

Corrosion of polyethylene

Optimization potential of polyethylene coatings for steel pipe

By Dr. Hans-Jürgen Kocks

Polyethylene is the state of the art in corrosion protection for steel pipelines. Considering the large number of modified materials, however, brings up the question as to whether and to what extent the properties and performance of such coatings can be optimized at the materials selection stage. Given that polyethylene has been used for coating buried pipelines for almost 50 years now, it appears appropriate that this material should be studied in detail with regard to its aging behaviour.

Introduction

The use of polyethylene for the coating of steel line pipe for drinking water pipelines, sewer systems and pipelines for the transmission of gases and other media that are hazardous to water is generally accepted as state of the art technology. In this respect, polyethylene has completely superseded bitumen as standard coating material for these applications. The introduction of polyethylene coating as a means of corrosion protection for buried pipelines dates back to the late 1950s. Compared to bitumen, polyethylene coatings stands out mainly for its significantly higher insulation resistance. For example, a single cathodic corrosion protection system can ensure effective condition monitoring of buried pipelines over a distance of 100 km and more.

The first polyethylene coatings were applied using a powder application. To start with, the

pipe was steel grit shot blasted to bright metal. In the coating facility, the pipe was rotated while polyethylene powder was spread on its surface, which was heated to approximately 300 °C. On contact with the steel surface, polyethylene powder fuses into a homogeneous coating. Compared to the later coatings applied by sleeve extrusion, the shortcoming of these powder coatings was their poor adhesion and elongation at break, because sintered polyethylene has a more brittle behaviour than extruded polyethylene.

Extruded plastic coatings, applied by either sleeve extrusion or sight extrusion process, were first introduced in the mid 1960s and have meantime completely replaced the sintering technique. Initially, they consisted of two layers, namely an adhesive agent and a polyethylene layer. The mid-1980s saw the launch of three-layer coating systems with an additional primer based on epoxy resin.

These practice-oriented systems achieve high adhesive strength at room temperature and can easily be cut back in the field as required by simply heating up the pipe ends. All polyethylene types – i.e. low (LDPE), medium (MDPE) and high density polyethylene (HDPE) – are used, with MDPE and HDPE preferred for higher service temperatures and because their higher strength makes them particularly suitable for the high stresses involved in pipeline construction.

The essential advantage of this material lies in its chemical resistance, which allows its application in soils of all classes, including severely aggressive environments. From a functional aspect, steel pipe coatings must act as a barrier to corrosive components in the soil. The material's chemical resistance prevents its degradation, but this should not be allowed to conceal the fact that polyethylene – like most materials – is susceptible to some form of corrosion.

Resistance to corrosion or aging must be verified for polyethylene coatings as part of the delivery conditions. As early as 1974, a combined heat and light aging test was required. The temperature measured using a black standard thermometer was 60 °C. The exposure time to xenon-arc light was 800 hours. The gauge of aging was determined to be the melt index, with the maximum allowable variation from the initial value being 25 %.

The 1980 version of DIN 30670 separated this combined test into two units. The resistance to heat aging was tested at 100 °C over a period of 2400 hours. The same period was specified for the light aging test, in conjunction with a maximum allowable black standard temperature of 45 °C. In both cases, the maximum allowable melt index variation from the initial value was 35 %. The current version of DIN 30670, published in 1991, stipulates an energy input of 7 GJ and a black standard temperature of 65 °C for the light-aging test. The requirements on the heat resistance of polyethylene have remained unchanged since 1980, while an exposure period of 4800 hours has been defined for the newly introduced coating type S for higher service

