PE-RT, A NEW CLASS OF POLYETHYLENE FOR INDUSTRIAL PIPES

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ABSTRACT
The development of a new family of PE materials with significantly improved processability and long-term strength at high temperatures is discussed. These polymers form the basis for a new ISO class of polyethylene materials: PE-RT (Polyethylene of Raised Temperature resistance) for hot and cold water as well as industrial pipe applications. These materials have a unique molecular structure and crystalline microstructure, which provides excellent Long Term Hydrostatic Strength at high temperatures without the need for cross-linking the material.

PE-RT type materials have been used successfully in domestic hot and cold water piping systems for more than 20 years, and in application areas such as underfloor heating and radiator connections. More recently, the easy processing and outstanding material properties have also made these resins attractive for use in many larger diameter industrial applications, where regular Polyethylene cannot be used due to its high temperature limitations. In this respect PE-RT can also compete with high-end engineering plastics, offering significant cost savings. The use of PE-RT materials provides significant process advantages to the converters, allowing high line speed pipe production and providing excellent flexibility and ease of installation for the application.

A recently developed PE-RT type material still offers higher long-term strength at high temperature and further improved processability, for example in larger diameter cooling water pipes in power plants. Pipes based on these materials can be connected via heat fusion welding or by the use of mechanical fittings. Furthermore, this material can be used in industrial applications, where its temperature resistance may limit traditional Polyethylene and metallic materials often suffer from corrosion. The excellent weldability of these materials provides various opportunities to connect even larger dimension pipes in industrial applications, an example of this being the use in multi-layer structured oil pipelines onshore and offshore.

This paper presents the material science and product design concepts that govern the high long-term hydrostatic strength at high temperatures. By controlling the molecular structure, the melt rheology and solid-state properties can be influenced, which results in a unique balance of processability and hydrostatic strength.

Also discussed are the product features and benefits of PE-RT materials. The paper shows examples of the application range for this type of product, using applications in the domestic pipes market as a reference.

INTRODUCTION
The adoption of new pipe materials and pipe-making processes continues to evolve, with the use of PE-RT moving from domestic hot and cold water systems, where the material has been installed for more than 20 years, to a broader range of industrial applications.

Industrial system designers and installers are responding to the mechanical and processing benefits of PE-RT resins in larger dimension pipe applications, where regular Polyethylene cannot be used, or is restricted by temperature limitations. The versatility of PE-RT and the ability to be used at higher temperatures without the need for cross linking, makes it a preferred choice for a wide range of applications where temperature profiles can range from sub-ambient to beyond what is considered normal for a traditional PE system.

To provide a series of technical and mechanical reference points, this paper focuses on PE-RT domestic pipe applications, with additional data on industrial applications where relevant.
Domestic pipe systems – a reference study
Domestic pipes can be described as pipes for hot and/or cold water in pressurized heating and drinking water networks within buildings. The requirements for these domestic applications are included in Table 1. Also belonging to this class are “snow melt” and “heat recovery” systems. Such piping systems typically operate at pressures between 2 and 10 bar and temperatures up to 80°C with malfunction temperatures up to 100°C. The conditions of use for the different hot water pipe classes/applications (under floor heating, radiator connectors and plumbing pipe) are described in ISO 10508.1

<table>
<thead>
<tr>
<th>Requirements</th>
</tr>
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<tbody>
<tr>
<td>Pressure: 2-10 bar</td>
</tr>
<tr>
<td>Temperature: 20 - 110°C (malfunction temperature 95-100°C, thermal stability up to 110°C)</td>
</tr>
<tr>
<td>Life time: minimum 50 years</td>
</tr>
<tr>
<td>Compliance with drinking water regulations</td>
</tr>
</tbody>
</table>

The domestic pipe market has traditionally been dominated by copper and galvanized steel pipe. Over the last 25-30 years, plastics have made significant inroads in this market. In most parts of the world, copper is still the dominating material. Penetration of plastics in Europe is furthest advanced with close to 50 percent market share. The consumption of plastics in hot water pipe applications is estimated at 120,000 MT globally, of which half is used in Europe.

The advantages of plastics are that they show no corrosion and are resistant to many chemicals. They are flexible and easy to install (also as "endless" pipe), are leak-tight by fusion welding and lightweight, which makes them easy to transport and to handle on site.

