

“Polybutene (PB-1) – Fascinating Polyolefin”

by Schemm, F., Van de Vliet, F., Grasmeder, J.

1. Historical Review

Polybutene-1 (PB-1) was first synthesised in 1954, one year after polypropylene. It took another 10 years until Chemische Werke HÜLS, Germany, started the first industrial production in 1964 (capacity: ca. 3 kt/a). *Vestolen BT* was introduced to the market. [1]

Independently, Mobil Oil in the US developed their own PB-1 process technology and built a small industrial plant in Taft, Louisiana, in 1968. In the early 70's the plant was taken over and operated by Witco Chemical Corporation. *Whitron 4121* was introduced to the market.

In 1973 HÜLS withdrew *Vestolen BT* from the market after some manufacturing issues in their polymerisation plant.

At the end of 1977 Shell Chemicals USA, a subsidiary of Shell Oil Company, acquired the PB-1 business from Witco, including the Taft plant. Shell then started a major investment program to improve the product quality and to increase the production capacity to about 27 kt/a. [2]

In 1998, the management of the polybutene portfolio was put in the hands of Shell's subsidiary Montell Polyolefins. Exactly two years later, in October 2000, Montell Polyolefins merged with Targor GmbH and Elenac GmbH to form Basell Polyolefins.

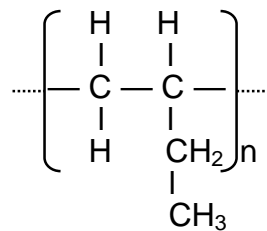
In December 2000 Basell's management board approved an investment to construct a new 45 kt PB-1 plant in Europe. It will utilise a new process technology, which has been developed by Basell's Research and Development centre in Ferrara, Italy. The new plant is currently under construction in Moerdijk, The Netherlands, and scheduled to come on-stream in January 2003. The existing plant in the US will be phased out by then.

In addition, Basell has invested in the construction of a small scale PB-1 plant in Ferrara. It has been operating since June 2001, benefiting from the same new process technology. In the first instance, the small scale plant helps to overcome the transition from US to EU production. From 2003 onwards, it will be used for the development of new PB-1 grades.

Apart from Basell, Mitsui Chemicals also manufacture PB-1 on their multi-purpose Tafmer plant in Japan.

2. Typical Properties of PB-1 Homopolymers [3] - [7]

PB-1 is obtained by polymerisation of butene-1 with a stereo-specific Ziegler-Natta catalyst to create a linear, high molecular, isotactic, semi-crystalline polymer. PB-1 combines the typical properties of conventional polyolefins with some characteristics of technical polymers.



Polybutene-1

Due to its similar structure, PB-1 is very compatible with PP. It can be used in blends to improve certain characteristics of PP. On the other hand, PB-1 is not compatible with PE. PB-1 copolymers are blended in PE film grades for use in peelable packaging.

Crystallisation Behaviour

Solid PB-1 can exist in 4 crystalline states. Three of them are meta-stable. During solidification from the molten state PB-1 mainly crystallises to tetragonal Form II. In course of a few days the material passes through a crystalline phase transformation to build the stable Form I (twin hexagonal).

The C₂H₅ side chains of PB-1 are long enough to create free volume between the molecules when the melt solidifies. During the recrystallisation phase the “voids” are filled and the material shrinks approx. 2 %. Hence, crystalline Form I is more dense and the product characteristics differ from Form II. The melt temperature, density, hardness, stiffness and yield stress increase, while the ultimate elongation remains unchanged.

Crystalline Form	Shape	Melt temperature	Density
I	twin hexagonal	121 – 130 °C	0.915 g/cm ³
II	tetragonal	100 – 120 °C	0.900 g/cm ³
III	ortho-rhombic	ca. 96 °C	0.897 g/cm ³
I'	hexagonal without twins	95 – 100 °C	

The recrystallisation continues over a long period but most of it is completed after 7-10 days (see figure 1).

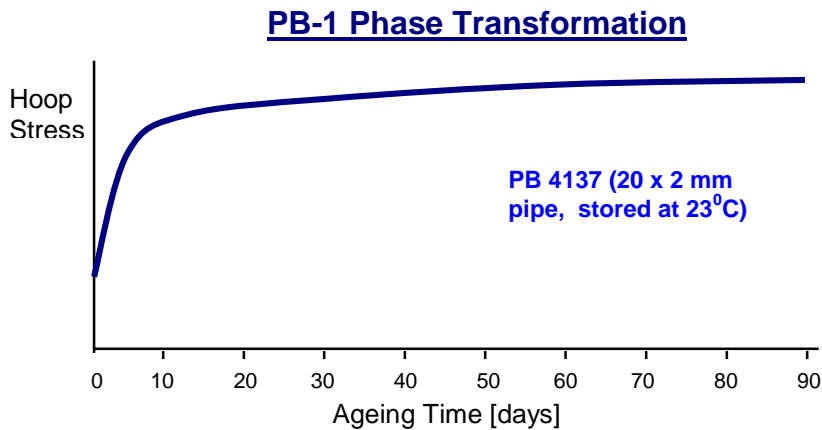


Figure 1: Hoop stress vs. ageing time of 20 x 2 mm pipes made from PB 4137

The speed of phase transformation depends on the temperature, hydrostatic pressure, structure, orientation and nucleation. The recrystallisation occurs fastest at room temperature. At 23°C and atmospheric pressure the phase transformation of PB-1 homopolymers takes about 1 week, however, at a pressure of 2000 bar it happens in only 10 minutes. Additionally, the phase transformation can be strongly accelerated by mechanical treatment, e.g. by multi-directional bending.

