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Investigation of an accident in a resins manufacturing site: The role of accelerator on polymerisation of methyl methacrylate

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HIGHLIGHTS

- The accelerator produces an increase in the initial rate of polymerisation.
- The accelerator increases the extent of polymerisation in certain conditions.
- The accelerator decreases the induction time due to the presence of inhibitor.
- Runaway reaction is more likely to occur in presence of the accelerator.
- The experimental data support the hypothesis about the accident.

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ABSTRACT

This paper analyzes the effect of an accelerator on the polymerisation of methyl methacrylate (MMA). This study is based on the results of an investigation of an accident in a manufacturing site for resins located in the United Kingdom. As sequence of event to cause the accident the following was assumed: during an unattended batch process a runaway undesired polymerisation of methyl methacrylate occurred, generating rapid vaporisation of monomer, which in contact with an ignition source, led to an explosion followed by a fire. Since no initiator for the polymerisation reaction had been jet added to the blend, it was supposed that the accelerator contributed to the onset of the undesired polymerisation. The accelerator involved in the accident t has therefore been tested by differential scanning calorimetry and adiabatic calorimetry. The experimental data allowed the authors to prove the hypothesis made and to define safety ranges for the polymerisation reaction.

1. Introduction

Chemical reaction hazards are one of the principal sources of risk in chemical and petrochemical industry, where processing, transportation, storaging and handling of reactive chemicals, of toxic or flammable liquids, vapours, gases and powders take place. Many industrial reactions are exothermic, so overheating of the system is likeable to occur [1]. A runaway reaction is the direct consequence of overheating in a chemical vessel [2] and is characterized by a positive feedback mechanism that makes the vessel behave approximately like an adiabatic system: a progressive increase of the temperature of the reacting mass makes the reaction rate to increase and so the heat accumulation in the system keeps rising [3]. A recent analysis of accidents involving chemical reactive substances showed that runaway reactions are statistically still one of the major concern in chemical industry [4].

In the past, several accidents caused by runaway reactions have occurred in polymerisation plants [5]. From an analysis of case histories, the development of accidents is often found to be due to a lack of understanding of the process chemistry and thermodynamics and poor reactor design [6] or are generated during storage and transportation of monomers [7]. According to the French Data Bank ARIA [8], between 2005 and 2010, 352 accidents involving sites of polymer production and manufacturing of plastic materials and resins occurred. The accidents happened in either process, transport or storage operations, and caused fires and explosions. In

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Abbreviations: ARC, accelerating rate calorimeter; DSC, differential scanning calorimetry; MeHQ, p-methoxy phenol; MMA, methyl methacrylate; DIPPT, N,N-diisopropyl-para-toluidine.

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Nomenclature

$(dT/dt)_{MAX}$	maximum temperature rate [°C/min]
ΔH_{reaz}	heat evolved by the reaction [J/g]
P_{max}	maximum pressure [bar]
Q/m	specific heat of reaction [W/g]
T_{max}	maximum temperature [°C]
TMR	time to maximum rate [min]
T_{onset}	detected onset temperature [°C]
X_f	final conversion [%]
ΔT_{ad}	adiabatic temperature increase [°C]

24 of the accidents considered people were injured and in 2 cases there were 2 fatalities. In 8 accidents the significant economic cost was incurred; in 6 cases, people living around the chemical plant had to evacuate the area because of the release of toxic substances. Several specific studies can be found in recent literature [9–13].

Loss of temperature control is one of the major reasons that can lead to thermal runaways in chemical reactors carrying out exothermic reactions. In the case of polymerisations of acrylic monomers, the loss of temperature control can also be caused by the self-acceleration of the process associated with diffusion phenomena; because of this the knowledge of the kinetic and the fluid dynamic regime of the vessel is necessary to prevent a runaway [13,14].

1.1. *Description of the accident and the investigated hypothesis*

This study is based on the results from an investigation of a recent accident that occurred in the United Kingdom in October 2009, when an explosion, followed by a fire, occurred in a resins manufacturing site. The explosion destroyed the factory and caused blast damage to adjacent buildings. Debris was spread across the surrounding countryside over a radius of approximately 50 m and a number of windows were broken in properties approximately 200 m distance away from the factory. No injuries were however sustained by the employees or members of the public. The entire building was consumed by the fire and the site has been completely demolished as it was deemed unstable.

