Characterisation of the Thermo-Oxidative Degradation of Polyethylene Pipes by Chromatographical, Rheological and Thermo-Analytical Methods

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Summary: In this work the influence of three different stabiliser systems on the stress rupture behaviour of high density polyethylene (PE-HD) pipes under constant internal pressure was examined at 60 and 80 °C with special consideration of the quasi-brittle failure by growth of a single crack in the failure regime preceding the global chemical degradation of the pipes. It could be proven that the pipes of the three formulations did not show global molecular and morphological differences in this failure regime and that the stabilisation was still intact. Therefore, the differences in failure times observed for the three formulations are believed to be a result of local ageing around the crack tip related to the combined influence of time, the elevated temperature, the presence of oxygen and water, and the high mechanical stresses in the immediate crack tip region.

Introduction

Thermoplastic polymers are extensively used to produce pipes for a wide range of applications including water services and natural gas supply. Depending on the specific area of use the service life typically required and to be achieved covers a time span from 20 to 50 years. The traditional method to compare different types and grades of plastics and to obtain information for pipe design consists of stress rupture experiments with pipes under constant internal pressure. The tests are conducted in a specified internal and external environment (usually water or air), at various pressure levels and frequently at several temperatures. The time to failure t_f is recorded and the data are presented on log hoop stress σ_{hoop} versus log time to failure coordinates yielding to so called stress rupture or creep rupture curves. Results of such investigations are available for essentially all plastics used in pressure pipes, in some cases covering a time span of more than 10 years.[1-3]

Based on the extensive amount of data available it is now well established that in general the lifetime of plastics pressure pipes is controlled by three principal failure modes,

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which may lead to stress rupture curves schematically illustrated in Figure 1.[1, 4, 5] In region A, associated with high applied stress levels, failure is characterised by extensive plastic deformations; in region B, at lower stress levels, failure occurs with little evidence of plastic flow as a result of the initiation of a (single) crack and subsequent propagation of the crack through the pipe wall in a brittle or quasi brittle manner. While there are hardly any experimental data, at least in principle there might be a region B′ associated with a certain threshold stress level below which no stress induced failure takes place, thus corresponding to a mechanical endurance limit; in region C, at low stress levels and long times, chemical ageing leads to global polymer degradation and brittle failure. Since in practice the purely mechanical failure cannot be separated from the chemical one, the higher loads in region B may be responsible at least for local ageing processes in region B.[3, 5-8]

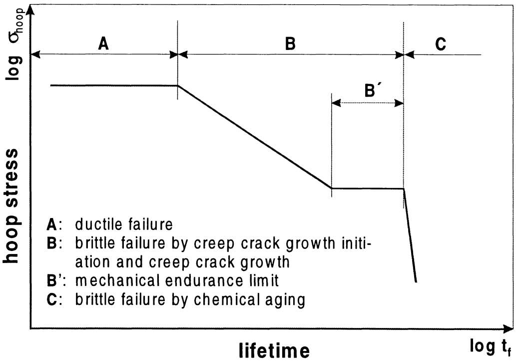


Figure 1. Schematic stress rupture curve of internally pressurised thermoplastics pipes illustrating the various regions of pipe failure.

In order to retard thermo- and photo-oxidative degradation processes and to ensure proper pipe performance, special stabiliser systems are added to the thermoplastic materials. It is well documented that stabilisers shift the transition to region C behaviour to higher failure times,[1, 3, 9] but it might also retard the very localised ageing processes in region B. Therefore, the aim of this work was to investigate the influence of different stabilisers on the stress rupture behaviour of high density polyethylene (PE-HD) pipes at 60 and 80 °C with special regard to region B failure. Chromatographical, rheological and thermo-analytical investigations of the pipes were used for material characterisation and for the determination of stabiliser consumption and thus for the indirect verification of global and local ageing processes.

Experimental

Materials

The investigations in this work were done with the base polymer (without standard additives) of a commercial grade PE-HD (Borealis, A). This type is usually recommended for extrusion blow moulding, but in this work it was used for the extrusion of pipes expecting shorter lifetimes also at lower testing temperatures (60 and 80 °C). Some characteristic material properties are summarised in Table 1.[10]

With this base polymer three formulations containing different stabiliser systems and stabiliser concentrations were produced. Formulation S was added 0.1 % of a sulphur containing secondary antioxidant (Santonox R; Monsanto, B). The formulations K1 and K2 contained 0.1 resp. 0.2 % of a mixture of a primary and secondary antioxidant (Irganox B 225, Ciba Specialty Chemicals, CH). The three material formulations were extruded to pipes on a commercial extrusion line using identical processing conditions. The nominal inside diameter of these pipes was 16 mm, the nominal wall thickness was 2 mm.