Melt Properties

The molecular weight, M_w , of PB-1 is typically around 750,000. Unexpectedly, the processability is not affected by the high molecular weight. PB-1 can be processed with conventional plastics manufacturing equipment. The melt strength is ca. twice as high as for PP, which results in better drawability and less sagging of the melt during extrusion. The rheological behaviour is very non-Newtonian, which means that the melt viscosity is shear-dependent. PB-1 is more sensitive to shear and orientation than other polyolefins. It is characteristically different in its processing behaviour compared to PP & PE and thus requires particular expertise in the manufacture of pipes and fittings.

PB-1 is easily weldable. Various joining techniques are feasible, socket welding, butt welding and electro-fusion welding are commonly applied for pipe installation.

Tensile Properties

Long molecular chains act as a link between the crystalline domains. The peculiar tensile behaviour of PB-1 (see figure 2) is based on these chain entanglements. Moreover, the glass transition temperature (ca. 78°C) and softening temperature (ca. 113°C) of PB-1 homopolymers are quite high. This explains why PB-1 has an excellent burst pressure resistance, no sensitivity to stress cracking, good impact strength, good abrasion resistance and retention of mechanical properties close to the melting point (see figure 3).

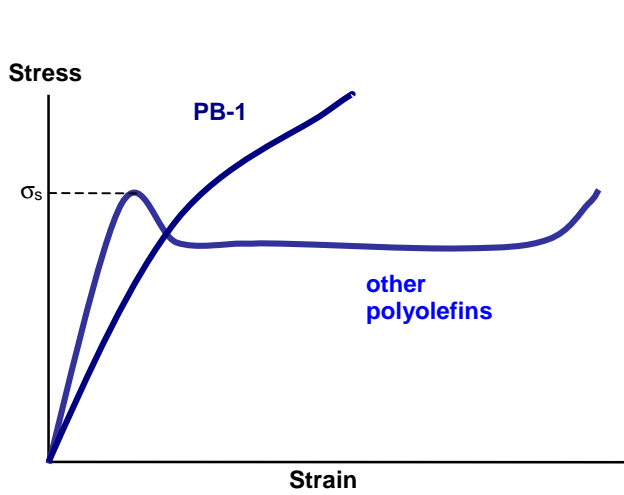


Figure 2: Tensile behaviour of PB-1 vs. other polyolefins

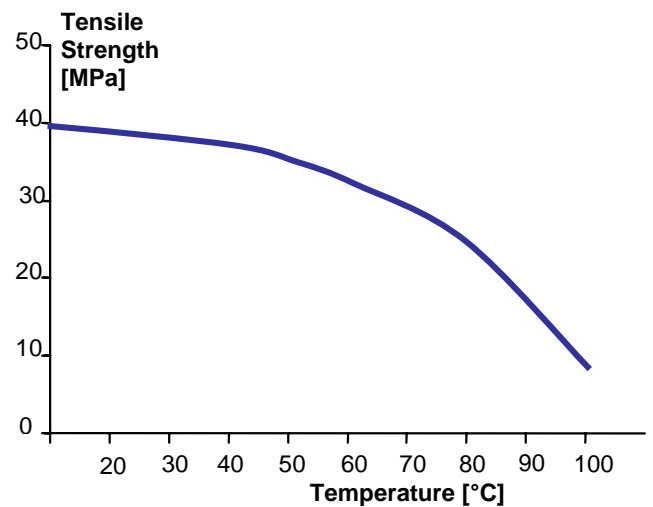


Figure 3: Tensile strength in function of the temperature

Having a tensile modulus of ca. 400 MPa, PB-1 homopolymers are more flexible than PP-R (min. 850 MPa) and PEX (min. 600 MPa). The flexibility remains high even at low temperatures and allows easier handling during cold seasons.

Impact Resistance

PB-1 resists well to impact. The IZOD notched impact strength (ISO 180) of PB-1 is classified “no break” at room temperature. The cold temperature performance is also very good because of the high flexibility and the low ductile/brittle transition temperature (ca. -18°C).

Creep Resistance

PB-1 behaves differently from other polyolefins under load (see figure 4). After the initial strain induced by a given stress, there is very little cold flow if the stress is below the yield point of PB-1 at that temperature. This property is dependent on the polymer morphology. The long-term

performance of PB-1 under mono-axial strain at different stresses and temperatures is depicted in figure 5.