In the formulation of acrylic coatings, the use of accelerators allows the application of the products at ambient temperature.

Accelerators are designed to increase the rate of polymerisation by promoting the decomposition of the initiator employed in order to start the polymerisation processes at room temperature. They are basically amine compounds that cannot generate radicals in the absence of peroxide or a similar oxidant. There should be no significant increase in the rate of the reaction until the stabilised monomer, in this study methyl methacrylate, containing the accelerator is added to the initiator (i.e. peroxides). However, calorimetric tests carried on after the accident indicated that the accelerator can affect the rate of polymerisation when no peroxide is present. This is a significant finding which warranted further investigation to establish the potential hazards associated with the use of accelerators in resin manufacture. The main process carried on in the site was to prepare an oligomer (pre-polymer) and blend it with methacrylate monomers and accelerators. No reaction was expected to take place at this stage, when no initiator for the polymerisation is present in the system. The blender involved in the accident was stirred and heated by hot water in order to maintain a lower viscosity of the blend. The temperature of the contents should have been approximately 40 °C, but apparently, due to an unknown malfunction of the temperature control system, temperatures as high as 80 °C could be reached inside the blender.

Table 1
Composition of the blender at the time of the accident. The batch was not completed because target weight when completed is 3060 kg.

Component	Weight [kg]	Composition [% by weight]
MMA	1770.0	65.0
Accelerator	23.0	1.0
Pre-polymer	939.0	34.0
Total	2732.0	100.0

In the facility being investigated, there was an incomplete batch of the process just described characterized by the presence of MMA, accelerator and pre-polymer (the detailed composition is shown in Table 1). No extra stabiliser had been added at the time of the accident, while generally a 10% solution of phenolthiazine was manually inserted at the end of the batch. The formulation of the final product was obtained by adding small quantities of substances which, apart from the inhibitor, were unlikely to affect the chemical properties of the intermediate.

The volume of the plant room was approximately 3000 m^3 which would require about 400 kg of MMA vapour to generate a stoichiometric mixture to fill it. The hypothesis made is that the flammable mixture could have resulted from a flammable liquid that had been heated to above its flash point. The most obvious source of vapour, composed mainly of monomer, would be from an uncontrolled runaway reaction within the blender, in which the top feeding port was found to be open.

2. Experimental

The experimental techniques applied in this study were mainly differential scanning calorimetry (DSC) and adiabatic calorimetry [15,16].

DSC tests were run first in scanning mode in order to identify a rough onset temperature for polymerisation; a sensitivity analysis of how the detected onset changes with the DSC heating rate was also performed. After this first screening, isothermal tests were carried out in order to focus on the different stages of the polymerisation reaction and to investigate how they are affected by the set temperature for the test. The isothermal results allowed considerations on the kinetic of the process. For each DSC test it is possible to evaluate the total heat evolved by the reaction. All these tests were performed for raw material, intermediate and product samples provided by the company as representative of the composition of the blend at different stages of the batch involved in the accident.

As this study was aimed at more general conclusions about the effect of the accelerator on MMA polymerisation, the same tests were run for samples containing different concentrations of the accelerator involved in the accident (Table 2). The monomer used for this purpose was commercial Sigma Aldrich (pure 99% contains < 30 ppm of MeHQ as inhibitor).

In each test, the quantity of sample in the DSC was nearly 60 μL (~50% of the available volume of the sample holder). The pans used were medium pressure steel crucibles (sealed with Viton O-ring) that could withstand pressures of up to 2 MPa and temperatures of up to 250 °C.

The experimental data from these tests allowed definition of a critical concentration for the accelerator in MMA so a more detailed calorimetric analysis could then be performed on them in an Accelerating Rate Calorimeter in *heat-wait-and search mode*. Adiabatic tests are useful to analyse the worst case scenario for the polymerisation, determining a more accurate onset temperature for the reaction, the adiabatic temperature rise and the time to maximum rate.