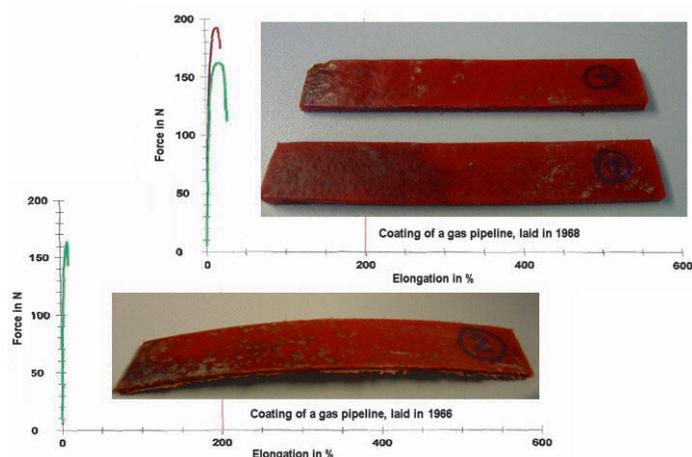


Fig. 1: Ultimate elongation of sintered polyethylene coatings



Fig. 2: Sintered coating affected by external forces



Fig. 3: Brittle fracture in an extruded polyethylene coating

embedded in rock-free material and not exposed to external forces such as point loads or point supports, the barrier effect of polyethylene will remain unaffected even in the case of significantly reduced elongation at break (**Fig. 1**).

This holds provided that there are no local peak stresses due to impermissible loads, which usually cause the formation of interlinking net-like cracks in the coating (**Fig. 2**).

Damage due to point loads or point supports is also known from extruded polyethylene coatings. **Figure 3** shows the fishbone-like cracks typical for this kind of damage. The coating shown here stems from a pipeline laid and buried in 1979. A closer look at the elongation at break in material aged in this way reveals a marked tendency to tough fracture and elongation values between 50 and 100 % in tensile test specimens, while bending leads to brittle fracture. In the tensile test, the material undergoes a reduction in cross-sectional area in addition to ultimate elongation (**Fig. 4**). The tough fracture behaviour in the tensile test is opposed by brittle behaviour during bending. This striking contradiction calls for a more detailed study of the extreme fibre elongation during bending.

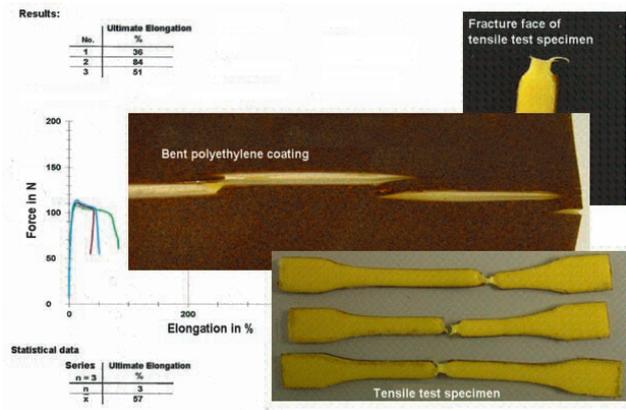


Fig. 4: Determination of the ultimate elongation of an embrittled polyethylene coating

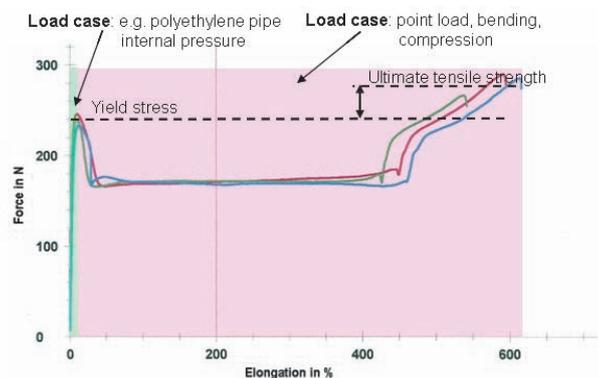


Fig. 5: Tensile tests on HDPE specimens (DIN 30670)

Elongation of extreme fibre

The evaluation of practical load cases must differentiate between two load ranges for polyethylene. Figure 5 shows the typical result of a tensile test on an HDPE specimen. The load case in the range below the yield stress up to between 8 and 10 % elongation (green) is used, for example, in plastic pipe design for internal pressure and is also assessed on a long-term basis as part of internal pressure creep testing.

The decisive factor influencing the material's behaviour is the rate of load build-up. Due to the viscoelastic properties of polyethylene, the achievable rate of stress equalisation decreases with decreasing service temperature. At high temperatures, this stress relief is strongly promoted, and the material can even out local stress concentration during bending.