Table 1. Characteristic properties of the PE-HD base polymer (ρ: density, MFI: melt flow index, E: elastic modulus, σ_y: yield strength, ε_y: elongation at yield).

ρ (ISO 1183)	$MFI_{190/2.16}$ (ISO 1133)	$E^{*)}$ (ISO 527)	$\sigma_y{}^{*)}$ (ISO 527)	$\varepsilon_y{}^{*)}$ (ISO 527)
g/cm^3	g/10 min	N/mm^2	N/mm^2	%
0.959	0.3	1450	31	8

*) 23 °C, 50 % r. H.

Test Methods

Internal Pressure Testing

The pipes were pressure tested with stagnant distilled water as the internal medium and moderately circulating air as the external medium at 60 and 80 °C at a test device designed and built in our laboratory.[3] At every single temperature and pressure level at least 4 pipes of each formulation with a length of 500 mm were tested. The hoop stress σ_{hoop} was calculated corresponding to the membrane stress theory (Equation 1) that is valid for thin-walled pipes:

$$\sigma_{hoop} = p \cdot \frac{d_a - s}{2s} \qquad (1)$$

where p is the internal pressure, d_a the outside diameter and s the wall thickness.

Size Exclusion Chromatography (SEC)

For all samples the molecular mass and its distribution of the samples were determined with the "GPC 220" chromatograph (Polymer Laboratories, UK) equipped with a differential refractive index (DRI) detector (Polymer Laboratories, UK), a differential viscometer 210 R (Viscotek, USA), and coupled with a low-angle laser light scattering (LALLS) photometer KMX 6 (λ=633 nm) (Chromatix, USA). A set of two columns was used, packed with crosslinked styrene-divinylbenzene (PLgel® Mixed-A LS, particle size: 20 µm, length: 300 mm, inner diameter: 7.5 mm; Polymer Laboratories, UK). The measurements were performed at 135 °C with 1,2,4-trichlorobenzene (Merck, Germany) serving as solvent and eluent.

The polymer solutions were prepared with amounts between 1 and 2 mg of the polymer in 10 ml of the solvent and were flushed with nitrogen for 15 minutes at room temperature to avoid oxidative degradation during the dissolution. The samples were then placed in an oven and were rolled by a self-assembled apparatus at about 3 revolutions per minute at 150 °C for 4 hours prior to injection. This procedure homogenises the samples with negligible mechanical stress and avoids oxidative degradation during SEC runs.

Rheological Analyses

The rheological characterisation of the materials was done with a Rheometrics RMS 800 (Rheometrics Inc., USA) with parallel plate fixtures (diameter: 25 mm, gap: 1.5 mm). In order to prevent thermo-oxidative degradation the tests were performed under nitrogen atmosphere. In frequency sweeps (0.01 – 100 rad/s) the complex viscosity η^*, the storage modulus G' and the loss modulus G'' were determined at a shear strain of 20 % in the linear viscoelastic deformation range at 180 °C.

The value of η^* as a function of frequency ω and the position of the crossover point G_c (intersection of $G'(\omega)$ and $G''(\omega)$ curves) were used as an indirect way to characterise the molecular mass of the materials. The zero viscosity η_0 (frequency independent value at low frequencies) is proportional to the weight average molecular mass M_w and from changes of η^* with ω, variations in the distribution of the molecular mass can be estimated.[11] Corresponding to Franck [12] the position of the crossover point with the coordinates G_c and ω_c gives an indication of molecular variations in a macromolecular material. An increase resp. decrease of G_c values indicates a smaller resp. broader molecular mass distribution and an increase resp. decrease of ω_c values a lower resp. higher average molecular mass.