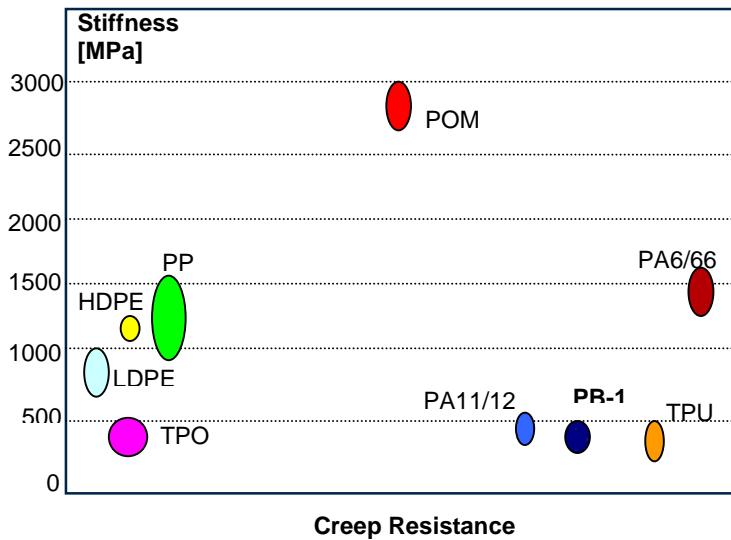


Figure 4: Stiffness and creep resistance of various polymers

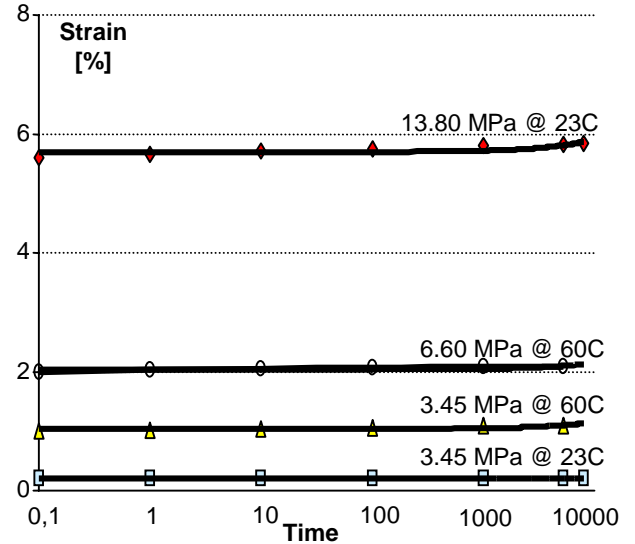


Figure 5: Creep strain of PB-1 at different stress and temperatures

Long-term Hydrostatic Performance

PB-1 resists also well to creep when submitted to multi-axial strain like in a pressurised pipe. Long-term hydrostatic testing of PB-1 is done at a max. temperature of 110°C. This is only 15°C below the melting point, and thus, a clear demonstration of polybutene's creep performance at elevated temperature.

The regression analysis according ISO/TR 9080 of PB-1 homopolymers has proven the minimum required strength MRS of 12.5 MPa. Thus, polybutene-1 is classified as PB 125.

Compression Set

PB-1 homopolymer is a very flexible and soft material for a pipe grade. Its elastic recovery is excellent even though it is not crosslinked. The compression set at 23°C is ca. 55 %, and at 70°C ca. 64 %, according ASTM D395-89, method B.

Abrasion and Wear Resistance

The wet abrasion resistance of PB-1 is excellent in sand/slurry type conditions. It performs as well as UHMW-PE which is well known for its outstanding abrasion and wear resistance. In dry conditions, however, PB-1 does not meet the high performance of UHMW-PE.

Sand slurry test at 23°C for 100 h (Basell internal method)	specific wear rate (weight loss)
UHMW-PE	0.46
PB-1 (MFR 0.1)	0.43
PB-1 (MFR 0.4)	0.44
HMW-HDPE	1.2
HDPE (MFR 0.1)	2.2
HDPE (MFR 0.3)	2.9
PP (MFR 0.8)	5

Environmental Stress Cracking (ESCR)

Polybutene-1 is very insensitive to environmental stress cracking. It does not show any failure after 15,000 hours of exposure in 10 % Igepal C0630 solution at 50°C according to ASTM D1693.

Melt Index [g/10min]	Density [g/cm³]	Exposure Time [h]	Failures [%]
Polybutene-1			
0.4	0.913	15,000	0
2.0	0.911	15,000	0
Polypropylene			
3.5	0.902	1,123	75
0.7	0.904	15,000	40
Polyethylene			
0.2	0.921	20	50
0.2	0.921	40	100
0.7	0.915	15	100
4.5	0.922	17	100
5.6	0.959	16	100

PB-1 is even used as additive in blend to improve the ESCR of certain PE grades. The addition of 2-5 % PB-1 improves the stress crack resistance significantly. Additionally, its unique rheology enables it to improve extruder throughput without increasing torque.

Chemical Resistance

Being a polyolefin PB-1 possesses excellent chemical resistance. It is resistant to most acids, bases, detergents, oils, fats, alcohol, ketones and aliphatic hydrocarbons. PB-1 is sensitive to oxidising acids, aromatic and chlorinated hydrocarbons. In this regards, it is similar to PP.

3. PB-1 in Piping Applications

Polybutene-1 homopolymers are used for various applications:

Outdoor

water distribution
district heating
industrial/chemicals

Indoor

hot and cold water transport
underfloor heating/wall heating/ceiling cooling
radiator connections

More than 25 years of service in the field have shown that piping systems made from PB-1 exhibit a unique balance of properties. Together with the characteristics described above (see chapter 2.), PB-1 has more to offer.

PB-1 pipes' easy handling and fast installation is determined by its light weight, flexibility (even at cold ambient temperatures), low memory effect and the variety of available jointing techniques.

Pipe fittings can be moulded from the same resin. The variety of jointing techniques (socket welding, butt welding, electro-fusion welding, push-fit systems) permits the production of a complete all-plastic piping network with homogenous connections.

For hot and cold water installations in buildings, from basement distribution via riser pipes up to final distribution to each consumer, water flows in a corrosion-safe and encrustation-free system. The thermal expansion, noise transmission and the friction inside the pipe (i.e. pressure loss) are low.

Currently, pipe diameters of 6 mm (for wall heating) up to 160 mm (for district heating) are being used.

The PB-1 pipe materials appreciate a broad recognition of international standards. PB 4137 Grey is formulated to meet the stringent water quality standards for drinking water systems even at elevated temperatures.

4. PB-1 in the European Market

Figure 6 shows the increase in overall plastics penetration in pressure pipe applications in Europe. The plastics share has grown constantly throughout the last ten years. The growth is mainly due to the substitution of traditional materials, and partially related to increased building activity.

