

## **THE BEHAVIOUR OF POLYSTYRENE IN A MICROCALORIMETER AT TEMPERATURES UP TO 353 K**

**J.C. Jones and K. Harper**

Department of Engineering, Fraser Noble Building, University of Aberdeen, King's College  
Aberdeen AB24 3UE, Scotland

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### **ABSTRACT**

Polystyrene samples are examined in a microcalorimeter. At temperatures far below those at which there can be measurable decomposition, strong positive heat release rates are observed. These are attributed to reactions between the solid material itself and atmospheric oxygen.

### **1. INTRODUCTION**

In the assessment of the fire propensity of polymers, cone calorimetry has found widespread application over about the last 15 years, and one reads relatively little about applications of microcalorimetry to such materials. The present authors have examined a number of polymers by microcalorimetry from temperatures ranging from just above room to 80°C. A considerable proportion of the time was devoted to polystyrene, novel results from which are reported and interpreted herein.

A microcalorimeter works at well below 'combustion temperatures', but low-temperature reaction is always a precursor to ignition of solids and aids such ignition by providing flammable degradation products. Hence the low-temperature behaviour is relevant to incipient combustion, arguably the stage of reaction to which preventive measures such as the incorporation of retardants ought to be directed. This point is further developed in the discussion.

### **2. EXPERIMENT**

The microcalorimeter used was a Thermometric 2277 Thermal Activity Monitor. A sample for testing was placed in a steel ampoule. The instrument had previously been stabilised at the desired temperature overnight. The ampoule containing the sample was then placed in the equilibration position. The reference ampoule, containing air only, was also placed in its equilibration position. Thermal equilibration of the samples took place over a one-hour period. The ampoules were then lowered into the measuring position and the signal followed at a potentiometric recorder (Linseis) connected to the instrument. The

ampoules were left in the measuring position for a few hours, either until the signal was steady or, at higher temperatures, until the peak heat release rate had declined and the signal was dropping markedly. When the final heat release reading at the recorder was taken, it was checked against that on the digital display on the microcalorimeter. The instrument was recalibrated at each change of temperature setting. The results given in the next section represent about 350 hours of instrument operation time.

The microcalorimeter provides a direct reading of the rate of heat release, that is, the rate at which the material is releasing heat. The measurement is basic and fundamental and trends in the measurement under different conditions lend themselves to interpretation in terms of chemical changes to the material.

### **3. MATERIAL**

The polystyrene was obtained from a local manufacturer as a transparent sheet having the nature of a sample such as might be shown to a prospective purchaser. It was subjected to no pre-treatment of any sort for the microcalorimetry work. Its date of manufacture is not known. Pieces for use in the experiments were cut off by means of a mechanical saw.

### **4. RESULTS**

The results are presented in Table 1.

Each section of the table, separated from the others by a horizontal space, gives information on tests performed on one sample. Both within the sections and across the entire table, the experiments are

described in the order in which they were carried out.

**Table 1: Tests performed on polystyrene**

Description of the sample	Temperature/ °C	Summary of results
Polystyrene, 270 mg	40	Left o/night, 0.3 - 0.4 μW
Same as in previous experiment	60	Left o/night, final reading 3.4 μW
Same as in previous two experiments	80	Rapid rise to about 44 μW followed by a sharp decline
Polystyrene, 700 mg	60	6 μW, steady after about 1 hour
Same as in previous experiment	70	Peak at 24 μW, rapid decline
Polystyrene, 410 mg	70	Peak at 21 μW, rapid decline
Polystyrene, 760 mg	60	Left o/night, peak at about 2 μW
Same as in previous experiment	85	Peak at about 40 μW
Same as in previous two experiments	70	Peak at about 3 μW
Polystyrene, 430 mg	55	Steady at 1.6 μW
Same sample as in previous experiment	80	Peak at 41 μW followed by a rapid decline
Same sample as in previous two experiments	55	2.7 μW
Same as in previous three experiments, heat soaked at 55°C for 24 hours	55	Steady at 0.8 μW
Same as in previous four experiments	80	Peak at 24 μW declining gently
Polystyrene, 420 mg, heat-soaked for 24 hours at 55°C	55	Steady at 0.8 μW

From the first set of three experiments, it is clear that at 40°C there is little exothermic reaction; an appreciable degree of reaction at 60°C and quite a rapid one, releasing heat at 44 μW, at 80°C. From the second set, comprising two tests, an important distinction is apparent: at 60°C a steady though quite small (6 μW) signal is achieved but not at 70°C, where, following a peak heat release rate, there is quite rapid decline. In the third 'set' - one determination only - the inability to obtain a steady result at 70°C is repeated, there being a peak at 21 μW. In the fourth set, a point of interest starts to emerge: once there has been an experiment at 85°C, there must have been some change to the chemical composition. This follows from the fact that a subsequent experiment on the same sample at

70°C gives only a feeble 3 μW signal, whereas a sample not having previously experienced temperatures as high as 85°C gives much higher heat-release rates than this at 70°C, as the earlier results in the table show.

