Looking Back. Production of PVC pipe in Bitterfeld, Germany, in 1935 ushered in the use of plastics for pipe production. This required exact knowledge of material properties, life expectancy and permissible loads. This was recognized from the very beginning and pursued systematically.

Materials for Pipes – Meeting Changing Requirements

EGON BARTH

VC pipe was not the very first plastic pipe, the literature contains reports on pipe made from vulcanized fiber, celluloid, synthetic resin and even thermosets, but does not record dates (Figs. 1 and 2). This pipe was usually processed into sleeves, bushings, cuffs and bearing shells, and used for craft projects, but not as industrial pipe. This field of application was first addressed by the "Igelit" and "Vinidur" pipe that originated in Bitterfeld, in central Germany. The PVC-U pipe produced there immediately found practical use in a wide variety of applications. The first PVC-U pressure pipe was laid in Bitterfeld and Salzgitter in 1935. Use in chemical plants is documented as of 1936. Application was not, however, restricted to industrial piping for conveying corrosive fluids, but rather wider in scope, so that the pipe very quickly found use in household plumbing systems and the food processing industry: in breweries and dispensing equipment, where it became favored because of its physiological harmlessness, minimal incrustation and - in transparent formulations - provided a visual means of checking cleanliness.

Besides the noteworthy pragmatic approach by which the new material best demonstrated its quality under real loads in practical use, investigations of the material properties did not stop, of course. Laying pipe out in the open (Fig. 3) was also a brave step, since the stabilizers employed at that time (soda and sodium

Translated from Kunststoffe 3/2010, pp. 14–19 **Article as PDF-File** at www.kunststoffeinternational.com; Document Number: PE110371 phosphate) protected the PVC against thermal loads during processing, but not against the action of the UV components of sunlight – an experience that many citizens of the former German Democratic Republic made in the 1960s with their Vinidur rainwater pipes that shattered at the slightest impact after several years of use. Walter Buchmann in particular is to be thanked for determining the material properties of Vinidur, including the temperature dependence of dimensional stability and welding conditions, almost completely within a few years [1]. Extensive "resistant to" lists were prepared by Walter Krannich [2].

It was also Buchmann who recognized that, contrary to the case with metals, the short-term integrity cannot be used to predict the long-term integrity, but that the integrity of macromolecular materials over time must be established on the basis of time- and stress-based investigations, and then conducted the first internal pressure investigations (Figs. 4 and 5).



Advertisement for "Trovidur" spiral pipe made from PVC-U; here, size NW 3000 (source: Dynamit Nobel company newspaper, June 16, 1970)

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He was thus able to state already in 1941: "The resistance of Vinidur to other materials has been investigated completely in a manner comparable to that for all commonly known metal-based materials. This fact, together with knowledge of scientific relationships, has proven to be the best way of exploiting the material's properties and avoiding incorrect use."

The second sentence in particular is not be disputed, especially in view of what we know today. Buchmann's investigations also provided the basis for the initial Standards for Pipe made of Polyvinyl Chloride-Pipe Type-in the form of DIN 8061 and 8062 in July 1941. Knowledge of the basic physical and chemical properties of the new material now existed and users were not entirely clueless. While it made sense to employ the pipe in company-owned and affiliated plants of I.G. Farbenindustrie, the willingness with which users in other fields, laboratories and state institutes participated in investigations of PVC-U and "reported back" their own experiences is noteworthy. Thus, after a few years, it was possible to lay the foundations for reliable use in the most varied of applications, as can be seen from a few examples of these initial feedback reports.

In the field of water supply, the first applications involved household plumbing installations in company-owned apartments in Bitterfeld in the years 1935-39. During this period of time, approximately 400 apartments in the Bitterfeld region of central Germany were equipped with PVC-U pipe for drinking and wastewater lines. In Steinfurth near Wolfen, a drinking water line was laid and still providing good service in 1992. Additional lines were laid in Salzgitter and

in apartments in southwestern Germany by I.G. Farbenindustrie. These lines were operated with pressures between 3.5 and 6 bar [3].

