



*Wirsbo-PEX 10 times around the world*

**Professor Thomas Engel**  
Professor at Université de Nice,  
Laboratoire de Chimie  
Organique de Fluor, Parc Valrose

*11/28/90*

## **POLYETHYLENE, A MODERN PLASTIC, FROM ITS DISCOVERY UNTIL TODAY**

Modern science assumes that the birth of our planetary system and of the universe started with a big bang. This is a hypothesis which is supported even by Professor Einstein, but whether or not it is actually true is still beyond our knowledge. On the other hand, there is no doubt that the birth of polyethylene started with a vigorous explosion. The equipment of a research laboratory was completely destroyed - windows were broken within a large radius and it was a stroke of good fortune that no one was injured.

What happened? In March of 1933, the behavior of ethylene and benzaldehyde under pressure and temperature was being studied as part of a series of experiments at the Imperial Chemical Industries Ltd. in England. It had already been noted there that previously unknown polymers can be produced under these conditions. Similar observations had also been made by Percy Bridgeman at Harvard University when he subjected organic substances to compression pressures of 20,000 bar. Such experiments are carried out in so-called autoclaves. These are extremely heavy steel containers into which the substances to be examined are placed and then subjected to pressure and temperature. And it was in just such an experiment that the explosion occurred. When the scientists opened the autoclave after the explosion they found a white, wax-like precipitate within it. The total amount was 8 grams. This was the hour of birth of polyethylene, since subsequent analyses showed that the molecular structure of the gas had been compressed to such an extent that it had become a solid. The laboratory was rebuilt and the experiment repeated. This time, however, with suitable precautionary measures and with the pipelines and valves reinforced.

When the autoclave was opened it was found to be completely empty. The reaction had not taken place and there was no white precipitate! The temperatures and pressure were changed and the ethylene was selected in a large variety of purity, but nevertheless when the autoclave was opened after each test, nothing but a gaping void was found. More and more the conviction grew that the first experiment had been a coincidence and years were to pass before the actual cause was found.

Sir Archie Renfrew, at that time Director of the I.C.I. in Welwyn Garden City, was present during a discussion in which all the scientists concerned with this project participated. He stated; "If all of these detailed tests have given negative results during the past years and not resulted in anything, then we must attempt to reproduce the precise operating conditions of the original test; that is, we must intentionally attempt to cause the unit to explode. Perhaps in that way we will come closer to our goal."

The experimental plant was therefore again made ready for operation. This time, to be sure, two places of intended rupture were provided in the piping. The heat was then turned on. The autoclave reached a temperature of 170 °C. The gas compressor was then connected and introduced ethylene at a pressure of 800 bars into the autoclave. The compression was increased further. It rose to 900 bars, 1000 bars, 1200 bars, 2000 bars. At 3400 bars the pipes suddenly ruptured and there was an explosion with a spontaneous drop in pressure within the reactor plant. When the clouds of smoke had disappeared, with expectant faces the scientists began to loosen the heavy bolts of the autoclave. When the lid had been removed, the same white waste as had been found two years previously upon the first test was seen. What had happened? Due to the explosion and the accompanying drop in pressure within the autoclave, oxygen had been drawn in from the air and acted as a catalyst on the ethylene.

This, in turn, led to the polymerization of the ethylene. The phenomenon was confirmed in subsequent tests by installing another feed pipe in addition to those which had been already installed. Oxygen was then carefully pumped through this pipe into the autoclave during the test and, the reaction was the same as in the forced explosion - the autoclave was filled with a thin layer of polyethylene!

The analyses carried out at that time had already clearly shown the outstanding properties of the samples - excellent chemical stability, similar to that known at the time only for chromium, nickel, gold and glass, improbable insulation values of an order of magnitude still unknown at that time and, last but not least, an extremely low density - an unbeatable advantage over metals.

It was therefore decided to construct a plant with which it would be possible to produce larger quantities of this polyethylene. The plant was constructed for an output of about 50 kg. No one at those days had the remotest idea that the day would come when polyethylene would be manufactured in millions upon millions of tons annually.

But the construction of the 50 kg plant was itself a masterpiece of technology because high industrial pressures of 3000 bars now had to be achieved. However, at that time there were no compressors capable of continuously producing such pressures. The first item was therefore to construct a high-pressure compressor, and once again many years were to pass before the first production plant could be placed in operation. This occurred in July 1939 and, for the first time, quantities were available which made it possible to test practically the possible uses of polyethylene.

It often happens that discoveries are made which scientists had been dreaming of for years. However, when the solution of the problem is found, one isn't quite so certain as to what is to be done with it. This turned out to be true also of polyethylene, until once again an accident came to their assistance. The Second World War was threatening. One of the problems at the time was the insulating of power cables in submarines. Such insulations were manufactured by the Bell Telephone Company using paragutta, a mixture of gutta percha, rubber and paraffin wax. This polymer, however, in no way had sufficient mechanical strength or dielectric constant. Polyethylene was to prove far more favorable - as a matter of fact-optimal. However, the problem then arose that there was no extruder by which this polyethylene could be extruded around the copper. Paragutta, in fact, has much better flow properties than polyethylene. Therefore they went to the United States where the polyethylene was extruded around the high voltage cable by means of a rubber extruder. These experiments were successful. The polyethylene-covered cable had excellent insulating values and high mechanical strength, and could be easily installed. I.C.I therefore quickly decided to construct an even larger production plant for polyethylene. This plant had a capacity of a few hundred tons a year. It was placed in operation in September of 1939. Due to the beginning of the Second World War, polyethylene was used solely for military purposes. It is thanks to polyethylene that Sir Robert Wattson was able to discover radar and develop it to perfection. "Find, fix, fight and finish the 'Scharnhorst'". Those were his words on the occasion of a sea battle between Germany and England. In fact, the British were able to sink the "Scharnhorst" only because they had been able to locate its position by radar much sooner than would have been true with any other instrument.