This observation was further investigated by 'heat soaking' a sample before measurement. This consisted of placing the crucible and contents in the equilibration position (not the measuring position) in the instrument, set at the 'soaking' temperature, for 24 hours. After this time the crucible would be removed and its atmosphere replenished by removing the lid before any measurements of heat release were subsequently made. In the fifth set of results, then, the initial

result at 55°C is about what was expected as is the result at 80°C. Whatever changes had occurred during the measurement at 80°C, which involved the sample in being at that temperature for 2-3 hours, actually activated the sample. This is shown by the fact that in a test afterwards at 55°C, the sample gave a significantly higher heat release rate than it had before the 80°C test. Accordingly, the sample was at this stage 'heat soaked' for 24 hours at 55°C, and afterwards its heat release rate at that temperature was found to have dropped to less than one third of what it had been before the heat soaking. The sample in this condition tested at 80°C gave a peak heat release rate just over half of that which had been displayed previously (row 2 of this section of the table). Finally, a fresh sample of the material was heat soaked at 55°C and then tested at that temperature, and its heat-release rate was greatly reduced by the heat soaking.

## 5. DISCUSSION

It is helpful to use the results to obtain an idea of the intrinsic reactivity of the material to oxygen. Coals, carbons and cellulose give heat-release rates of  $10^{-3}$  to  $10^{-2}$  Wkg<sup>-1</sup> at temperatures just above room, say at 38°C [1]. At 55°C, a sample of the polystyrene weighing 430 mg gave a steady signal at 1.6 μW, which converts to  $4 \times 10^{-4}$  Wkg<sup>-1</sup>. If the activation energy is about 100 kJmol<sup>-1</sup>, this will be roughly an order of magnitude lower at 38°C, indicating that the substance is much less reactive than those with which it is being compared.

The degradation of polymers is important in understanding their combustion. Beyler and Hirschler make this point very directly in their recent review [2] of polymer decomposition: '*polymers cannot burn if they do not break down*' (their italics). One index [2] of the tendency of polymers to break down is the minimum thermal decomposition temperature, usual symbol  $T_d$ , which is determined by thermal analysis in an inert atmosphere at 10 Kmin<sup>-1</sup> heating rate and is the temperature at which decomposition begins. Another index [2] is the temperature at which decomposition has occurred to an extent of 1% - symbol  $T_{1\%}$  - which is determined under the same conditions as those appertaining to the measurement of  $T_d$ . For polystyrene,  $T_d$  and  $T_{1\%}$  are given [2] respectively as 436 and 603 K (163 and 330°C). With a 10 Kmin<sup>-1</sup> heating rate, the time interval between these must be just over 15 minutes. The same source [2] states, in a different context: 'Polystyrene shows no appreciable weight loss below 575 K (202°C)'.

The microcalorimetric results herein show that, under conditions certainly different from those used in determining  $T_d$  and  $T_{1\%}$ , significant reaction does occur at much lower temperatures than these indices would suggest. An important further question posed is whether it is the different heating conditions that is the origin of the difference, or whether it is the presence in the microcalorimetric experiments and absence in the thermal analysis experiments of an oxidising atmosphere.

Comparison of decomposition temperatures with those of the microcalorimetric tests is not, however, necessarily the most helpful way of examining the results. Whatever reactions are causing the heat release in the microcalorimeter are unquestionably reactions of the solid *per se*: flammable decomposition products once released into the atmosphere inside the ampoule are too dilute to give a heat release signal. Even a reactive and volatile liquid such as methanol having its saturated vapour pressure at the microcalorimeter temperatures will not give a signal [3]. It therefore appears that the reactions occurring in the microcalorimetric tests on polystyrene are akin to those which, at lower temperatures, cause discolouring and general deterioration over extended periods. Using, again, an activation energy of 100 kJmol<sup>-1</sup>, and assuming an Arrhenius temperature dependence, the extent of reaction reached during heat soaking for 24 hours at 55°C would be achieved in 163 days at 15°C. The correspondence of time scales is semi-quantitative, and supports the view that reactions of the solid - not decomposition and subsequent oxidation of the products - are responsible for the heat release at temperatures accessible to a microcalorimeter. Such reactions are also thought responsible for the composition changes reflected in the unsteady thermal behaviour at higher measurement temperatures and the effects of heat soaking, since all of these observations were well below decomposition temperatures.

In summarising, we return to a point made at the beginning: that in understanding (and, therefore, controlling) polymer combustion, the low-temperature processes which are the necessary precursor to combustion are quite possibly a more suitable focus for fire prevention measures than combustion behaviour itself. A number of retardants act by slowing down propagation of combustion after ignition. Is a slowly moving flame, enhanced in toxicity by the presence of the retardant, necessarily any less of a hazard than one moving more rapidly without the toxic effect of the inhibitor? Better surely to inhibit ignition, with the aid of knowledge of the low-temperature

chemistry that provides the degradation products for ignition.

## **6. CONCLUDING REMARKS**

At temperatures well below those required for thermal decomposition, polystyrene samples display in a microcalorimeter positive heat release signals which are attributable to reaction of the solid itself with atmospheric air. Composition changes occur as a result of such reactions, resulting in irreproducibilities of the heat release measurements.

## **ACKNOWLEDGEMENT**

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