A higher rate of load build-up will inevitably lead to local stress concentration beyond the permissible maximum and hence to elongation exceeding the permissible rate of 8 to 10 % (at room temperature). Such conditions arise for line pipe exposed to alternating wet and dry phases during handling, storage and laying as well as for buried pipelines in the case of point loads or point supports resulting from soil subsidence due to alternating frost-dew cycles or other reasons. This range, which extends from above approximately 10 % elongation to ultimate elongation (red), is relevant for load cases such as compression or bending (as described in the model case below), i.e. load cases whose assessment requires a detailed

temperatures. The tests mentioned here do not claim to provide a basis for assessing the long-term behaviour of polymers but serve as minimum requirement regarding the stabilization of the material used.

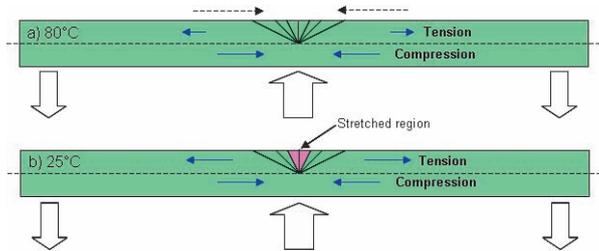
The currently discussed draft version of ISO 21809-1 requires that, in addition to light and heat aging tests, the OIT (Oxidation Induction Time) must also be determined. To do this, a polyethylene specimen is exposed to an oxygen atmosphere at 210 °C until it starts degrading. However, the OIT test can only be used to assess the performance of the stabilizers in the tested polyethylene for production conditions at higher temperatures. It does not provide an indication of the material's aging behaviour under service conditions. This is confirmed by practical examples,

where polyethylene specimens aged under service conditions revealed excellent OIT values, although the elongation at break was significantly reduced [1]. While the determination of the elongation at break as a gauge of stabilization has been specified in the various versions of DIN 30670, the current draft version of ISO 21809-1 additionally stipulates a comparison of the elongation at break and melting index of the input material with the corresponding values of the extruded coating.

The reason why the corrosion properties of polyethylene have become an issue for in-depth discussion is based on a number of incidents where coating damage was clearly attributable to the reduction in elongation at break and thus embrittlement of the material. As long as polyethylene coated pipelines are

look at edge fibre elongation. Even a single incident of stress application beyond the 8 to 10 % limit will trigger the yield process at a low stress level. This means once the stress maximum has been exceeded, the material's long-term behaviour in terms mechanical properties is no longer calculable even under normal service conditions (Fig. 6).

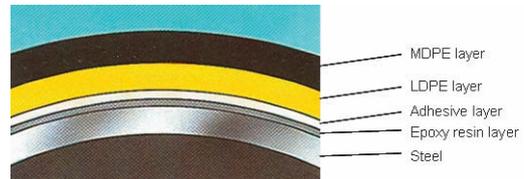
Fig. 6: Bending of polyethylene at various temperatures



For a material behaviour that shows increasing stress with increasing elongation, edge fibre elongation is relatively subcritical (green). Polyethylene shows such behaviour, especially at high temperatures (Fig. 6a).

At room temperature, this behaviour changes significantly (Fig. 6b). The yield stress reaches a maximum (cf. Fig. 5) at elongation in the range of 8 to 10 %. If this elastic limit is locally exceeded during bending, the material in this area will sacrifice itself in favour of those areas strained below the elastic limit, i.e. it will be completely stretched even under the lower stress (red). In this state, the stress increases once again (cf. Fig. 5). If it reaches the yield point, previously unstretched material can be strained beyond the 10 % limit, whereupon the stretching process will commence once again. This shows that elongation as a function of the rate of load build-up during bending is not a

Fig. 7: Steel pipe coating of LDPE with MDPE top layer for added protection (Product information Röhrenwerk Gebr. Fuchs GmbH 1988)



smooth process but occurs in a discontinuous fashion. This behaviour is critical insofar as, macroscopically, a component with subcritical extreme fibre elongation may be completely stretched in other areas (red region).