Thermo-Analytical Analyses

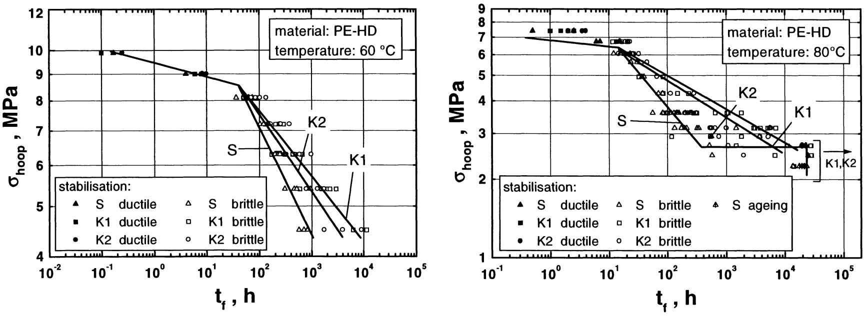
Both, the degree of crystallinity X_c and the oxidation temperature T_{ox} were determined using a Du Pont 910 Differential Scanning Calorimeter (DSC; TA Instruments, D) at a heating rate of 10 K/min in air. The sample weight was approximately 5 mg with samples covering the entire pipe wall thickness. Values for X_c were calculated based on the relationship $X_c = \Delta H_s/\Delta H_c$ with ΔH_s representing the experimental melting peak area and assuming a value for ΔH_c for 100 % crystalline PE of 293 J/g [13]. T_{ox} was defined as the temperature at the intersection of the extended baseline with the extrapolated slope of the exotherm.

The oxidation induction time (OIT) was measured under isothermal conditions at 180 °C in air with an isothermal long-term differential thermal analysis (ILDTA) device designed and built in our laboratory [14]. The sample weight was also in the range of 5 mg. The deviation from the baseline when oxidation starts was used as a criterion for induction time, which was obtained by extrapolation, by drawing a tangent to the steepest portion of the exotherm.

Results and Discussion

In Figure 2 the stress rupture curves of the three formulations are shown at 60 and 80°C. As expected the stress rupture curves were shifted to lower hoop stress levels and failure times at 80 °C. In the flat part of the curves with ductile failure no differences in failure times as a function of stabilisation could be determined at both temperatures. Also the ductile/brittle transition of the pipes was found to be independent of the stabiliser-type (80 °C: σ_{hoop} = 7 MPa, t_f = 10 hours; 60 °C: σ_{hoop} = 8.5 MPa, t_f = 30 hours). However, with increasing duration of the tests in region B, where pipe failure is caused by crack growth initiation and crack growth, the failure times got sensitive to the stabiliser systems.

Despite the high scatter in the data a careful analysis of the results reveals that stabilisation S showed the lowest failure times followed by K2 and K1. Region C has as yet been reached only for stabilisation S at 80 °C after passing a mechanical endurance limit. While the existence of an endurance limit has been suggested earlier,[4, 5] to our knowledge such an endurance limit was verified experimentally for the first time in this test series. As the transition to region C with substantial global ageing and molecular degradation of the polymer has as yet been reached only for stabiliser S at 80°C, future work will provide further insight into the significance of such a regime.



(a) (b)

Figure 2. Influence of the three stabiliser systems on the stress rupture curves of PE-HD at (a) 60 °C and (b) 80 °C.

In order to identify the reasons for these findings, the molecular and morphological structure as well as the state of stabilisation of the pipes was investigated. The degree of crystallinity was determined by dynamic DSC scans. After extrusion of the pipes no differences could be found in the degree of crystallinity between the three formulations (about 63 %). With higher testing times the pipes showed a slight increase in the degree of crystallinity to a level of about 69 %, what is supposed to be a result of temper effects.

In Figure 3a and b the results of the investigations of molecular mass measured by SEC are depicted as a function of pipe failure times. No differences in weight average molecular mass M_w and molecular mass distribution M_w/M_n (M_n= number average molecular mass) could be detected between the three stabilisations up to pipe failure times of about 400 hours; then formulation S showed a continuous decrease in molecular mass and molecular mass distribution, whereas the values for K1 and K2 have remained constant until actual testing times. The sharp drop in the values after 17.000 hours for stabilisation S is in good correlation with extensive molecular degradation in region C.

