TA Instruments

Thermal Analysis & Rheology

EVALUATION OF HAZARDS POTENTIAL BY DSC

by

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INTRODUCTION

Differential scanning calorimetry (DSC) is an analytical technique which measures the heat flow into or out of a material as that material is exposed to a controlled thermal profile. DSC provides both qualitative and quantitative information about material transitions including glass transitions, crystallization, curing, melting and decomposition. For several of these transitions, DSC provides not only transition temperatures and a measure of the heat involved, but also provides information about the rate of reaction/decomposition (i.e., kinetics information) as well as related characteristics such as hazards potential.

Because DSC kinetics are based on dynamic heating rate measurements and because the typical sample size is small (1-5 mg), the results obtained from DSC should be used in combination with larger scale tests and other tests which provide complementary information (e.g., pressure build-up and vent sizing) to gain a more complete perspective of a material's hazards potential. Nevertheless, DSC is still very useful for rapidly comparing and/or screening potentially hazardous materials.

EXPERIMENTAL

Hazards evaluation by DSC is based on kinetic treatment of a material's exothermic decomposition profile using ASTM Test Method E698. This method is an implementation of the variable heating rate method of Ozawa in which several samples of the same material are decomposed at different heating rates between 1 and 10°C/minute.

This method assumes Arrhenius behavior, first order reaction kinetics, and that the extent of reaction at the peak of the decomposition exotherm is constant and independent of heating rate. The equation used to describe the process is:

$$d\alpha / dt = Ze^{-E/RT} (1 - \alpha)$$

where: $d\alpha / dt$ = reaction rate (1/sec)
α = fractional conversion
Z = pre-exponential factor (1/sec)
E = activation energy (J/mol)
R = gas constant = 8.314 J/mol K
T = temperature (K)

A plot of the natural logarithm of the heating rate versus the peak temperature provides the information necessary to calculate E, Z, k (rate constant) and the half life ($t_{1/2}$). These parameters, in turn, can be used to generate isothermal and isoconversion predictive plots, as well as the "figures of merit" specified by ASTM Test Method E1231 including:

- Time to thermal runaway (estimation of the time required for an exothermic reaction to reach thermal runaway in an adiabatic [no heat loss or gain to the environment] container)
- Critical half thickness (estimation of the half thickness of a sample in a container in which heat losses to the environment are less than the retained heat, resulting in build-up of internal temperature leading to thermal runaway)
- Critical temperature (estimation of the lowest temperature of a container at which the heat losses to the environment are less than the retained heat leading to a build-up of internal temperature leading to thermal runaway)
- Adiabatic decomposition temperature rise (estimation of the temperature that a material would attain if all the heat of decomposition were absorbed by the material)

These "figures of merit" can be determined for a wide variety of shapes (sphere, infinite slab, cube, box, cylinder) assuming either an unstirred (Frank-Kamenetskii) or a stirred (Semenov) model for the container. The former is generally preferred for DSC determinations because it results in more conservative projections (i.e., is more likely to overstate the hazards potential of the material).

Two additional assumptions of this DSC hazards evaluation are that the material does not disappear (evaporate or sublime) before decomposition occurs and that the only reaction occurring is decomposition. Hence, it is important that the DSC heating experiments be conducted in a way that eliminates these potential sources or error. Figures 1-3, for example, show DSC results for the decomposition of chloroperoxybenzoic acid (CPBA), a common pharmaceutical precursor, obtained in several different DSC pans. In aluminum hermetic pans, the decomposition appears to be a multi-stage process (Figure 1). However, other analytical tests indicate that this decomposition is not multi-stage and that the heat of decomposition is higher than that obtained by DSC. This erroneous result is undoubtedly due to sample volatilization and gradual leakage from the pan before and during decomposition. Evaluation in commercially available stainless steel pressure pans (Figure 2) also yields incorrect results due to catalysis of the decomposition by the metal pan. These pans are able to contain the sample and prevent volatilization prior to decomposition and thus yield the appropriate heat of decomposition. However, the temperature range where decomposition occurs, and more importantly the shape of the exotherm obtained, are not indicative of the expected first order reaction. Evaluation in sealed glass ampoules, on the other hand, yields the expected melting and exothermic decomposition peaks (Figure 3).