At room temperature and, especially, at the temperatures prevailing underground polyeth-

ylene can only react in this way as long as – to put it in simplified terms – the ultimate tensile strength, taking into account the effective geometries, is higher than the yield point (cf. Fig. 5). If the ultimate tensile strength is reduced due to aging, it is impossible for the material to integrate further areas into the stretching

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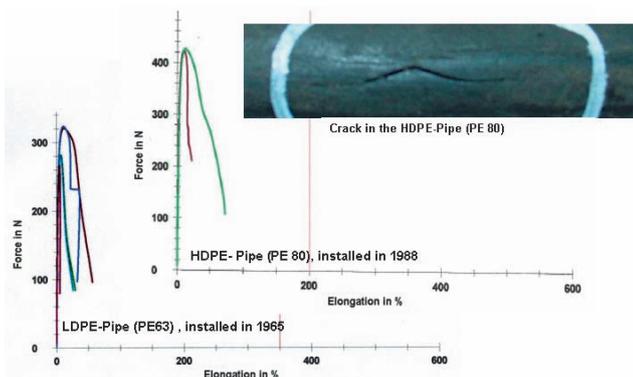


Fig. 8: Tensile tests to DIN 30670 on specimens from LDPE and HDPE pipe

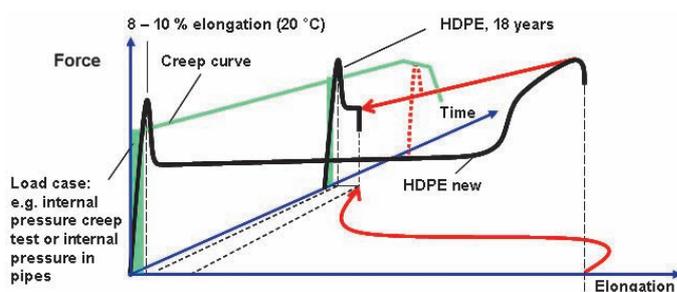


Fig. 9: Corrosion behaviour of HDPE

process in order to evade the stress by means of elongation until it breaks. This shows that the reduction in ultimate tensile strength is not a continuous aging-induced process but is related to a given load case that has exceeded the elastic limit. As a result, the fracture mechanical behaviour is changed and the risk of cracking increases.

From the model described above it is clear that crack initiation takes place on the side facing away from the pressure point (Fig. 6b) [2, 3]. In the past, a second, higher-strength layer of MDPE was frequently extruded over the LDPE coating to protect it from mechanical damage (Fig. 7). Such a layer has a certain protective function in that it prevents the coating from being affected by the sort of scratches that occur, for example, when pulling a pipe string through the soil by the HDD method. Nevertheless, it cannot prevent crack initiation in the presence of a point load or point support, if the ultimate tensile strength of the underlying LDPE layer has been reduced due to aging. That is why experts now generally recommend a top coat of cement mortar for such load cases.

Changes in fracture mechanical properties can be verified in a tensile test at room temperature. It should be noted, however, that elongation determined in the tensile test (here in accordance with DIN 30670) depends primarily on the specimen geometry. As long as the yield stress does not exceed the material's elastic limit, a rod coupon will be fully stretched in the tested region, especially in the case of the extruded polyethylene types

for buried pipelines discussed here. If the ultimate tensile strength drops below the limit value required for a given load case, the elongation reached depends primarily on which sections of the symmetrically shaped tensile test specimen exceed the elastic limit (between 8 and 10 % elongation) at roughly the same time. These and only these areas will be fully stretched in the tensile test and will show the typical reduction in cross-sectional area. Elongation beyond the 8-10 % limit relevant for the yield stress therefore does not necessarily mean the absence of the hazard of aging-induced crack formation. Embrittled material can show apparently ductile fracture behaviour in the tensile test and still fail after it has undergone a certain elongation. Under these conditions, significant variations in the results of elongation rate measurements are only to be expected. In any case, assuming that materials in a new condition have been fully stretched in a tensile test, it is possible to verify aging-induced reduction in ultimate tensile strength on the incompletely stretched part of the tested area, even if the initial values of the ultimate tensile strength are unknown.

Aging behaviour of polyethylene

For many years now, engineers have looked to material developments for plastic pipe when selecting the starting material for polyethylene coatings. In fact, in some cases the same material has been chosen for both pipe and coating.