Preferred plastic materials used in domestic pipe applications are Polyethylene (PE), followed by Random Copolymer Polypropylene (PP-R) and Polybutene (PB) and, to a lower extent, Chlorinated PVC (C-PVC). Whereas PP-R, PB and C-PVC have inherently good high temperature properties, traditionally PE was not suitable for this market, because of an upper service temperature that was too low.

To enable these higher temperature requirements, cross-linking of the polyethylene (PEX) was needed to obtain the desired Long Term Hydrostatic Strength (LTHS) at high temperature. PE-RT allows these same properties to be obtained without the need for chemical modification or post extrusion curing and can easily be manufactured on a conventional PE extruder.

The benefits of PE-RT can easily be transferred to larger dimension pipe applications, such as industrial and multilayer structured pipes. This allows users to extend the use of such piping system to higher temperatures than is currently possible with conventional HDPE based pipes.

New Product Design Principles
High Density Polyethylene is known to have a good mechanical strength at elevated temperatures and is therefore often used in packaging applications where a good high temperature performance property is required. However, the limited long-term creep characteristics of HDPE at these higher temperatures are often unsuitable for durable applications, such as hot water pipe. The creep properties of PE may be improved by reducing the resin density, but unfortunately this will negatively affect the long-term hydrostatic strength (LTHS).

Major advances have been made in understanding the structure property relationships of PE polymers. Through improved process design and catalyst development, the incorporation and placement of the co-monomer into the polymer backbone can be controlled. This greater accuracy in defining the micro-crystallinity of the polymer allows a new combination of

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1 ISO 10508, Publication date: 1995-10 Thermoplastics pipes and fittings for hot and cold water systems
performance parameters to be observed, as seen in Table 2. PE polymers combining high
temperature performance with flexibility or better long-term creep for a given crystallinity are now
possible.

Tie chains play a key role in long term ductile creep behavior. By introducing short side chains via
the incorporation of co monomers, imperfections in the polymer structure are created. The hexyl
side group, from the octene co-monomer, is too big to be incorporated in the lamellar crystal
structure and the polymer chain is pushed out of the crystal. When this chain now is incorporated
in another crystal, a tie chain is formed.

**TABLE 2: NEW PE PERFORMANCE THROUGH MOLECULAR ARCHITECTURE**

<table>
<thead>
<tr>
<th>Optimization of tie chain concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control of how co-monomer is incorporated in the polymer backbone: crystalline microstructure</td>
</tr>
</tbody>
</table>

Graphic 1 shows how tie chains are formed. The crystalline structure of a linear polyethylene
without side chains or short chain branches is shown at the left. The polymer chain folds to form a
lamellar crystalline structure.

**GRAPHIC 1: EFFECT OF THE MICROSTRUCTURE ON THE CRYSTALLIZATION PROCESS**

The lamellar crystal structures are connected through amorphous polymer segments: the tie
chains. The probability of tie chain formation increases with the polymer chain length. Tie chain
molecules are known to increase toughness and ESCR or long-term creep properties, by “tie-ing”
multiple crystals together. Tie chains show extensibility and mobility and can as such absorb and
dissipate energy. This is graphically presented in Graphic 2.

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3 Butterworth Scientific (1983)
Tie Chains have extensibility and mobility (can absorb / dissipate energy)

GRAPHIC 2: TIE CHAIN MOLECULES INCREASE RESIN TOUGHNESS

The type of co-monomer incorporated also has an influence on the tie chain concentration. Octene-1 is more efficient than shorter $\alpha$-olefins (Graphic 3). The reason for this is that the octene-based side chains are longer and therefore more difficult to incorporate in the growing crystal. For a given concentration of co-monomer, this results in a higher probability of tie chain formation.

![Tie Molecule Probability at Optimum Density, %](image)

**GRAPHIC 3: COMONOMER TYPE INFLUENCES TIE MOLECULE PROBABILITY**

An important design aspect is the control of the amount of co-monomer and the way it is incorporated into the polymer chain. Graphic 4 shows Crystaf curves for different density ethylene-octene copolymers produced in the Dow proprietary solution process. By steering the co-monomer incorporation, different polymer morphologies with a different balance of properties can be obtained. The Crystaf curve below is actually a fingerprint of the resulting molecular architecture from a heterogeneous polymerization process. Linear molecules with the highest crystallinity crystallize at the highest temperature. Since a heterogeneous polymer is composed of molecules with varying co monomer concentration, the Crystaf curve below represents a distribution of co-monomer. The molecules crystallizing at an intermediate temperature have the highest chance of forming tie chains at a fixed molecular weight. Controlling the co monomer distribution, along with the polymer molecular weight controls the tie chain concentration.