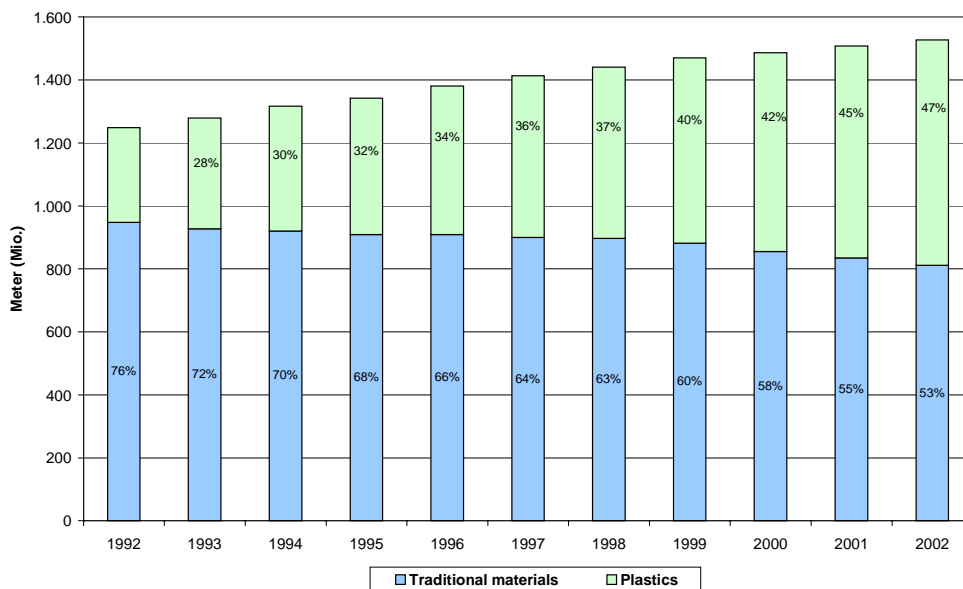


Figure 6: Overall plastics penetration for pressure piping applications in Europe (source KWD)

The multi-layer composite pipes (MP) are booming, while PP-R and PVC-C are in regression. PB-1 has a small market share. However, its two digits average annual growth is encouraging and future prospects are bright. Figure 7 shows the evolution of the plastics pressure pipes in the past 10 years.

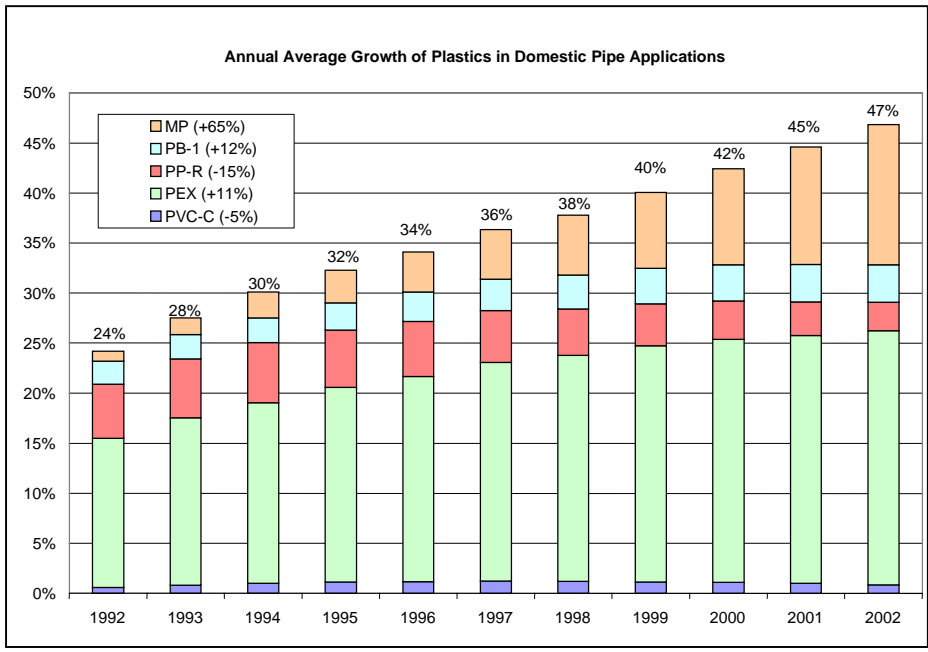


Figure 7: Annual average growth of plastics in piping applications (source KWD)

Every country has different drivers, e.g. pipe flexibility, safety factor, fitting system, local plumbing tradition etc., and a different starting point with regards to plastic penetration. Figure 8 depicts the plastics penetration per country and the PB-1 share within the plastics.