Figure 8 shows examples of tensile tests on LDPE and HDPE pipe specimens. The most striking phenomenon is that the effect of reduced ultimate tensile strength and elongation at break can be observed much earlier in HDPE than in the LDPE material. While the LDPE lasted through between 30 and 35 years exposure before a reduction in elongation at break became noticeable, it was significant in HDPE after less than 20 years. This has not only been verified by our own measurements but is also mentioned in the literature [1]. Reports describe the phenomenon of incomplete stretching of the tested area and the reduced elongation at break in aged pipe specimens. Here too, reduction in elongation at break was observed significantly earlier in pipes made from PE 80 (HDPE) than in those made from PE 63 (LDPE).

Figure 9 shows the aging-induced changes and/or corrosion verified in tensile tests on a new and on an 18-year-old HDPE specimen. While the tested area in the service time segment considered here remains unaffected by the aging process up to max. 10 % elongation, the ultimate tensile strength and, as a secondary effect, the elongation at break, are reduced. Account is taken here of the fact that, as described above, the elongation at break is not reduced in a continuous process but in leaps induced by loads exceeding the applicable elongation limit.

With polyethylene, unlike for example polypropylene, chain scission only plays a minor role in the first step of oxidative decomposition. Oxidative decomposition leads primarily to chain extension and branching. If a tensile load is applied, the cross links between the molecular chains ensure that not all the chains are integrated into the elongation process. Accordingly, the ultimate tensile strength decreases as the number of cross links increases (Fig. 10).

The change in the fracture-mechanical behaviour of polyethylene described at the beginning of this article is associated with the aging-induced changing of fracture mecha-

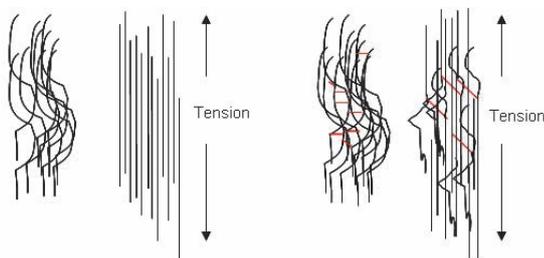


Fig. 10: Tensile stress distribution in new and aged polyethylene

nics properties. Aging processes below the 8 – 10 % limit in polyethylene pipe are normally examined by internal pressure creep tests. Assessing the starting materials for the polyethylene coating as extruded hollows in an internal pressure creep test is theoretically conceivable, but hardly promising. It has to be remembered that, under these test conditions, corrosion processes in polyethylene will only be detected when the material has completely lost its mechanical properties with regard to load cases such as point loads, point supports, compression and bending, etc. An internal pressure creep test detects changes up to the yield point. It provides no information at all about changes in the ultimate tensile strength and elongation at break as a function of time beyond the 8–10 % elongation limit.

In addition it has been shown that the mechanical properties, especially of service-aged materials, change dramatically under the effect of heat, even after short exposure periods [4]. For example, by exposing aged LDPE to heat, its ultimate tensile strength can be raised from values well below 100 % to over 400 % (Fig. 11).

This behaviour has been verified for both service-aged coating specimens and specimens from LDPE pipe (PE 63). It cannot be excluded that, in stage of aging examined here, embrittlement takes place primarily in the amorphous regions of the semicrystalline polyethylene microstructure. Under the effect of heat treatment the immobilized amorphous regions may undergo transformation to the crystalline state, and formerly crystalline regions may form new amorphous regions, enabling the material to resume its original behaviour.

This effect has also been described in the literature in reports about aged pipe specimens that passed the internal pressure creep tests despite their reduced ultimate tensile strength [1]. Based on the test results alone, the fact of the reduced ultimate tensile strength and elongation at break would be unknown and, consequently, disregarded which means that they could easily be released again and approved for a service life of 50 years. However, this apparent contradiction can also be explained by the changes taking place in the material during heat treatment. Heat can rehabilitate the material. For this reason, test results obtained under the effect of heat are of no use when it comes to assessing the service behaviour of aged material. In light of these findings, even tests on new materials must be viewed critically with regard to their value and validity for the long-term service behaviour of the tested material.