Fig. 1. "Trolit"

from 1928

advertisement from **RWS** Troisdorf dating

(source: M Dederichs)

In addition to I.G. Farbenindustrie, which was interested in promoting new fields of application for its PVC-U pipe out of its own self-interest, the water authorities responsible for providing drinking water quickly recognized the outstanding properties of this new pipe material. Accordingly, between 1936 and 1941, test lines in various sizes were laid by the water authorities in the German cities of Leipzig, Dresden, Magdeburg, Berlin, Hamburg, Cologne, Heidelberg and Wiesbaden, among others. They were operated with pressures of up to 6 bar and observed carefully. The test lines passed with flying colors and even withstood additional loads such as pressure surges of up to 18 bar at a frequency of 10 pressure changes per minute in fatigue tests. Many of these test lines were destroyed in the course of the war. Installations that survived the war undamaged continued in service long after the end of the war without major difficulties. These include, for instance, 480 apartments in central Germany such as the household connecting lines (d = 32 mm) laid in 1938 by Berlin's water authorities and, at least until the 1960s, the Mipolam pipe $(22.5 \times 1.6 \text{ and})$ 16.5×1.6 mm) installed in Hamburg in 1937. Even the PVC-U water lines from Bitterfeld installed in the Olympic Stadium in Berlin are reported to have remained in use until long after the end of the war [4–6].

The good resistance of PVC-U to chemicals was also recognized very quickly. As early as 1937, Hans Lutz reported that Mipolam pipe "exhibits remarkable resistance to chemical attack" [7].

The good performance of the pipe when exposed to corrosive chemicals in particular led quickly to use of the pipe produced in Bitterfeld in neighboring chemical plants. By 1938, initial feedback reports on the pipe installed in 1936 were available. Similar positive reports were issued, for instance, by the ammonia plant in Merseburg, Germany, in 1938 regarding 3,900 kg of pipe: "Igelit was used primarily and with good results for a wide variety of acids, bases and gases (especially sulfuric acid and hydrochloric acid)." At the same time, extensive investigations into the physiological harmlessness of the pipe were being conducted in the company's own laboratories and in state institutes. The assessment:

- The police chief in Berlin, Department IV on August 22, 1938: "We have no concerns regarding use of these Mipolam hoses as the moving part in the carbon dioxide pressure line."
- The Institute for Brewing and Starch Production in Berlin on February 27, 1940: "Contact of about 40 to 45 cm? of pipe surface with about 330 cm? of bier (i.e. about 8 cm? of beer 1 cm?) over a period of 3 weeks produced no changes in flavor or aroma or other changes, especially no degradation in this regard. Neither of the two production samples of Vinidur Pipe MP indicates any need for concern or restrictions in this respect regarding their suitability and use in beer dispensing equipment."
- And on March 31, 1941: "Surprisingly the Vinidur material, which after all is \rightarrow



Fig. 2. Pipe, profiles and knobs made from "Trolon" (source: M. Dederichs)

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Fig. 3. "Vinidur" pipe laid outdoors (source: W. Krannich)

synthetic and organic in origin, is a material that even under the rigorous test conditions applied (long action time, large contact surface, amount in relation to the volume of spirits etc.) has no effect whatsoever on the brandies, liquors or spirits with which it is in contact in various degrees of dilution and is itself not noticeably changed by these spirits."

After receiving official confirmations of the physiological harmlessness, the Igelit pipe quickly found use in drinking water installations, the dairy industry, food processing industry, beverage industry etc. since no degradation of the food or beverages involved was to be expected from these pipes.