In the middle of the Second World War it then suddenly became evident to German scientists that the British not only had discovered polyethylene but were also able to manufacture it on a large industrial scale. This became clear when an English bomber was shot down over Germany. Upon examination of the wreckage the peculiar nature of the cable insulation was noted. When the material was analyzed it was found that it was actually polyethylene.

The Second World War came to an end. Germany, fully involved with reconstruction, was approaching the start of the "economic miracle". Contacts were established again between the large chemical companies, and B.A.S.F. was the first company in Germany to obtain a license for the manufacture of polyethylene from I.C.I. London. In this way, polyethylene came to Germany and was to experience here the same triumphal march as it had in all other countries in the world.

Polyethylene is a thermoplastic resin, that is, it softens under heat and hardens upon cooling, comparable, if you like, to a wax candle whose wax can be softened and liquefied and then resolidified as frequently as desired. This is a great disadvantage for the use of polyethylene. Its suitability for long-term use was thus limited to about +70 °C. It was therefore obvious to look for ways of increasing polyethylene's resistance to temperature. And it seemed that this should be possible in view of its molecular structure, that is by connecting the chains of the molecules to each other so as to produce a network. This would considerably, or even completely, prevent the flowing of polyethylene at elevated temperature.

Similar observations had already been made, namely in the case of caoutchouc. Caoutchouc is by nature a sticky mass. Only when the American Goodyear had come upon the idea of adding sulfur to caoutchouc under pressure and heat did caoutchouc become what we today call rubber. The vulcanisations of caoutchouc is a Goodyear discovery.

In 1965 I was together with various scientists of the Phillips Petroleum company in Bartlesville, Oklahoma, and we were discussing specifically this matter - namely, the cross-linking of polyethylene. I decided at that time to study the problem, naturally with the realization that the chemists of all raw-material companies were also working on this problem. It was possible at that time to cross link polyethylene by means of highly active radiation. The problem, however, lay not only in the extremely expensive and somewhat dangerous equipment but also in the fact that this method of cross linking was suitable only for very thinwalled films and sheets. Cross linking was feasible only for wall thicknesses of up to 0.5 mm. The important uses for cross-linked polyethylene would, however, always be for thick-walled parts having a wall thickness of 1 to 10 mm.

I began my studies using an extruder and I very rapidly found that this technique is not feasible. This was followed by lengthy experiments with laser beams.

Finally I decided in favor of a compression method with intermolecular friction, telling myself that the cross linking of the molecules would have to be easier if I could heat them rapidly and bring them closer together by high pressure so as then to cross link them in the presence of a catalyst. Years of intensive research followed, finally culminating in success. Here, too, the result was a handful of glittering white plastic which came out of the autoclave.

With this small treasure in my pocket, I flew back to Phillips Petroleum in the United States, where we carried out the analysis. We found that I had actually obtained 97% cross-linking.

As a result of the cross-linking process the thread-shaped chains of molecules had been connected directly to each other via the C-C atoms. We were all somewhat speechless. The joy was immense. Again and again we heated the polyethylene. The plastic simply would no longer melt into a shapeless mass. A fascinating picture! But what was to be done with it and into what could it be fabricated?

I traveled from one chemical company to another in the hope of selling a license, but received always the same answer:

"Marvelous, but what do we do with it?"

It was not possible to sell a license.

Naturally, this development and cross-linked polyethylene were discussed in the trade and general press.

In our neighborhood there was a chicken farm, and one day I was asked whether I could make pipes of this material which could be laid in the ground. In this way the hens would have a larger amount of heat and would lay more eggs. In my despairing search for a field of use I decided to modify the autoclave so as to be able to extrude a pipe with it. We installed the pipe successfully on the chicken farm. The laying of my pipe in the Olympia Stadium in Munich was then the first highpoint of its use. However, if a shoe factory had been present in my vicinity at that time, we would perhaps today all be walking around on shoe soles made of cross linked polyethylene. The paths of life are frequently this strange.



One day Sir Archie Renfrew came from London and called upon me in my laboratory. I demonstrated the cross-linking of polyethylene to him: "All of this reminds me of our work in 1933," he said, "when we were desperately attempting to produce pressures of more than 3000 bar. No one thought at the time that polyethylene could be compressed with 10,000 bars, and when I see what influence your high compression has on the molecular structure of polyethylene I can only repeat that chemistry is still only at the very start of a development, the extent of which no one can foresee."

The process for cross-linking of Polyethylene is today a well established technology throughout the world. Wirsbo Bruks AB, Sweden has played a very important role in the industrialisation and marketing of cross-linked pipe. 400 Million meters Wirsbo pipes have successfully been installed for heating and hot water supply throughout the world. In many respects Wirsbo cross-linked PE Pipe has similar properties than those of copper pipe. However to produce copper pipe requires 7 times more energy than needed for Wirsbo pipe. This of course means 7 times more pollution. On top of this, Wirsbo pipe can be installed much easier. Already these facts lead cross-linked Wirsbo pipe into a very promising future.