Tests with wetting agents are similarly unable to contribute quantitatively or qualitatively to the clarification of this question. Test results obtained from new materials cannot be transferred to aged material whose fracture behaviour or fracture mechanical properties,

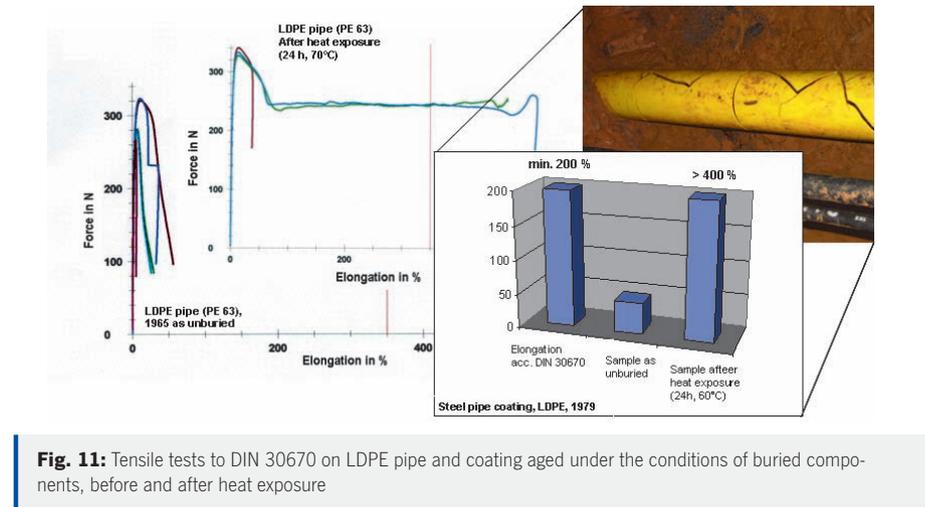


Fig. 11: Tensile tests to DIN 30670 on LDPE pipe and coating aged under the conditions of buried components, before and after heat exposure

as in the case described here, have changed fundamentally over the course of just 20 years. This has also been expressly emphasized in the literature [5, 6, 7]. Moreover, a test using a wetting agent examines a purely physical phenomenon, namely the diffusion of a medium that incorporates a wetting agent into the polymer microstructure. However, the actual subject of the test, namely the aging behaviour of the polyethylene, is a chemical process [8]. Although the correlations between creep tests and tests under the effect of wetting agents are frequently brought forward, they are in fact based on a similar linear dependence on time of two quite different failure mechanisms. It stands to reason that the change in marginal conditions to be assessed for the one process cannot be established by using the other process. This is also shown by the fact that published results of tests carried out in the presence of wetting agents do not even mention the clearly more favourable behaviour of the previously used material for PE 63 types compared to the more recent material for PE 80 types, especially in the context of material properties to be assessed – e.g. under point loads – beyond the 8-10 % edge fibre elongation.

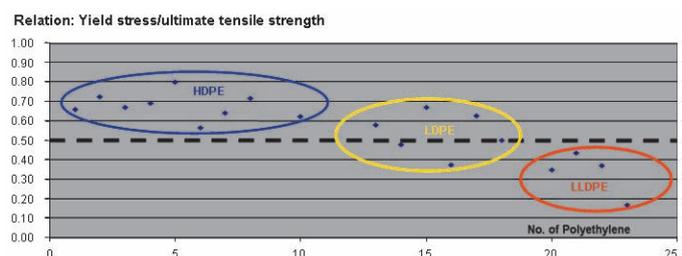
When the mechanical characteristics of the polyethylene types and the effects described are taken into consideration, the somewhat unfavourable aging behaviour of HDPE in respect of the described effects perhaps becomes more comprehensible. Further, an increase in yield stress, will under no condition lead to a comparable increase in ultimate tensile strength. So the relation between

yield stress and ultimate tensile strength will reach higher values from LLDPE over LDPE to HDPE (Fig. 12).

Figure 12 plots the relation of yield stress and ultimate tensile strength for various PE types which are typically used for buried components. Assuming that the reduction of a given ultimate tensile strength in a completely stretched material with similar stabilisation is related to roughly the same period of time, this relative consideration will necessarily lead to a more favourable aging behaviour – independently of the PE type – as the distance between yield stress and ultimate tensile strength increases. Following this approach, HDPE may have become completely brittle, while components made from LLDPE still have enough tensile strength to resist the forces acting on them. LDPE holds a position between the two here, which has already gained its distinct advantages, judging from practical observations.