Use of PVC pipe in piping systems requires a way to connect to the individual pipes to one another permanently. This meant that fittings such as T-pieces, elbows, reducers, valves etc. would be needed. And these were also developed in the I. G. Farben plants. Pipe connectors and elbows were relative simply to fabricate by means of warm forming. They were attached by means of adhesives or welding, which was developed by A. Henning in Merseburg [8]. Production of other fittings and valves was more difficult. The first shaped parts were machined from blocks of material and assembled manually. Later, pipes with different diameters were welded or shrink-fitted together (Fig. 6). The breakthrough came with development of impact molding in Bitterfeld as well [9].

Rapid and successful development was interrupted by the Second World War, but resumed very quickly after 1945. While Bitterfeld was the largest producer in the world in 1945 (with production capacity of about 9,000 t/a), plants with much higher capacity were built primarily in the USA, Japan and Western Europe.

The breakthrough to mass production also occurred in West Germany after a slight delay, where almost all successors to I.G. Farben introduced polymerization of PVC. At this time, suspension polymerization, which had already been developed by Wacker in1934, quickly replaced emulsion polymerization. Rapid expansion of the fields of application required not only improving polymerization methods, stabilization and processing techniques. The development of extrusion technology that was started in Bitterfeld in 1942 had, in the mean time, reached the point where pipe could be produced continuously from thermoplastic resins and output and pipe dimensions continued to increase.

New Pipe Materials

Along with PVC-U, polyethylene must be counted among the first-generation plas-



Fig. 4. Creep strength and fatigue strength of "Vinidur" after extended testing of tensile specimens cut from Vinidur pipe (x-axis: durability; y-axis: creep strength; Dauerstandfestigkeit = fatigue strength) (source: W. Buchmann)

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Fig. 5. Short-term burst pressure values for "Vinidur" pipe (left-hand scale) and fittings (right-hand scale) for the three standardized pressure series at 40 °C (source: W. Krannich)

tics in the pipe sector. R. O. Gibson at JCJ in England had already presented the high-pressure process for polymerization of ethylene to low-density polyethylene (PE-LD) in 1933 and the first large-scale plant with a capacity of 200 t had been put into operation by JCJ in 1939. In 1945, BASF announced its own high-pressure process. The first "Lupolen" PE-LD pipe for drinking water was laid in 1949 after its physiological harmlessness was confirmed by the German Department of Health in Berlin-Dahlem. Follow-up investigations after a service period of eight years showed no changes whatsoever in properties or deformation of the pipe cross-section. The interior surface was still smooth with no deposits. Internal pressure testing of PE-LD pipe at 20 °C was initiated in the USA already in 1950.

Development of polyolefins benefited significantly from the work of Karl Ziegler, Essen, Germany, and Giulio Natta, Milan, Italy, as a result of the catalyst technology they developed. On the basis of Ziegler catalysts, Phillips and Standard Oil developed the low-pressure process to produce PE-HD in 1953. Natta succeeded in polymerizing polypropylene (PP) and polybutylene-1 (PB) in 1954.

After the first internal pressure fatigue trials had confirmed the longterm integrity PVC-U, PE-LD and PE-HD pipe and reliable data regarding the quality and load-bearing capacity of these pipe materials became available in the form of the DIN Standards 8061, 8062, 8074 and 8075, vigorous development ensued with the objective of achieving larger pipe dimensions and opening up new fields of applications. In Germany, use of the low-pressure process was expanded further by Hoechst AG. This led to production of the first pipe in 1954 and in only three years development of a practical PE-HD pipe material with the designation Hostalen GM 5010. PE-HD pipe was subjected to extensive testing (Fig. 7) and for 42 years has now been in use for drinking water applications, as sewer lines, as cable conduits and, since the end of the 1960s, even as gas lines with great success. In these applications, it has almost totally displaced PVC-U pipe in Germany. PE-HD was continually developed further. While the first PE-HD Standards DIN 8074 and 8075 from 1960 referred to pipe for which the permissible stress at 20 °C was 6.3 N/mm² over 50 years, PE-HD pipe able to withstand 8 and 10 N/mm² is available today.

