precision of the DSC degree of cure analyses, for a given molded DAP part, has been found to be ±1%. (1)

The rapid turnaround time of the DSC analysis has proven to be very useful to Mound's Mold Shop. Samples can be run overnight, using the DuPont Dual Sample DSC with the DSC Autosampler, and results returned the next morning. Any problems in the molding operations can be spotted quickly and results of experimental molding conditions returned rapidly. Even under "normal" molding conditions, variations can be found in DSC degree of cure (from ~80 to ~100%) depending on part geometry and molds employed. If different molding temperatures are used for a given DAP component, much greater differences in degree of cure result. (2) Fig. 1 illustrates these differences for one type of molded DAP part. The sample with the lowest DSC degree of cure also "failed" the chloroform extraction test. Mound engineers have used these and similar results to set the degree of cure acceptance standards for the molded DAP components.

DTA and TG/DTA of Ceramics and Pyrotechnics

DTA and high temperature TG/DTA are used for production q.c. and surveillance testing of glass ceramics and of pyrotechnic blends at Mound. The high temperature TG/DTA research on Ti/B blends has been described previously. (4) It has resulted in a standard method for the TG/DTA analysis of blends of either pure Ti/B or Ti/B mixed with an additive, such as Al_2O_3. This method involves heating 10-20 mg of the blend in a tungsten crucible at 30°C/min in high vacuum (10^{-5} mbar) to a maximum temperature of ≤2200°C in the 2400°C Netzsch STA 429 TG/DTA. (Conditions such as sample weight and final temperature are varied depending on the Ti/B blend type). Fig. 2 is a thermogram of a Ti/B blend containing 21% Al_2O_3. It includes the Ti/B reaction exotherms and the endothermic Al_2O_3 melt, which are accompanied by a small TG weight loss during the Ti/B reaction and a larger one on evaporation of the Al_2O_3 in the high vacuum.

DTA is also used for analysis of other pyrotechnic blends, such as $B/CaCrO_4$, which cannot be analyzed by DSC, and for production q.c. analyses of glass ceramics. An example of a DTA analysis of a borosilicate S-glass is shown in Fig. 3. The first transition observed is the glass transition. Information obtained by thermal analysis is important in setting the correct processing temperatures for glass ceramics in Mound production.

DSC of Secondary Explosives

The majority of the thermal analyses performed at Mound for surveillance are DSC of explosives and pyrotechnic blends. As part of this program, statistical analyses are done on a number of DSC runs of reference or baseline explosive or pyrotechnic materials. These are used later for comparison with the DSC analysis of the component materials (component baselines are also run at the beginning of a program, but are only duplicate analyses due to material limitations). When weapon components are returned from the field, they are disassembled and all explosive or pyrotechnic materials analyzed by DSC or DTA. All thermal activities (melting, reaction exotherms) are monitored.

An example of this type of comparative DSC data is shown in Fig. 4, in which a DSC scan from a reference secondary explosive, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), is plotted along with a DSC scan of an artificially aged HMX sample (12 years @ 120°C). Even after such drastic aging conditions, the only statistically (within 2 σ limits) significant differences observed were a lowering of the HMX reaction exotherm peak and onset temperatures, and an increase in the endothermic β-δ phase change temperatures. (5) No significant differences were observed in either the exotherm or endotherm enthalpies. One other difference noted was the disappearance of the small melting

endotherm normally observed coinciding with the HMX decomposition exotherm. (DSC conditions used were ~0.7-mg samples run in crimped aluminum pans at 10°C/min heating rate, with 100 mL/min argon gas flow.) While this is an unusual example, these are the types of changes looked for by DSC in the surveillance program.

TMA of Adhesives

Another thermal analysis performed as part of the weapons surveillance program is TMA, which is used to follow any changes in the Tg of adhesives. Silicone-based adhesives are frequently used, and sub-ambient Tg analyses are required for these. For example, a typical Sylgard seal adhesive has a Tg of -47°C by TMA. TMA is the method of choice for these Tg determinations, due to its greater sensitivity over DSC.

CONCLUSIONS

As shown through the examples here, thermal analyses play an important part in Mound's production q.c. and weapons surveillance programs. The quality of the results and efficiency of operation (aided by the use of robotics) are vital in both areas.

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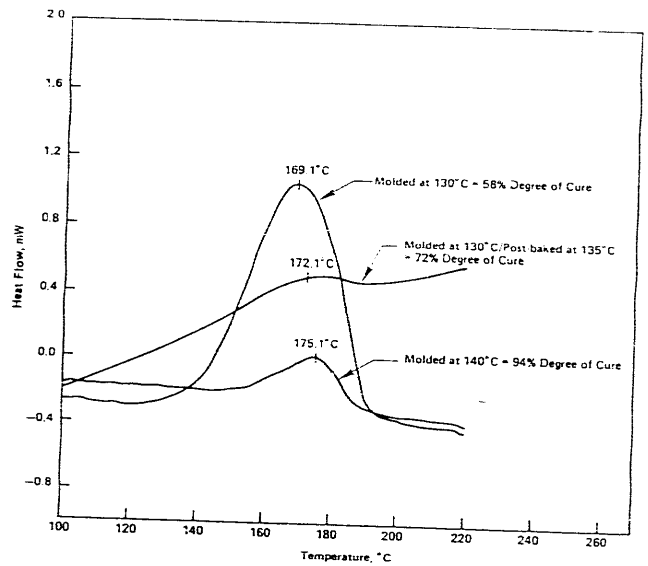

Figure 1 - Effect of molding conditions on DSC degree of cure of molded DAP component.