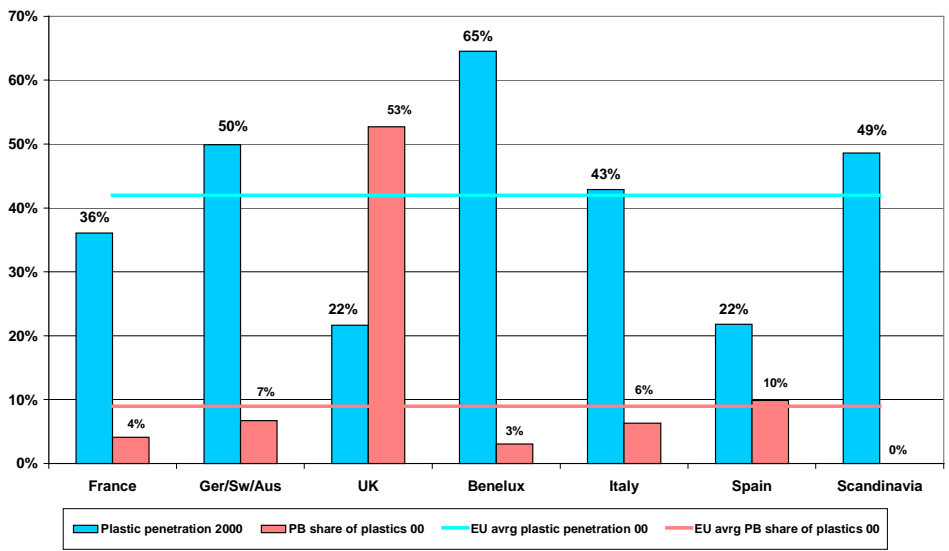


Figure 8: Plastics penetration and PB-1 share of plastics per country (source KWD)

In most European countries PB-1 is considered as a niche product. In the UK PB-1 owns a big part of the plastics share, even though the plastics penetration is still relatively low.

Figure 9, 10 and 11 show the plastics penetration and the PB-1 share within the plastics in underfloor heating, radiator connections and plumbing. Although the building industry is currently stagnating or even regressing, the PB-1 has grown steadily throughout Europe.

The overall potential for PB-1 to replace the traditional materials like copper and galvanized steel is enormous. PB-1 can contribute to the increase of the plastics penetration in domestic piping applications.

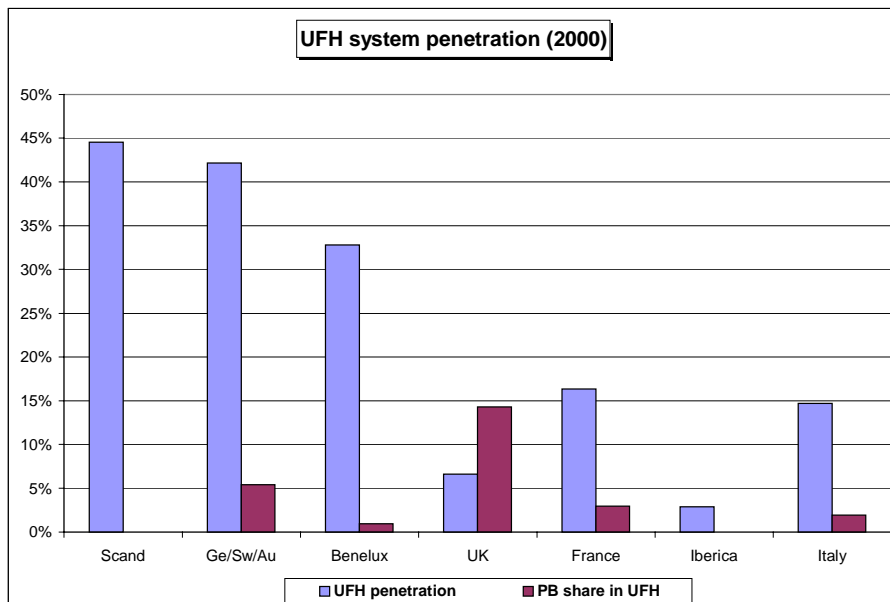


Figure 9: Plastics penetration in underfloor heating and PB-1 share of plastics per country (source KWD)

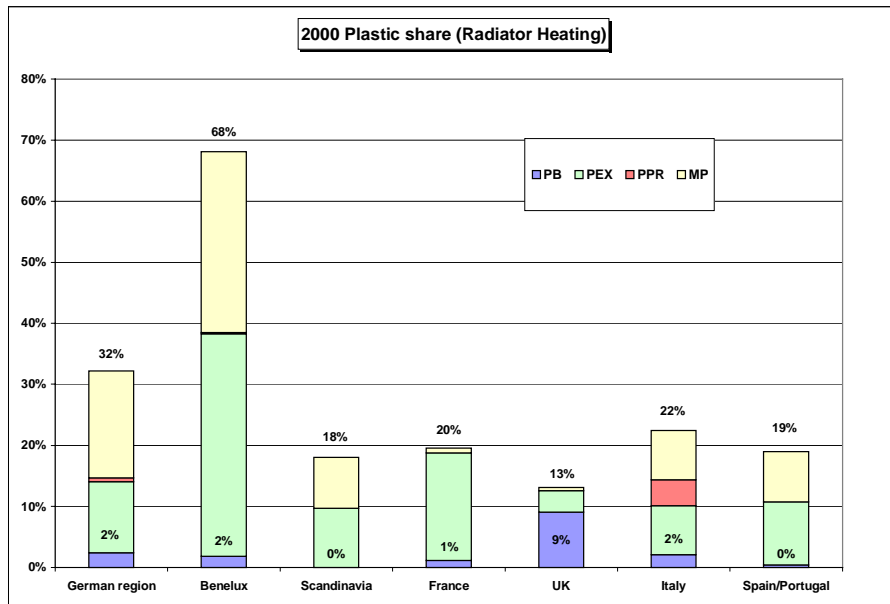


Figure 10: Plastics penetration in radiator heating and PB-1 share of plastics per country (source KWD)