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*Fig. 16.4.9. Steps in the ductile (crimp) deformation of polyethylene (© 1983, Reprinted from Fig. 16.4.8. Initial steps in the deformation of polyethylene (© 1983, Butterworth Scientific).*
GRAPHIC 4: CHEMICAL COMPOSITION DISTRIBUTION OF DIFFERENT ETHYLENE-OCTENE COPOLYMERS

By applying these design concepts, a new family of DOWLEX™ PE resins for the hot and cold water pipe market was developed.

These developments formed the basis for the creation of a new class of polyethylene materials for high temperature applications. These resins are defined in ISO-1043-1\(^4\) Polyethylene of Raised Temperature Resistance (PE-RT). PE-RT shows excellent Long Term Hydrostatic Strength without the need for cross-linking. This results in significant processing advantages versus PEX for the pipe producers. PE-RT materials can be used in all hot water pipe applications, described in ISO 10508.

The first DOWLEX PE resin for pipe in this category is DOWLEX 2344, an ethylene-octene copolymer, produced in the Dow proprietary solution process. This product is designed to combine very good Long Term Hydrostatic Strength with excellent flexibility.

DOWLEX PE resins have been used successfully for nearly 20 years in hot water pipe applications. Its good Long Term Hydrostatic Strength at high temperature combined with a very high flexibility, made DOWLEX 2344 the material of choice for heating pipe applications.

The features of DOWLEX 2344 are summarized in Table 3. Pipe made out of DOWLEX 2344 shows excellent Long Term Hydrostatic Strength without the need for cross-linking. This makes the product particularly suitable for hot water pipe applications for which the resin has many different approvals in many countries. For example, DOWLEX 2344 is approved in, e.g.: Germany: DIN 16833\(^5\) (PE-RT) and the relevant application standard DIN 4721; the Netherlands: KIWA\(^6\) approval for all hot water applications; USA: PPI listing \(^5\) 180°F (DOWLEX 2344 as the

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\(^4\) ISO 1043-1, Publication date: 1997-03, Plastics – Symbols and abbreviated terms – Part 1: Basic polymers and their special characteristics
\(^5\) DIN 16833, Publication date: 2001-06
\(^7\) PPI listing, TR4/2001, HD/PDE/MRS listed materials

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only non-cross linked PE) and for multi-layer pipe ASTM1282-01A\(^6\) and ISO 24033 (PE-RT) and the relevant system standard ISO DIS 22391 part 1 to 5 (PE-RT for hot and cold water).

Pipe made from DOWLEX 2344 is extremely flexible, which facilitates installation of pipes for domestic and industrial applications. Pipe can be produced at high rates without cross-linking, which allows subsequent welding. The high smoothness of the DOWLEX 2344 pipe surface offers reduced pressure loss and results in minimum deposit formation.

Due to the absence of the cross linking step, the processing of PE-RT resins offers improved economics over PE resins needing cross linking. This advantage is biggest for multi-layer composite pipes.

<table>
<thead>
<tr>
<th>TABLE 3: FEATURES OF DOWLEX 2344 AS A HOT AND COLD WATER PIPE RESIN MATERIAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Approval for hot water pipe in many countries, e.g.:</td>
</tr>
<tr>
<td>o DIN 16833 (PE-RT); KIWA for all hot water pipes</td>
</tr>
<tr>
<td>o PPI listing at 180°F; ASTM F 1282 (multi-layer pipe)</td>
</tr>
<tr>
<td>o ISO/FDIS 24033 system standard for Plastic piping systems</td>
</tr>
<tr>
<td>o ISO/FDIS 22391 part 1-5 for Plastics piping systems for hot and cold water installations</td>
</tr>
<tr>
<td>• Low cost production process: 1 step, no cross-linking</td>
</tr>
<tr>
<td>• High flexibility = ease of installation of mono-layer pipe</td>
</tr>
<tr>
<td>• Superior weldability</td>
</tr>
<tr>
<td>• Material of choice in the fast growing composite pipes segment, due to significant process advantages</td>
</tr>
</tbody>
</table>

The newest member of the DOWLEX PE pipe resin family is DOWLEX 2388, a product that is designed to combine superior Long Term Hydrostatic Strength (Graphic 5) with excellent processability.