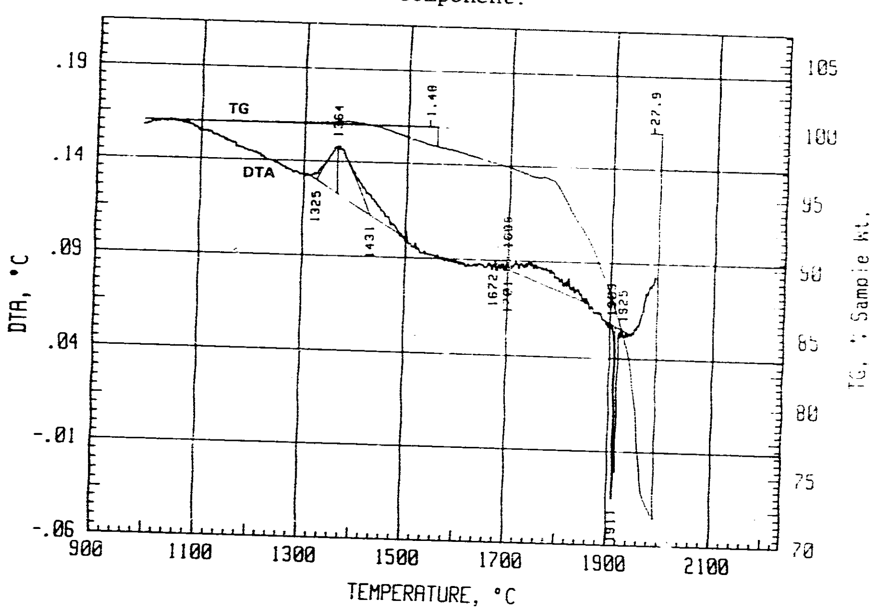

Figure 2 - TG/DTA of blend TBM-11 - in vacuum, W crucible.

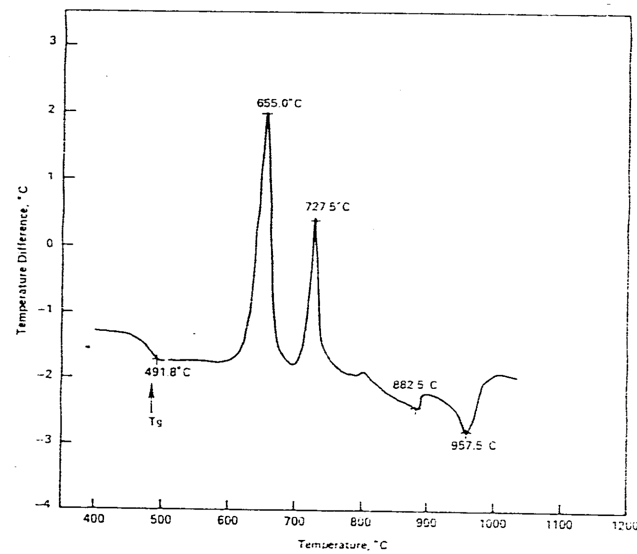

Figure 3 - DTA of Z-24 glass ceramic.

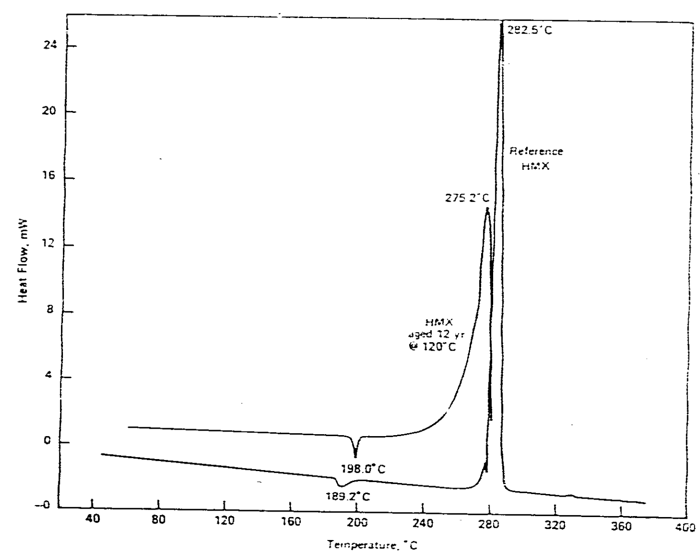

Figure 4 - DSC scans of a reference HMX explosive and HMX aged 12 years at 120°C.

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