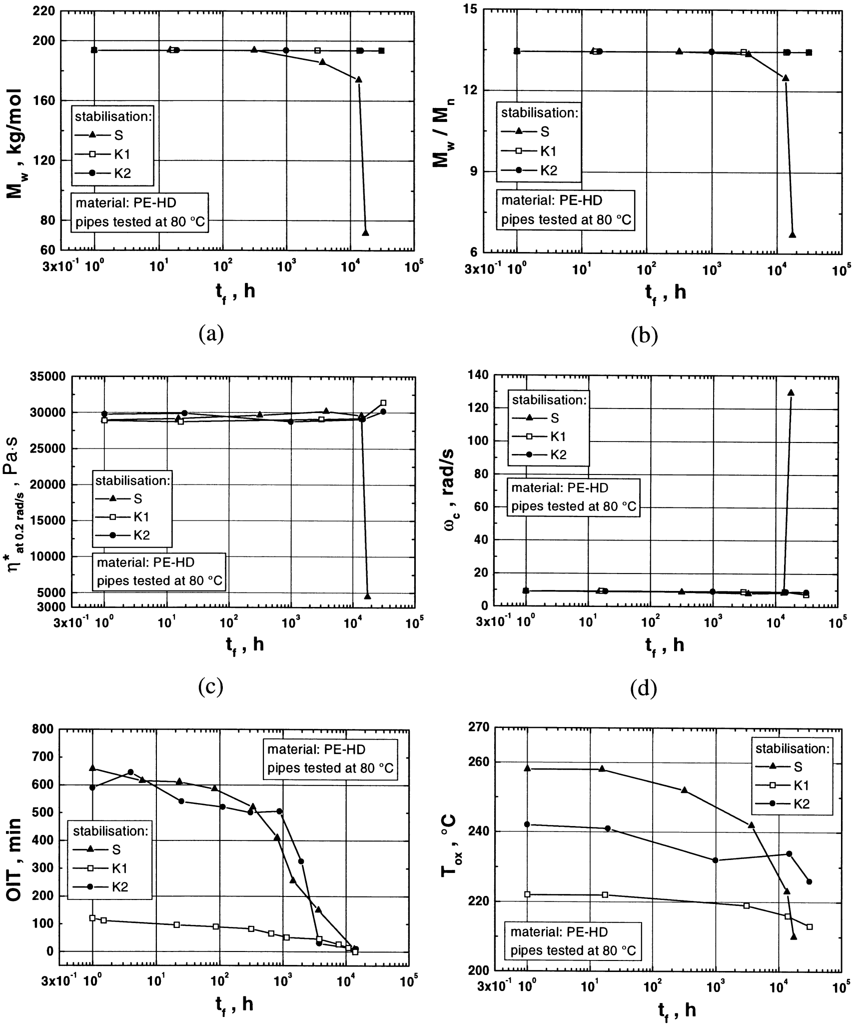
The rheological characterisation of the materials could confirm the results of SEC. No differences in complex viscosity (Figure 3c shows the data at a frequency of 0.2 rad/s) and crossover point (Figure 3d shows the data for ω_c) were found for the three stabilisations in region A and B of pipe failure. The continuous decrease in molecular mass and molecular mass distribution beginning with failure times of about 400 h for stabilisation S could not be detected in this kind of tests. The sharp drop in these properties for stabilisation S at about 17.000 h, however, could be documented by considerably lower values in complex viscosity (Figure 3c) and a shift of the crossover point to lower values for ω_c (Figure 3d) and higher values for G_c.

In the run of the hydrostatic stress rupture tests the concentration of the stabilisers in the pipes is reduced by loss to the environment and by reactive consumption. In this work the decrease of OIT [15, 16] and T_{Ox} [17, 18] was used to characterise these changes in stabiliser content.

In Figure 3e the reduction of the OIT values measured at 180 °C is illustrated as a function of the pipe failure times at 80 °C. Generally the value of the OIT depends on the stabiliser system as well as on the test temperature. Without additional information the absolute value of the OIT, however, does not allow any comments on the efficiency of the stabilisation or on the extent of ageing. The OIT of the pipes of the three stabilisations began already to drop after a few hours from the level of the original pipes, a significant knee in the curves, however, could only be observed much later. For the pipes tested at 80 °C this drastic drop of the OIT was detected after about 3.000 hours for all three formulations. A correlation between the ductile/brittle transitions in the stress rupture curves (10 hours at 80 °C) and the strong drop in the OIT values, as found in reference 19, could not be seen in these measurements. At failure times of approximately 10.000 hours the stabilisers of the formulations seem to be consumed at 80 °C, since the OIT values fell almost to 0. Nevertheless the pipes still exhibited a thermo-oxidative stability, because global chemical degradation could be suppressed for lifetimes of about 17.000 hours for formulation S and is still suppressed for K1 and K2 (actual testing time: 32.000 hours).