In light of the findings presented in this article, the fact that – corresponding to developments in polyethylene pipe – practically all the pipeline projects now use HDPE coatings, the selection of this material must be subjected to a very critical analysis. It may be that materials such as the LLDPE types with their relatively more favourable yield stress-to-ultimate tensile strength ratio offer a much better solution, considering the mechanical loads involved. However, the tests which are currently being frequently discussed provide no meaningful statement – either quantita-

Fig. 12: Relation of yield stress/ultimate tensile strength of various PE types (manufacturer's data)



tively or qualitatively – regarding the long-time service behaviour of these materials. When new materials are tested, aging-related changes are not registered, especially when they concern the load case beyond the 8-10 % elongation limit. What is more, tests in a hot atmosphere change the material's microstructure and conceal aging-related changes. Here, several points need to be clarified, not only regarding the suitability of the test methods, but also concerning the materials themselves, such as the presence of the tertiary carbon content in LLDPE.

Outlook

The questions raised here are being investigated within the framework of several research projects in cooperation between steel pipe producers, universities and institutes. In addition, public utility companies are providing aged specimen material for the tests. Current research activities primarily aim to optimize the mechanical properties of polyethylene coatings with regard to impermissible interference. In this context it must be considered that, provided the required care is applied in pipe laying and operation, the polyethylene coating merely has to follow the elongation of the steel base material, which is significantly lower than 0.5 %, even if the permissible internal pressure is fully utilized. Under these conditions, the polyethylene coating will lose none of its efficiency, even in a fully embrittled state, as a measure of corrosion protection for the steel pipe it covers [8].

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Author:

Dr. rer. nat. Hans-Jürgen Kocks
Salzgitter Mannesmann Line Pipe GmbH,
Siegen, Germany



Phone: +49 271 691170
E-mail: hans-juergen.kocks@smlp.eu

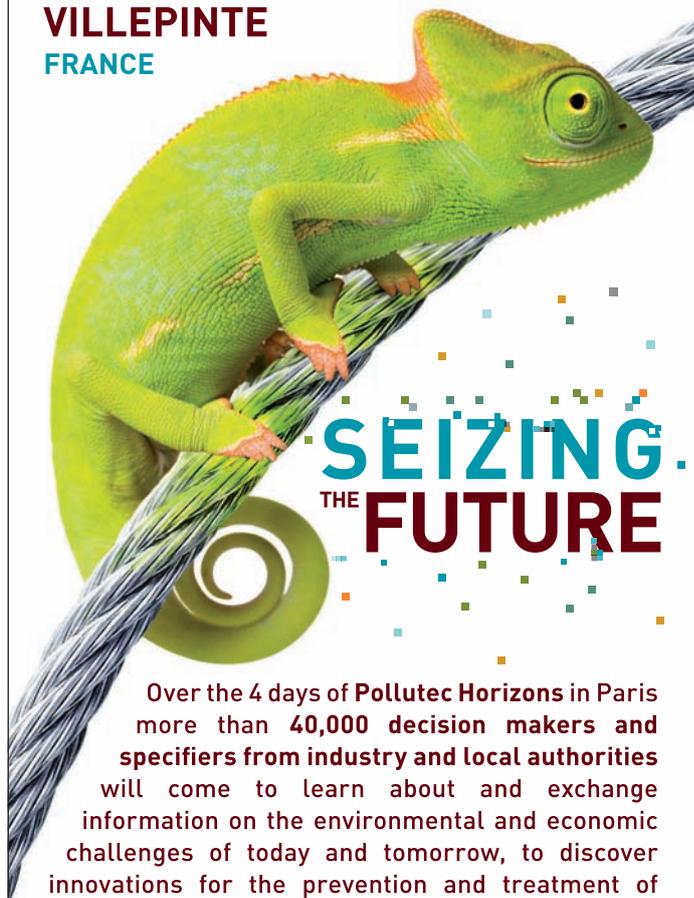
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