**Graphic 5: HOOP STRESS PERFORMANCE OF DOWLEX 2388, SEM ACCORDING ISO 9080**

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\(^{6}\) ASTM F 1282, Publication date: 2001
Standard Specification for Polyethylene/Aluminum/Polyethylene (PE-AL-PE) Composite Pressure Pipe
Test times well above one year at 110 °C allows extrapolation of the pipes performance beyond 50 years at 70 °C, using the ISO 9080\(^9\) extrapolation factors. This material has a design stress, comparable to PEX materials, but without the need for cross-linking. The design stress is the basis for the wall thickness calculations for the various conditions defined in ISO 10508 and national pressure classes.

Table 4 shows a comparison of the design stress for DOWLEX 2388, PEX and PE-RT for sanitary pipe (class 1 to 5 of ISO-10508). Because of their comparable design stress, the required wall thickness will be the same for pipe made out of DOWLEX 2388 and PEX for all pipe dimensions.

### TABLE 4: DESIGN HOOP STRESS DOWLEX 2388, AND PEX

<table>
<thead>
<tr>
<th>ISO 10508</th>
<th>Application area</th>
<th>PE-X DIN 16892*</th>
<th>CUAP for Type II DOWLEX 2388</th>
<th>DOWLEX 2388 (PE-RT type II)#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1</td>
<td>Hot water supply at 60°C</td>
<td>3.86</td>
<td>3.81</td>
<td>4.17</td>
</tr>
<tr>
<td>Class 2</td>
<td>Hot water supply at 70°C</td>
<td>3.55</td>
<td>3.54</td>
<td>3.95</td>
</tr>
<tr>
<td>Class 4</td>
<td>Underfloor heating and low temperature radiators</td>
<td>4.01</td>
<td>3.84</td>
<td>4.02</td>
</tr>
<tr>
<td>Class 5</td>
<td>High temperature radiators</td>
<td>3.25</td>
<td>3.10</td>
<td>3.41</td>
</tr>
</tbody>
</table>

*Minimum requirements from DIN norm
# Data generated by Bodycote Polymer AB

Table 4 shows the calculated life times for pipes made of DOWLEX 2388 at elevated temperatures. These numbers are based on the extrapolation of the data points measured at 110°C, following the ISO 9080 calculation methods. Extrapolation factors Ke are defined in ISO 9080, following Arrhenius principles, which allow for extrapolation to lifetimes at lower temperatures. For a difference in temperature of e.g. 40°C the Ke factor is 50, which practically means that testing of one year at 110°C allows for an extrapolation of 50 years at 70°C. Typically the basis of the extrapolation is the logarithmic average of the five longest test times at the highest test temperature.

### TABLE 5: EXTRAPOLATION TIME LIMITS ACCORDING ISO 9080

<table>
<thead>
<tr>
<th>Extrapolation time limits [years]</th>
<th>DOWLEX 2344</th>
<th>DOWLEX 2388</th>
<th>Ke factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average 110 °C</td>
<td>1.55</td>
<td>1.47</td>
<td>1</td>
</tr>
<tr>
<td>100 °C</td>
<td>3.86</td>
<td>3.66</td>
<td>2.5</td>
</tr>
<tr>
<td>95 °C</td>
<td>6.18</td>
<td>5.86</td>
<td>4</td>
</tr>
<tr>
<td>90 °C</td>
<td>9.27</td>
<td>8.79</td>
<td>6</td>
</tr>
<tr>
<td>85 °C</td>
<td>18.55</td>
<td>17.59</td>
<td>12</td>
</tr>
<tr>
<td>80 °C</td>
<td>27.82</td>
<td>26.38</td>
<td>18</td>
</tr>
<tr>
<td>75 °C</td>
<td>46.37</td>
<td>43.97</td>
<td>30</td>
</tr>
<tr>
<td>70 °C</td>
<td>77.29</td>
<td>73.29</td>
<td>50</td>
</tr>
<tr>
<td>60 °C</td>
<td>&gt; 100</td>
<td>&gt; 100</td>
<td>100</td>
</tr>
</tbody>
</table>

* Log average of 5 data points at 110°C

\(^9\) ISO/DIS 9080, Publication dates: 1998-02
Plastics piping and ducting systems - Determination of the long-term hydrostatic strength of thermoplastics material in pipe form by extrapolation (Revision of ISO/TR 9080:1992).
Another feature of DOWLEX 2388 is its excellent processability. Graphic 6 compares the viscosity curves of DOWLEX 2388 and DOWLEX 2344.

