

# Thermal Decomposition of Polymeric Materials

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## Project Description

In March 2004, Sandia National Laboratories (SNL) and the All Russian Research Institute of Automatics (VNIIA) initiated a material-science project to study thermal decomposition of polymeric materials pertinent to weapons safety analyses and numerical modeling.

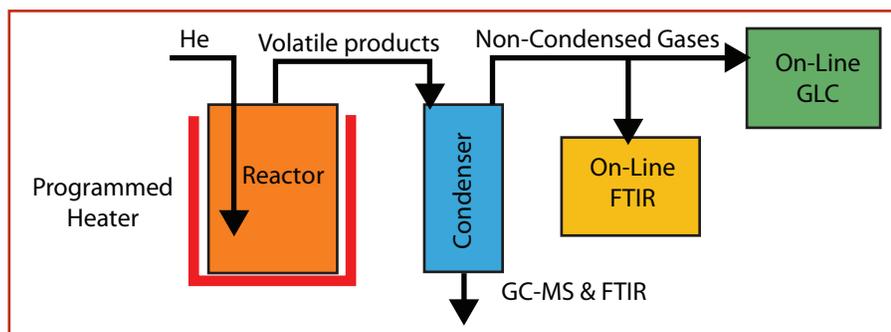
The project includes tasks for both experiments (Tasks 1-3 and Task 7 subtasks) and modeling (Tasks 4, 5, and Task 7 subtask). The initial objectives of the project were to: (1) determine chemical mechanisms and kinetics controlling thermal decomposition of polymers subjected to heating rates between 5°C/min and 10,000°C/min and (2) develop submodels for thermal decomposition, based on kinetics and physical properties, which could be incorporated into numerical models for safety analyses. A third objective, agreed to by SNL and VNIIA during FY06 was to develop models for heat transfer and pressure growth caused by thermal decomposition of polymer foams in closed containers in fire environments. (Experimental work is specified in Option Tasks 10 and 11 for FY08. Modeling work is specified in Tasks 8 and 9 authorized in FY07 and Option Task 11 for FY08.)

The project is now in its fourth year and has been primarily funded by Defense Programs (experimental work) and by ASC (modeling work). The first three years of the project were very successful. During FY05, thermal decomposition experiments were completed with epoxies and polyurethanes at heating rates ranging from 5°C/min to 10,000°C/min. The materials were similar to, but not identical to, those studied by Erickson et al. at Sandia using complementary techniques. During FY06, experiments were completed that involved quantitative chemical analyses of the solid, liquid, and gas-phase products from constant-temperature decomposition of 20 to 40 gram samples. Joint experiments were done at SNL (April 2006) and VNIIA/Mendeleev Institute (June 2006) involving complementary capabilities. Several low-molecular weight gas-phase products were quantitatively determined, which provided needed data for refining decomposition mechanisms and kinetics. Submodels for decomposition of the materials studied were developed from the experimental data.

The objective of new work in FY07 is to develop models for heat transfer and pressure growth caused by thermal decomposition of polymer foams in closed containers in fire environments. This work has direct application to Directed Stockpile Work's (DSW's) assured safety issues of foam decomposition and pressurization, for which C6 and ASC (PEM) projects currently exist.

## Technical Purpose and Benefits

This work will produce submodels that will be useful for determining the chemical reaction mechanisms and kinetics controlling thermal decomposition of selected polymer materials subjected to a large range of relevant heating rates. This work will further produce models for heat transfer and pressure growth caused by thermal decomposition of polymer foams in closed containers in fire environments.



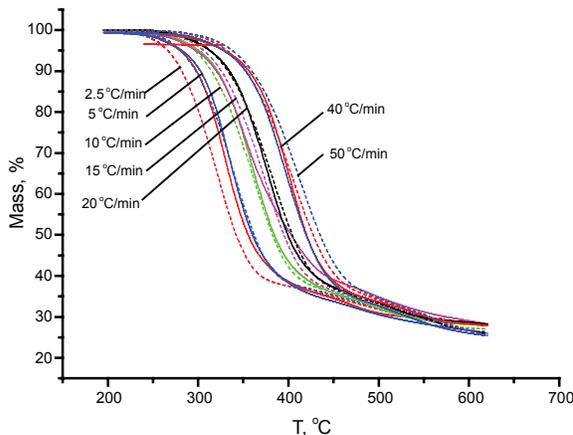
Schematic large sample thermal decomposition.