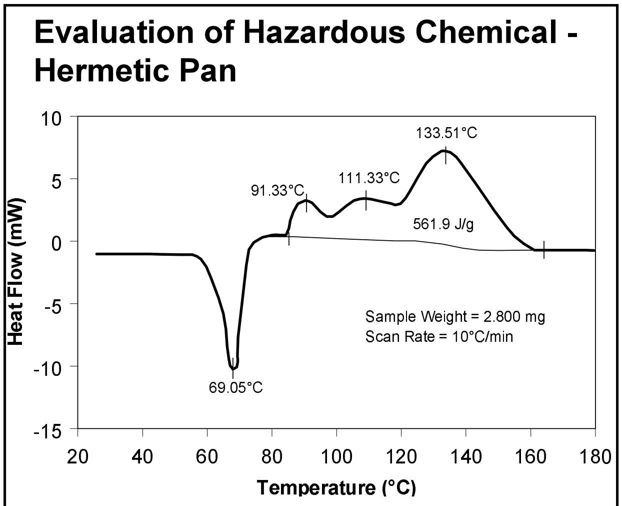

Figure 1

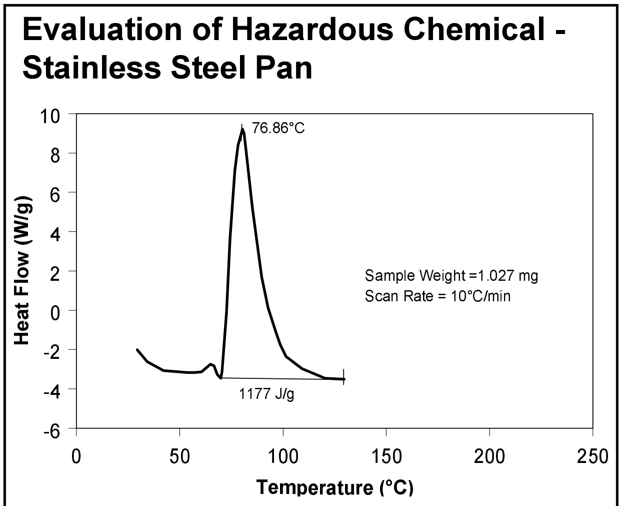

Figure 2

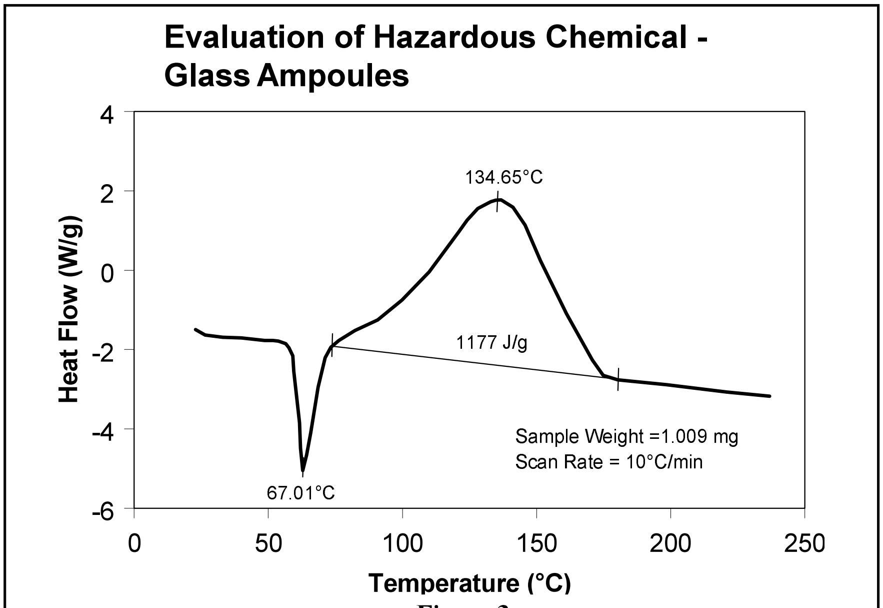

Figure 3

TA Instruments provides all the hardware (including stainless steel high pressure pans, as well as glass ampoules and an ampoule sealing accessory) and software (ASTM hazards kinetics software with figures of merit calculations based on the Frank-Kamenetskii model, and isothermal kinetics software for autocatalytic reactions) required to perform comprehensive DSC hazards evaluations. Contact your local Technical Representative for more details.

APPLICATIONS

The following sections describe “real-world” examples where DSC hazards evaluations were used to rapidly assess or compare materials.