As the aftermath of war was increasingly overcome, the development of plastics expanded worldwide. Optimism prevailed in all branches of industry and drove innovation in polymer chemistry. The machinery industry continually improved the mixers, calenders, extruders etc. needed for processing to achieve higher output. The joining and pipe laying



techniques were improved in equal measure. Plastics increasingly made inroads into new fields of application. The expression "age of plastics" was sometimes used in a state of euphoria. In close cooperation with resin suppliers, plastic pipe manufacturers sought out new applications and materials. Activity focused on expanding the range of application to higher temperatures and larger dimensions (**Title photo**).

After PVC and PE pipe had expanded from drinking water and chemical pipe applications into use as wastewater pipe in sewer systems (1966), PVC pipe was the first to find use for gas distribution in the first half of the 1960s. In the meantime, PE has almost completely displaced PVC pipe for gas distribution. Polypropylene then appeared as the new material in the pipe sector.

Polypropylene. Development of plastics able to withstand higher temperatures began as polypropylene became available on a large scale in 1957. Compared to other plastics, that was a relatively short time span from its initial synthesis in 1954 by Natta. Initial difficulties with stability were quickly overcome. The lower impact strength of PP as compared to PE was improved through co-polymerization with PE and PP polymer blends. PP pipe found its fields of application very quickly in the 1960s. Underfloor heating represented a very specific niche application until pipe made from cross-linked polymers (PE-X) became dominant. Together with PVC and PE, PP is now a commodity resin that because of its ability to withstand elevated temperatures can be employed at operating temperatures of up to 90°C.

Chlorinated PVC. In 1959, chlorinated PVC (PVC-C), which was already produced by BF Goodrich in the USA in 1934, was used for the first time to produce pipe. In an attempt to increase the service temperature limit to above 100 °C, ever higher Cl content was sought in the 1960s. For instance, PVC-C pipe with Vicat temperatures of up to 140 °C was successfully extruded in Troisdorf, Germany. However, with increasing Vicat



Fig. 6. Straight seat valve. The valve body consists of individual shrink-fitted "Vinidur" pipes. The valve is constructed from machined Vinidur parts assembled to the valve body by means of threads, welding and adhesive

temperature, extrusion becomes more difficult and the material more brittle. The PVC-C pipe used today on a large scale has Vicat temperatures between 105 and 110°C, and thus a service temperature of up to 90°C.

Polybutylene-1. Similar operating temperatures were also achieved with polybutylene-1 (PB) pipe. Although initially synthesized by Natta in 1954, it was not until 1964 that pipe was first extruded from this polyolefin by the Chemische Werke Hüls, Germany. In 1968, Mobil Oil in the USA also began production.

Polybutylene-1 exhibits one peculiarity: when crystallizing from the melt, a tetragonal crystal structure forms. In this modification, the material is rubbery and can be easily deformed, i. e. easily extruded. Then, depending on the pressure, temperature, orientation and other factors, recrystallization into a twin hexagonal crystal structure occurs. At normal pressure and room temperature, the recrystallization is complete after about one week. The material becomes harder and stiffer, and the melting point increases to 125-130°C. The pipe can withstand stress only in this modification and then up to at operating temperature of 90 °C. Unfor-

Pipe designation	Min. degree of cross-linking [%]	Cross-linking method	
		Physical	Chemical
PE-Xa	75	Peroxide cross-linking	
PE-Xb	65		Silane cross-linking
PE-Xc	60	Electron beam cross-linking	
PE-Xd	60	Azo cross-linking	

Table 1. Cross-linking method and degrees of cross-linking for pipe made from cross-linked polyethylene



Fig. 7. Early time-to-rupture internal pressure tests conducted at the materials testing laboratory of Hoechst AG

tunately, production of PB at Hüls ended after a few years. Today, PB is produced only by Shell (with a capacity of 30,000 t/a) and in smaller amounts by Mitsui in Japan.