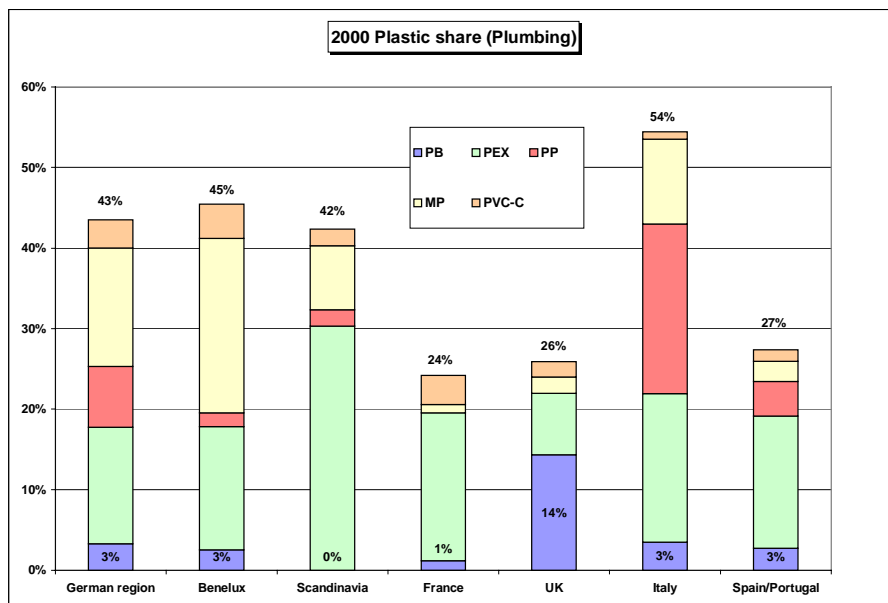


Figure 11: Plastics penetration in plumbing and PB-1 share of plastics per country (source KWD)

5. Polybutene-1 and the Environment

In order to have an objective and factual comparison on the impact of piping systems, it is necessary to find an evaluation method that compares products of different nature which are used in the same application.

The plastics technology department of the Technical University Berlin has conducted an environmental analysis on drinking water installation systems, utilising the self-developed standardised comparison method VENOB (German: vergleichende normierende Bewertung). The work was supported by the Kunststoffrohrverband (KRV) and various pipe producers.

The environmental analysis is based on scientific fact. It summarises and compares the energy consumption and the emissions in air, water and soil during the individual stages from raw material production to the installation in the building.

The TU Berlin looked at 6 different raw materials for pipes used in drinking water installations according to DIN 1988 Part 3, for a multiple dwelling with 16 apartments with central warm water distribution (pressure of supply: 4 bar).

Stage of life-cycle	Metals (galvanised steel, copper)	Plastics (PE-X, PB-1, PP-R, PVC-C)
Raw material production	ore mining	crude oil extraction
Raw material processing	<i>mechanical crushing, classifying</i>	oil refining (naphtha)
Refining	metal refining	steam cracking (ethylene, propylene, butene)
Pipe material production	smelting (recycling ratio: 35 % steel, 49 % copper)	polymerisation
Pipe manufacturing	rolling	extrusion
Fittings manufacturing	casting, reshaping	injection moulding
Heat insulation	foamed PE-LD tubing	foamed PE-LD tubing
Installation	soldering, screwing	welding, clamping, gluing

The life cycle of the pipe starts with the raw material production and ends with the installation of the pipes in the building. The currently applied recycling ratios of 35 % for steel and 49 % for copper were taken into consideration for the stage of metal processing (smelting).

The discharge or recycling of the pipes and fittings after service-life was not included because one cannot reliably predict the recycling scenario in 50 or 80 years time.

The raw material production and manufacturing of metal pipes consumes much more energy than plastics. The overburden from ore mining and the emissions from smelting pollute the environment considerably. On the other hand, the recycling ratio of metals is very high. The energy consumption of 1000 kg pipes and fittings are depicted in figure 12.

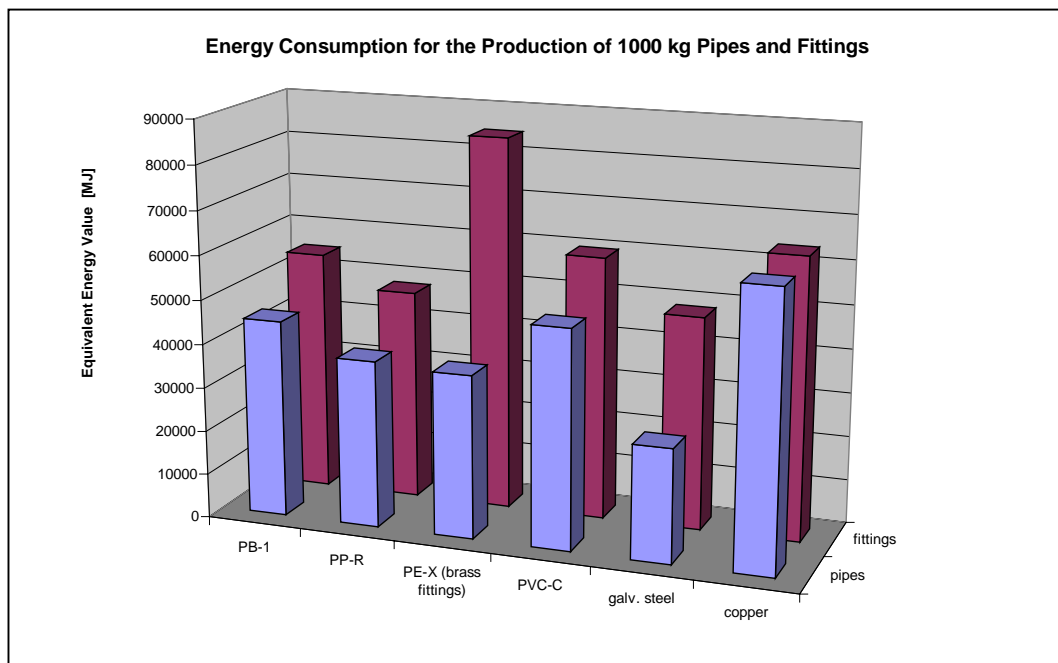


Figure 12: Energy consumption of 1000 kg pipes and fittings of various pipe materials

Of course, it is not the 1000 kg of pipes and fittings which are relevant for the determination of the energy equivalence value of the complete piping system, but the required length and dimension of the pipes and the numbers of fittings used. Figure 13 shows the weight of the complete piping network for the multiple dwelling with 16 apartments.