- Comparison of Alternative Raw Materials

Figure 4 shows the critical half thickness (i.e., radius) versus temperature curves for three materials used as reaction accelerators or catalysts. These plots project the relative stability of the materials when stored in cylindrical containers (e.g., 50 gallon drum) as a function of temperature. Clearly, nitrocellulose is the most stable of these materials over a wide range of conditions.

- Comparison of Storage Configurations

Figure 5 illustrates the relative stability for a raw material stored in different configurations. These curves indicate that regardless of the material’s thickness, spherical containers always provide a more stable environment than an infinite cylinder or infinite slab. This relationship, where storage in spherical containers is more stable, holds for many materials. However, the relative comparison between shapes may vary.

Frank-Kamenetskii Calculations for Three Different Materials (Cylindrical Container)

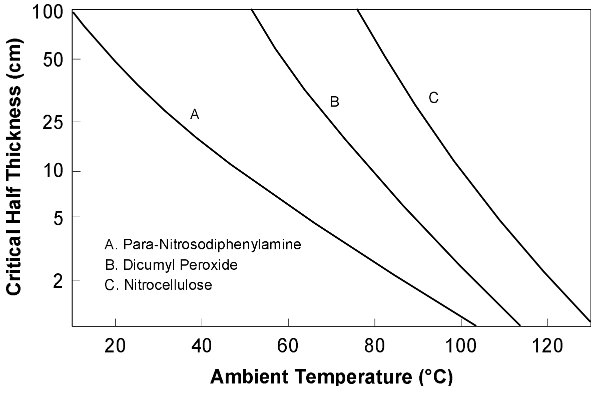

Figure 4

Relationship Between Critical Temperature and Semi-Thickness (Frank-Kamenetskii Equation)

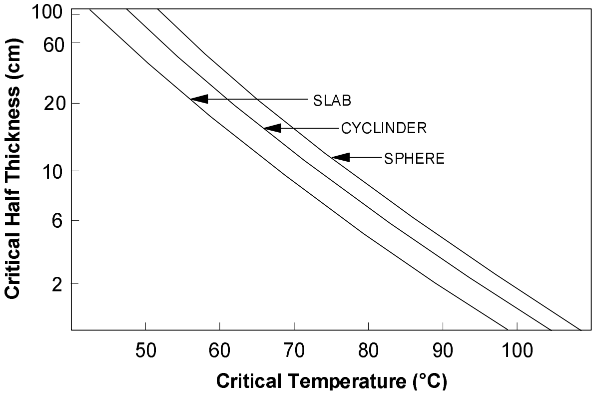

Figure 5

- Optimization of Processing Conditions

The relative stability results obtained from DSC can be used to monitor the results of changes in plant process conditions. Figure 6 shows a series of relative stability curves for a cellulose process.

The curves indicate the effects that the process reaction temperature and pH have on the stability of the product. In this case, decreasing the pH from a caustic to a neutral or slightly acidic situation increases the stability.

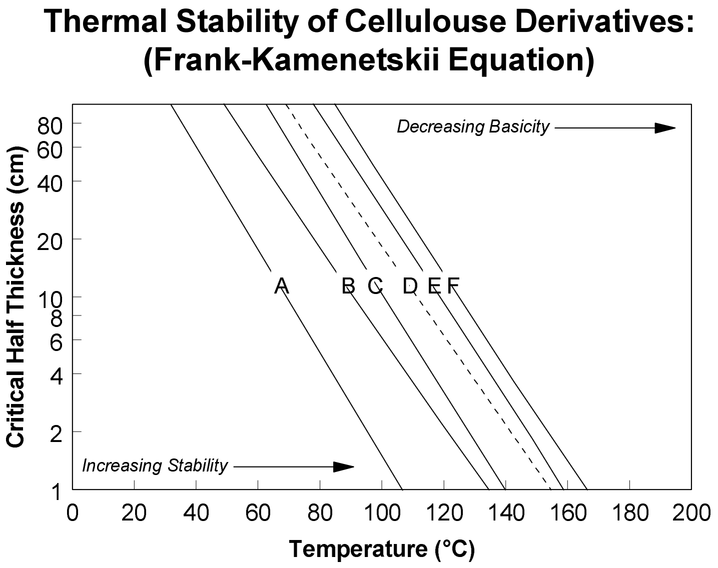

Figure 6

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