Polyester and epoxy resins. A further extension of the temperature range then became possible with glass fiber-reinforced polyester and a epoxy resins. Polymerization of these resins had already been successfully achieved in the 1930s (unsaturated polyester resins (UP) by Hermann Staudinger in 1934 and epoxy resins (EP) by Pierre Castan in 1938 in Zurich, Switzerland).

In 1942, the United States Rubber Comp. was already using structural parts made from glass fiber-reinforced UP resins. This technology developed very rapidly and has become well established for construction of storage containers and vessels, in the aircraft and aerospace industries and in boat construction. Not until 1961, however, were the first spun glass fiber-reinforced pressure pipes with a diameter of DN 1000 produced. Because of their high strength, these pipes then quickly found use in industry. It was only after Drostholm in Denmark developed the winding process that production of such pipe became more economical and a breakthrough into the pipe sector was achieved.

Cross-linked polyethylene. With the discovery in the mid-1950s that polyethylene can be cross-linked, the foundation for an additional successful pipe material was laid. Cross-linking of PE molecules can be achieved in various ways. Peroxide cross-linking was patented by Th. Engel in 1969. The cross-linking methods

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and degrees of cross-linking achievable for pipe made from cross-linked polyethylene (VPE and PE-X) are presented in **Table 1**.

Development of PE-X pipe coincided with the introduction of underfloor heating in highrises. Here, PE-X pipe found an almost custom-tailored field of application. Today, PE-X underfloor heating pipe enjoys a market share of about 80 % and has almost totally displaced not only metal pipe, but also the PP and PB pipe (approx. 15 %) initially used in this sector.

Styrenic polymers. Pipe made from acrylonitrile-butadiene-styrene (ABS) and acrylonitrile-styrene-acrylic ester (ASA) or blends thereof must be counted among the "late bloomers", at least in Germany. By the same token, the styrenic polymers also belong to the "old" plastics. Polymerization of the styrene was probably first observed by the pharmacist Eduard Simon in 1839 in Berlin. At the request of Liebig, Blith and Hofmann achieved intentional polymerization into glasslike blocks in 1845. The company Nangatuck in USA achieved the first technical preparation in 1925 and BASF followed in 1930 with continuous polymerization in Ludwigshafen, Germany. Extrusion of ABS pipe probably first started in the USA. ABS pipe was first extruded in Germany between 1965 and 1970. Because of its better weatherability, however, ASA has been preferred since the 1970s.

Polyvinylidene chloride (PVDF) is for now the last plastic to have become established as a pipe material. The history of fluoropolymers began in 1886 with preparation of the gaseous tetrafluorocarbons by the Frenchman Henri Moissan. Between 1930 and 1940, numerous gaseous fluorine compounds that served as refrigerants and propellants were developed. The leader was the USA, but I.G. Farben also received a patent in 1934 for polytrifluoroethylene, which, however, was not produced until 1950 by Hoechst AG.

Except for special applications, the breakthrough in the pipe sector was first achieved by polyvinylidene fluoride. It was first synthesized in 1944 by Du Pont and introduced in 1961 by the Pennwalt Corp. under the name Kynar. In Europe, PVDF first became known at the end of the 1960s through imports. Solvay & Cie SA, Brussels, Belgium, took up development of PVDF in 1970 and launched its product in 1972/73 under the designation Sole. The commercial products Forefront from PC Urine Cullman and Dilfer 2000 from Dynamite Nobel, Troisdorf, Germany, followed in the year 1973. Extensive internal pressure fatigue testing of PVDF pipe began in Troisdorf already in 1974. More than 1,200 pipes were tested there at temperatures between 20 and 140 °C. The first time-to-rupture curves were published in 1980. PVDF pipe has been in use since the mid-1970s, primarily in chemical plants. With this pipe, a thermoplastic pipe material is now available that, in addition to very good resistance to the action of chemicals, also permits operating temperatures of up to 140 °C. Because of their good properties, PVDF systems have, in the meantime, even become an alternative to glass in the food processing and pharmaceutical industries.

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