The values of T_{ox} were also reduced with increasing testing times of the pipes (see Figure 3f). However, a sharp drop could be detected only for formulation S at about 13.000 h. Apparently, changes of the oxidation temperatures reflect the overall ageing conditions of the pipes in a better way than those of the OIT, because the latter results correspond rather well with the data from pipe testing (global chemical ageing of formulation S at about 17.000 h, still no signs of global chemical ageing of formulation K1 and K2 at 32.000 h).

The morphological and molecular characterisation of the pipes tested at 60 °C confirmed that at least in the early stage of region B failure no global molecular and morphological changes occurred in the pipes and the global stabilisation of the pipes was still intact.



(a) (b)

(c) (d)

(e) (f)

Figure 3. Influence of the three stabiliser systems on molecular, rheological and thermo-analytical properties of internally pressurised PE-HD pipes as a function of pipe failure times at 80 °C; (a) weight average molecular mass (M_w), (b) distribution of molecular mass (M_w/Mn), (c) complex viscosity (η^*) at a frequency of 0.2 rad/s, (d) frequency of crossover-point (ω_c), (e) oxidation induction time (OIT) at 180 °C, (f) oxidation temperature (T_{ox}).

Hence, the differences in lifetimes observed for the three formulations are believed to be a result of local ageing around the crack tip related to the combined influence of time, the elevated temperature, the presence of oxygen and water, and the high mechanical stresses in the immediate crack tip region (see Figure 4).[20, 21] As crack growth initiation times and crack growth rates are very sensitive to molecular and morphological changes, this local ageing process may influence failure times in pipes. As stabilisers delay the auto-oxidation and degradation of the polymer, they should also be effective near the tip of the crack and thus should influence local ageing and the lifetimes of pipes.

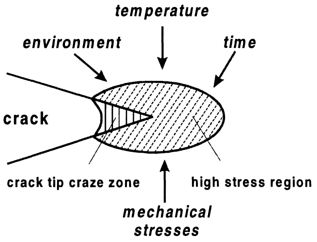


Figure 4. Schematic illustration of the crack tip region in PE-HD along with the parameters controlling local crack tip ageing.

The increasing differences in failure times between the three stabiliser formulations with decreasing hoop stress levels in region B (see Figure 2) apparently reflect, that the influence of stabilisers becomes more pronounced as longer crack growth initiation times and low creep crack growth rates are involved providing sufficient time for potential local crack tip ageing processes. Consistent results could be found in fracture mechanical creep crack growth experiments with the same formulations, where also differences in crack growth rates in the low speed region could be found.[6, 7, 22, 23] Surprisingly, but in quite good agreement with the fracture mechanical creep crack growth investigations,[6, 7, 22] pipes of the formulation K1, containing only 50 % of the antioxidants of K2, indicate higher lifetimes than K2. The mechanisms involved are not yet clear. There are two possible explanations for this anomalistic behaviour of the formulations K1 and K2. On the one hand agglomerates of stabilisers in formulation K2 might morphologically weaken the polymer [24, 25] and lead to lower failure times of the pipes. On the other hand molecular or morphological changes during processing on an extreme local scale beyond the sensitivity of the characterisation methods used might influence pipe lifetimes. Consistent with the findings above Gebler could prove in his measurements [9] that after achieving the boundary of sufficient stabilisation of a polymer global ageing (region C failure) cannot be shifted to longer times. Gebler found that an increase of the concentration of a not closer specified stabiliser from 0.1 to 0.2 % in PE-HD did not lead to an improvement of the failure behaviour of the pipes but reduced the failure times to a certain extent.

Conclusions

Hydrostatic stress rupture tests were done with three differently stabilised PE-HD pipes at 60 and 80 °C. While within the area of ductile failure no differences in lifetimes between the formulations could be detected, the pipes within region B of the stress rupture curves, where failure is characterised by crack growth initiation and crack growth, indicated different service lives. Pipes of the formulation S failed after the shortest times, followed by K2 and K1. Region C of the stress rupture curves with global chemical ageing has as yet been reached only by formulation S after passing a mechanical endurance limit.

The characterisation methods used could prove that the stabilisation for all three formulations was still intact in region B and also global polymer degradation could be excluded. Thus the varying lifetimes are explained by the occurrence of local thermo-oxidative degradation in the immediate environment of the crack tips. As stabilisers delay the auto-oxidation and degradation of the polymer, they should also be effective near the tip of a growing crack and thus influence local ageing and crack growth rates corresponding to their individual performance.

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