The lower viscosity at high shear rates of DOWLEX 2388 allows increased line speeds in pipe extrusion, especially in high shear rate processing, like thin wall pipe and PE/Al/PE composite pipe extrusion. During trials at extrusion equipment manufacturers, pipe of 20mm diameter with a 2mm wall thickness was produced at line speeds > 60 m/min.

DOWLEX 2388 covers all ISO 10508 classes of hot water pipe applications, domestic and industrial. DOWLEX 2388 is particularly designed to compete effectively in monolithic plumbing pipe (covered by ISO 10508 class 2), due to its higher Long Term Hydrostatic Strength at high temperature. Another application area where DOWLEX 2388 offers advantages is in high-speed extrusion PE/Al/PE composite pipe. For industrial applications it might be interesting to use the outstanding long term thermal stability of DOWLEX 2388 (e.g. 70°C for more than 73 years or 80°C for more than 25 years) together with the excellent weldability to install large dimensions of pipe by butt-welding or electro fusion welding.

**Offshore Oil and Gas Industry**

The acceptance of PE-RT over a prolonged period in such a demanding application has given confidence to pipe manufacturers and end users to consider this material for a wide variety of alternative applications other than domestic hot and cold water pipe. It is clear that the benefits of having a PE material that encompasses a much wider temperature range than a traditional polyethylene will extend the range of applications. New attractive markets are being considered where polyethylene traditionally would have been excluded.

One such area is in the use of PE-RT as a cost effective liner in water injection flow lines as used by the offshore oil industry where temperatures up to 80°C are common. To allow economic extraction of the oil from a source, well water is commonly injected down a flow line to preserve the reservoir pressure. In addition to its high temperature resistance, the use of PE-RT as a liner allows both flexibility and minimal flow loss due to the smooth surface characteristics of the PE.
However, the use of water injection may result in the formation of \( H_2S \), which accelerates the corrosion rate of the metal flow line resulting in a substantial increase in corrosion rate. Corrosion is a major concern since the cost of replacement or rehabilitating the pipeline in flexible steel pipes can determine the ultimate lifetime of a well. Prolonged lifetime expectations can extend the working life of such oilfields. The good chemical resistance allied to its working temperature range makes PE-RT a suitable resin for this highly demanding technical application.

**Industrial Applications**

The very wide operating temperature range of PE-RT makes it an ideal pipe material for any project where huge temperature differences are observed. This may be particularly relevant for industrial chemical applications where temperatures can change from sub-zero up to 70 °C. Although many of the examples given have required high temperature resistance PE-RT may be also be used for cold temperature applications. For example, PE-RT may be used for the refrigeration of glycol / water mixtures in the making of an ice arena, where the fluid transported may reach as low as – 40 °C.
Heat Exchangers

PE-RT resins are not just limited to the production of pipes, but may also be molded into articles used in higher temperature applications. When chemical resistance and corrosive properties are key in material selection, consideration of PE-RT is often the best choice. Metal heat exchangers as used in chemical plants often require maintenance and replacement due to the corrosive nature of the chemical at elevated temperature. By using PE-RT, the lifetime of such heat exchangers can be significantly enhanced.

CONCLUSIONS

Through advanced molecular architecture and improved process control, the manufacture of polyethylene with superior Long Term Hydrostatic Strength at high temperatures is now possible. These polymers form the basis for a new class of Polyethylene materials: PE-RT (Polyethylene of Raised Temperature resistance) for industrial and domestic hot water pipe applications.

The uniqueness of these materials is that they do not need to be cross-linked to deliver the desired Long Term Hydrostatic Strength at high temperature. This results in significant processing advantages over PEX systems. PE-RT is suitable for use in all hot water pipe applications.

DOWLEX 2344, the first member of the DOWLEX PE pipe resins family is designed to provide high flexibility and good Long Term Hydrostatic Strength at high temperature. This combination makes this resin the material of choice for heating pipe applications (covered by ISO 10508 classes 4 and 5).

The newest member, DOWLEX 2388, offers an even higher Long Term Hydrostatic Strength at high temperature, enabling effective competition in monolithic plumbing pipe (class 1 & 2 of ISO 10508) and industrial applications.

Another benefit of DOWLEX 2388 is its excellent processability, which results in higher line speed extrusion, especially for composite PE/Al/PE pipes.
The advantages of PE-RT can be translated to larger dimension pipes and molded products, such as industrial and multilayer structured pipes. This allows users to extend the use of such piping systems to higher temperatures than is currently possible with conventional HDPE based pipes while maintaining the advantages of polyethylene’s inherent good low temperature performance, flexibility and chemical resistance.