



# Plastic fantastic

**Y**ou can't miss polyethene (PE). It's in your house, in the streets and roads, in supermarkets, in your garden and maybe even in you. The list of PE products is endless – shampoo and detergent bottles, gas and plumbing supply pipes, electrical insulation, car wheel arches and petrol tanks, food packaging and crates, and milk, ketchup and healthcare bottles. Polyethene is also used in bullet proof vests, in hip and bone replacements, and as a waterproof coating on skis, sail boards, and canoes. So ubiquitous is this plastic – PE is the most widely used plastic, commanding ca 36 per cent of the total European market – that it's hard to imagine life without it. And yet, like many other products we have come to rely on for our current lifestyles, polyethene was discovered by accident.

## A serendipitous discovery

In March 1933, Reginald Gibson and Eric Fawcett, two research chemists at ICI's Winnington Laboratory in Cheshire, were working on high pressure and high temperature reactions. They were trying to develop new products for ICI's rapidly growing dyestuffs industry. They reacted ethene and benzaldehyde (benzene carbaldehyde) at 2000atm (1atm = 101325Pa) and 170°C in the hope of producing either phenyl ethyl ketone or phenyl allyl alcohol, two potential intermediates in the manufacture of dyes.

The high pressure apparatus, comprising a mercury gas compressor, had been designed by Dutch chemist Dr A. Michels, with whom Gibson had worked with at the University of Leiden a few years earlier. Benzaldehyde

was contained in an inverted glass tube, sealed with mercury and placed in a steel tube, which was placed into a reaction vessel. The vessel was sealed and put in an oil thermostat, regulated to 170°C. Ethene was bubbled through the mercury into the benzaldehyde – mercury separated the gas from benzaldehyde rather like a piston.

Gibson and Fawcett started the experiment on Friday 14 April in the afternoon, and left it to run over the weekend. When they returned on the Monday morning, they found that the pressure in the system had fallen to ca 500atm because of a small leak in the oil system. Ethene had expanded and forced the benzaldehyde through the mercury into the oil system. They couldn't replace the benzaldehyde so, having fixed the leak, they restored the pressure by adding more ethene. After a few hours they stopped the reaction, allowed it to cool and dismantled the apparatus. No liquid product had formed, as they had hoped for, but instead a trace amount – 0.2g – of a waxy solid had formed on the inside wall of the glass tube. Spectroscopic analysis revealed that this contained only hydrogen and carbon in the same ratio as ethene. They had discovered polyethene.

Unfortunately, though, when they tried to repeat the experiment, decomposition of ethene to carbon occurred, which being exothermic caused an explosion, bursting a pressure joint near the oil thermostat and setting it on fire. ICI management immediately stopped high pressure work on ethene until safer premises could be found. That might have been the end of the story but ....

## Polyethene – rediscovered

Two years later, and in an isolated building with walls one-foot thick, Michael Perrin, another research chemist who had also worked with Michels, decided to do some more experiments with ethene.

Frank Bebbington, now 94 years old and one of Perrin's research assistants at the time, told *Education in Chemistry*, 'On 20 December 1935 I assembled equipment in a deliberate attempt to polymerise ethylene [ethene] under the same conditions that Gibson and Fawcett had used, but on a smaller scale. Immediately, we put the pressure up to 2000atm, the pressure in the reaction vessel started to fall away very slowly, and again we thought there was a small leak in the system. I felt embarrassed because I had assembled the equipment. I compressed more ethylene to take the pressure back up to 2000atm. At 1.00pm everybody, except me, went to lunch; I was left to keep the pressure at 2000atm. When they came back we stopped the experiment, and cooled the vessel. We opened it up, and to our amazement, it contained white powder – 8.5g of the stuff to be precise. We had rediscovered polyethene. We immediately called the research director, Dr J. Swallow, who took the powder in his fingers and said "I wonder if it's a plastic?"'.

The next couple of attempts to repeat the experiment, however, gave only 0.5g, 1g and an explosive decomposition reaction. 'But', says Bebbington, 'once you've made 8.5g of something, you know you can do it and we were determined to find out how'.

Bebbington remembers, 'after about 200 experiments, we discovered that the key to the successful polymerisation of ethylene [ethene] was an impurity in the ethylene – ie oxygen. Too much O<sub>2</sub> – ca 500–1000ppm (parts



Polyethene – it's so useful

In its simplest form polyethene consists of a long backbone of carbon atoms with two hydrogen atoms attached to each. This is called linear polyethene or high density polyethene (HDPE). Sometimes the hydrogen atoms are replaced by other PE molecules, which gives branched or low density polyethene (LDPE) – the molecules don't pack together so well. Approximately two thirds of all injection moulded PE items are made from HDPE – industrial containers, such as crates and pallets, gas and water pipes, canoes, car parts, and food containers, carbonated bottle bases and caps; LDPE is used mainly for food packaging films, waterproof films, and electrical cable insulation.

per million) – led to decomposition of the ethylene, 20–200ppm of O<sub>2</sub> gave polyethylene, and no oxygen – no polyethylene'. 'Oxygen', explained Bebbington, 'was acting not as a catalyst but as an initiator because it was being used up during the polymerisation reaction'.

By April 1936 the first pound of polyethene had been made. It was sent to the Nobel Division of ICI in Ardeer, Scotland, where the only injection moulding machines existed, and a few small pill boxes were made. Back at Winnington, Perrin and his team made more polyethene and started testing their new material. The PE that they had made was low density polyethene (see Box). Its excellent insulating properties at high frequencies soon attracted the telephone industry, which was quick to spot it as a replacement for gutta-percha to insulate telephone cables. (Gutta-percha – latex from rubber trees in the Far East – was becoming increasingly difficult to obtain because of the imminent war.) On 1 September 1939 polyethene became an official product of ICI.

During World War II all PE was made for the Government, specifically for high frequency experimental radar cable. The successful development of radar is said to have shortened the war by years. A polyethene tube, called Pluto, was also laid across the Channel for transferring petrol from the UK to France.

Since its discovery over 70 years ago, there have been many improvements to the synthesis of polyethene. These have centred around the development of several types of catalyst – notably Ziegler–Natta catalysts in the 1950s and metallocene catalysts in the 1970s – so that the polymerisation can be done at lower pressures and temperatures, thus using less energy and making the process more environmentally acceptable.

Kathryn Roberts



The original apparatus used to discover PE

Science Museum, London