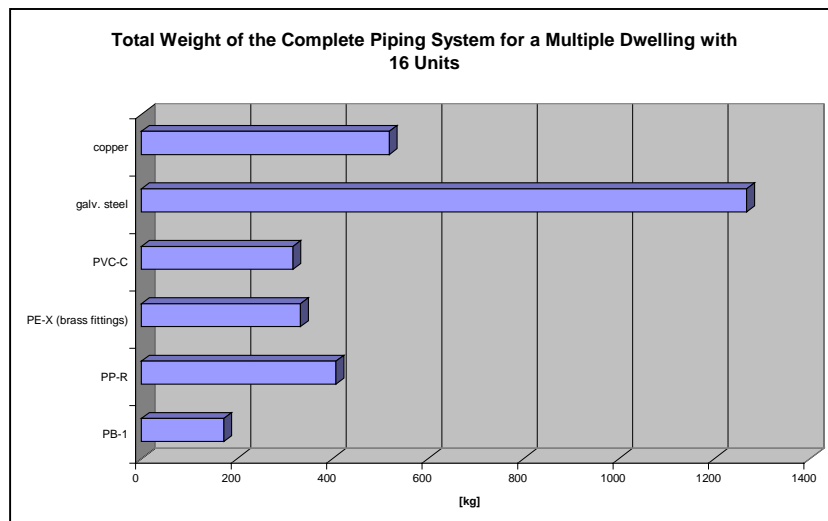


Figure 13: Weight of the complete piping system for a multiple dwelling with 16 apartments acc. DIN 1988 for the various pipe materials

To fit the application requirements the various pipe systems have to be dimensioned according to the mechanical strength of the individual material. The layout of the piping system of this multiple dwelling requires the following dimensions per material:

- PEX d40 x 5.5 mm
- PP-R d50 x 10.0 mm
- PVC-C d40 x 4.5 mm
- PB-1 d40 x 3.7 mm

Due to its superior burst pressure resistance PB-1 permits the manufacture of pipes with lower wall thickness.

The weight of the piping network is not an important criterion for building installations. But it influences the overall energy consumption. Thanks to their light weight, plastics materials have a distinct advantage over metal pipes. The total energy consumption for the production of metal pipes needed for the piping system of one multiple dwelling with 16 apartments is significantly higher than for plastics pipes. Figure 14 shows the energy equivalent value which takes the total weight of the piping network per material into consideration.

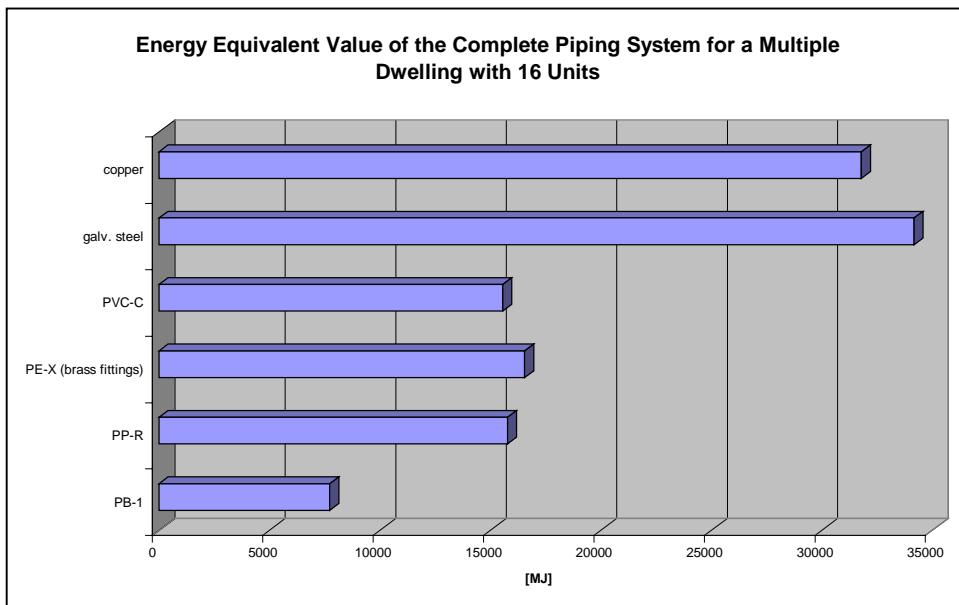


Figure 14: Energy equivalent value of the complete piping network of a multiple dwelling with 16 apartments acc. DIN 1988 for the individual pipe materials

Emissions in soil, water and air according VENOB

The impact on the environment during all stages from raw material production to installation inside the building needs to be included in the determination of the energy equivalent values of the various pipe materials.

A lot of different emissions of various kinds are obtained from the environmental analysis. Merely listing the values does not allow a comparison of the pipe systems. TU Berlin has developed the standardised comparison method VENOB. This method allows a simplified and straightforward interpretation of the emissions data.