The project has significantly benefited US/DP, ASC, and the Russian Federation, and the data exchange between laboratories has been mutually beneficial. The project has contributed to quantitative understanding of polymer behavior in accident and fire scenarios. Results have contributed to engineering analyses supporting systems safety and structural vulnerability studies based on accident and fire scenarios. Specific examples include:

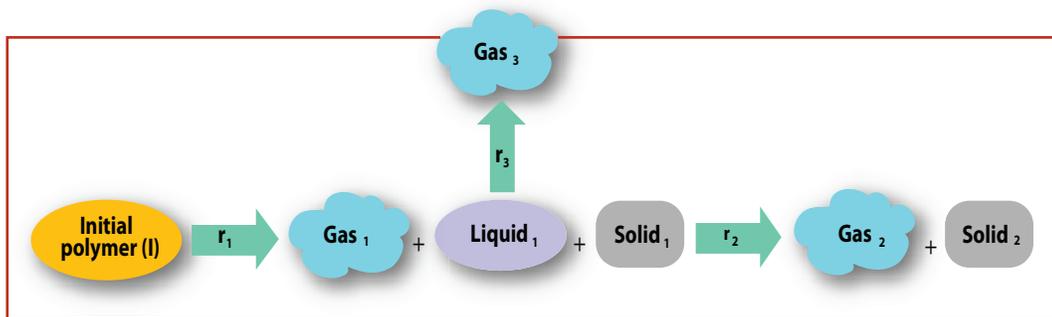
(1) Results from high-heating rate decomposition experiments showed that mechanisms change little below heating rates of about 800 °C/min. This supported theoretical arguments made by Erickson as part of the FY04 Level I V&V milestone, during which the external panel expressed concerns about the effect of heating rate on the adequacy of rate expressions used in the numerical simulations of validation experiments.

(2) From recent work, the quantitative analyses of low-molecular-weight decomposition products will provide input for determining equations-of-state for use with models for predicting pressurization of sealed containers in fire environments.

(3) The decomposition submodels that were developed support engineering analyses for systems safety studies and provide a basis for the new work to develop models for heat transfer and pressure growth caused by thermal decomposition of polymer foams in closed containers in fire environments.



Predicted and experimentally observed mass loss during TGA experiments with polyurethane foam at a variety of heating rates. Solid lines are experimental results, and dotted lines are predicted results.



$$\begin{aligned} d[I]/dT &= -r_1/B; \\ d[\text{Solid}_1]/dT &= (r_1\alpha_1\alpha_2 - r_2)/B; \\ d[\text{Liquid}_1]/dT &= r_1\alpha_1(1 - \alpha_2)/B - r_3; \\ d[\text{Solid}_2]/dT &= r_2\beta_1/B; \\ d[\text{Mass}]/dT &= (-r_1(1 - \alpha_1) - r_2(1 - \beta_1)) B - r_3; \end{aligned}$$

where

B = dT/dt = sample heating rate.

t = time

T = sample temperature

$$r_1 = k_1 \exp(-E_1/(T+273)) [I]$$

$$r_2 = k_2 \exp(-E_2/(T+273)) [\text{Solid}_1]$$

$$r_3 = B \cdot k_3 \cdot \exp(-E_3/(T+273)) [\text{Liquid}_1]$$

$k_1, k_2, k_3$  = pre-exponential multipliers;

$E_1, E_2, E_3$  = the activation energies, referred to gas constant;

$\alpha_1$  = mass of (Solid<sub>1</sub> + Liquid<sub>1</sub>) formed per unit mass of initial polymer consumed by  $r_1$

$\alpha_2$  = mass of Solid<sub>1</sub> formed per unit mass of (Solid<sub>1</sub> + Liquid<sub>1</sub>) formed by  $r_1$

$\beta_1$  = mass of Solid<sub>2</sub> formed per unit mass of solid1 consumed by  $r_2$

**For polyurethane foam:**

$r_1$  = decomposition rate of urethane groups with formation of CO<sub>2</sub> (Gas<sub>1</sub>), aromatic amines and isocyanates (Liquid<sub>1</sub>), and secondary polymer (Solid<sub>1</sub>)

$r_2$  = decomposition of secondary polymer (Solid<sub>1</sub>) with formation of H<sub>2</sub>O, CO<sub>2</sub>, olefines, propylene glycols (Gas<sub>2</sub>) and coke (Solid<sub>2</sub>)

$r_3$  = rate of evaporation of aromatic amines and isocyanates (Gas<sub>3</sub>).

Collaboration between Sandia National Laboratories, Albuquerque, NM, USA, and All Russian Research Institute of Automatics (RFNA-VNIIA), Moscow, Russia

