DETERMINATION OF THERMAL HAZARD FROM DSC MEASUREMENTS - Investigation of Self Accelerating Decomposition Temperature (SADT) of AIBN

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Abstract

Some chemicals have the potential to cause fires or explosions, and, as hazardous materials, are handled with appropriate care to minimize accidents. The category of hazardous materials includes a group of chemical substances called "reactive or self-reactive chemicals" which may initiate exothermic decomposition by themselves without reacting with oxygen in air. The estimation of the hazard probability, especially for packaged materials during transport conditions, is commonly performed using the Self Accelerating Decomposition Temperature (SADT) [1].

The method of determination of the thermal hazard properties of such reactive chemicals from DSC experiments is illustrated by the results of SADT simulations performed with Azobisisobutyronitrile (AIBN). When considering the intrinsic properties of the chemicals during simulations of their thermal behaviour one has to take into account important additional factors influencing the predictions, namely the possibility of the simultaneous occurrence of a phase transition (endothermal melting) and a chemical reaction (exothermal decomposition). For the prediction of the hazard properties for the materials such as AIBN in which melting occurs before or during the decomposition, the kinetic parameters and heat balance computed for the liquid state can be inapplicable to predict the reaction kinetics and thermal behavior in solid phase. In such situation, the experiments should be performed isothermally at temperatures below the melting point. The kinetics of decomposition of AIBN in the solid state was investigated in a narrow temperature window of 72-94°C, just below the sample melting. The kinetic parameters of the decomposition were evaluated by differential isoconversional method. The very good fit of the experimental results by the simulation curves, based on the determined kinetic parameters, indicated the correctness of the kinetic description of the process. Application of the kinetic parameters, together with the heat

balance performed by numerical analysis, allowed scale-up of thermal behaviour from mg- to kg-scale and simulation of SADT. The study presents the evaluation of the influence of the overall heat transfer coefficient *U* on the SADT value. The results obtained clearly illustrate also the dependence of SADT on the sample mass. The ten-fold increase of the mass from 5 to 50 kg results in the decrease of the SADT from 50°C to 43°C. Determination of the reaction kinetics, describing the rate of heat generation, and the heat balance in the system, based on Frank-Kamenetskii approach, was calculated using AKTS-Thermokinetics and -Thermal Safety software [2-3]. Determined SADT values were verified experimentally with a series of large-scale experiments (UN test H.1 [1]) performed with packaging of 5, 20 and 50 kg in an oven at constant temperatures.

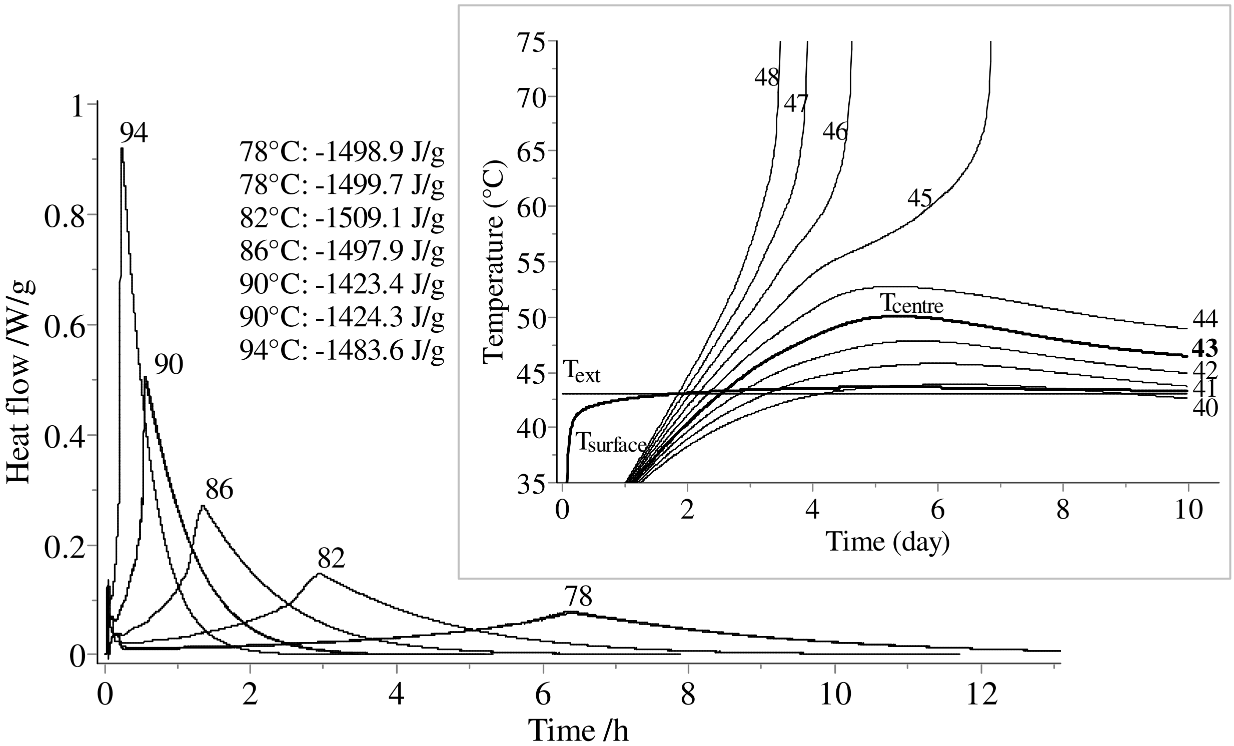

Fig.1 Heat flow traces of AIBN recorded by DSC under isothermal conditions at different temperatures as a function of time, and values of the heat of reaction determined at the respective temperatures. The values of the temperatures in °C are marked on the curves. Inset: Simulated thermal behaviour of AIBN for mass of 50 kg with λ =0.072 W m^{-1} K^{-1} and U = 5 W m^{-2} K^{-1}, respectively. Temperatures of SADT are marked in bold. Centre temperature profiles for other external temperatures between 40 to 48°C are reported too.

[1] UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 5th revised edition, United Nations, New York and Geneva, 2009, 28.3.7.
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