The single emissions are recorded, standardised and then summarised in three individual and independent parameters:

1. emissions in soil
2. emissions in water
3. emissions in air

The lowest specific value of the 6 pipe materials is set to 1.0 and the other values are adapted accordingly with the same factor. This is done for all three VENOB parameters individually. Figures 15, 16 and 17 summarise the emissions according the standardised comparison method.

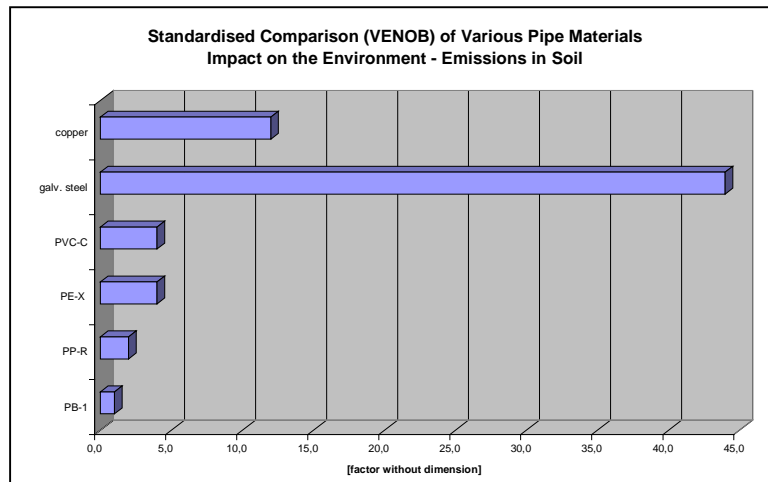


Figure 15: Standardised comparison according VENOB of various pipe material – impact on the environment, emissions in soil

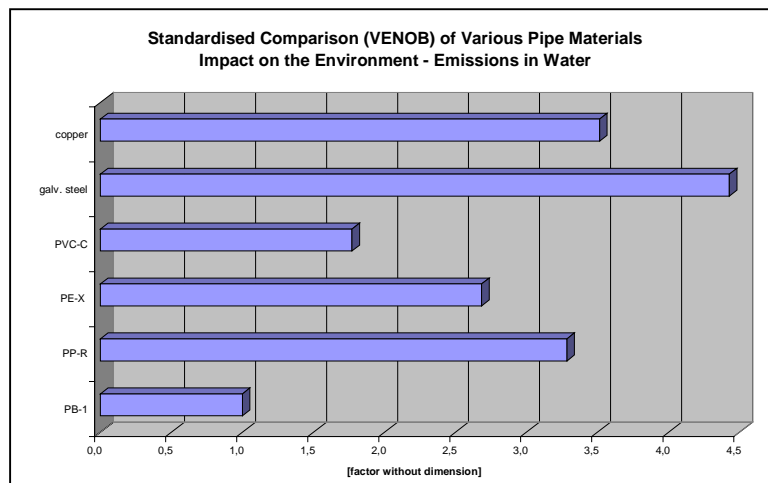


Figure 16: Standardised comparison according VENOB of various pipe material – impact on the environment, emissions in water

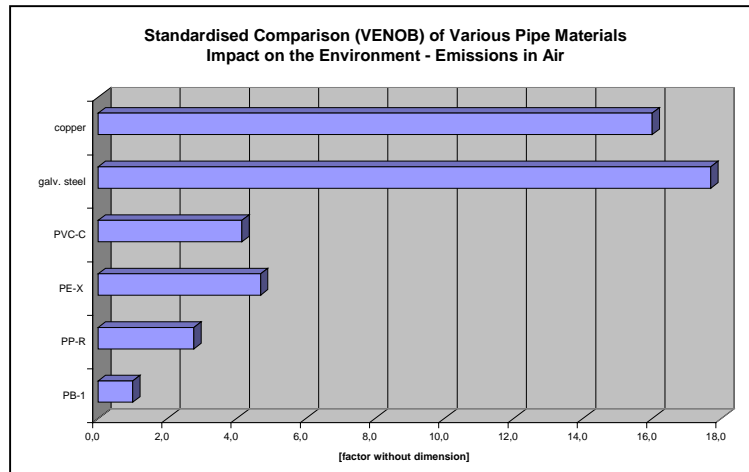


Figure 17: Standardised comparison according VENOB of various pipe material – impact on the environment, emissions in air

The emissions in soil are very high for metals because a large part of the electrical energy is being generated by coal combustion. Coal mining and ashes from incineration pollute the environment considerably. Although copper has a high recycling rate (nearly 50 %), the consumption of electrical energy is very high, too. This is because the copper fraction in ore is very low (average 1.2 %).

Sulphate, oil and solid emissions in the water are the main reason why metals perform less favourably than plastics when it comes to water pollution.

Large quantities of sulphur dioxide, carbon dioxide and particles emissions derive from the use of coal in steel production. [8],[9]

6. Conclusions

PB-1 is a unique polyolefin with a number of properties that make it an excellent choice as a pipe material, evidenced by its continuing market acceptance growth in both Europe and Asia. In common with other polymers, it demonstrates numerous environmental benefits over the use of traditional materials. Rigorous codes & standards are in place to ensure long life and suitability for potable water and demanding high temperature applications. PB-1's unique properties will ensure that it retains its position alongside the better-known polymers used in piping in the years to come.

7. Acknowledgement

The authors wish to thank the members of the Polybutene Piping Systems Association (PBPSA) for their contribution.

8. Literature

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Note: Basell does not sell PB-1 for use in pipe applications intended for use in North America, and requires its customers not to sell products made from PB-1 into pipe applications in North America.