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Durability of cross-linked polyethylene pipes under pressure

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This article summarizes about 20 years of experimental studies on the durability of cross-linked polyethylene (XPE) extruded pipes for hot water transport. The time to failure was determined against hoop stress and temperature (in the 20–120°C range). The XPE samples (16 distinct materials) were compared to classical PE ones (6 distinct materials). It appears clearly that cross-linking suppresses the ductile-brittle transition (average coordinates: $t_C = t_{C0} \exp(Q/RT)$ with $\ln t_{C0} = -24.2$ and $Q = 84.6$ kJ mol^{-1} but does not modify significantly the behavior in ductile regions. It can be assumed that, for XPE, the ceiling conditions are determined by the oxidation embrittlement of which the (tentative) coordinates could be given by $t_E = t_{E0} \exp(H_E/RT)$ with $\ln t_E = -24.45$ and $H_E = 116$ kJ. Thus, XPE performs better than PE in the $(t_C - t_E)$ interval. On this side of t_E, the lifetime t of XPE is linked to the hoop stress σ and the temperature by an equation of which a simplified form could be: $\sigma = \alpha(T_M - T)(\beta - \log t)$ where $\alpha = 4 \times 10^{-3}$ and $\beta = 30$ for $T \leq 80$°C and $\alpha = 6 \times 10^{-3}$ and $\beta = 20$ for $T \geq 80$°C, σ being in MPa, t in hours and T_M being the melting point (137°C). © *2002 Kluwer Academic Publishers*

1. Introduction

It is well known that the durability of polyethylene (PE) pipes under static pressure is essentially limited by the existence of a ductile-brittle transition at which there is a sudden slope change in stress (σ)-time to failure (t_F) curves. N. Brown and coll [1, 2], for instance, express the lifetime as a power law of stress and show that the exponent varies by a factor of about 10 at the transition. The results of empirical approaches of durability improvement in the last decades, clearly indicate that the best performance must result from a compromise. For instance, very high molar masses would be favorable from the point of view of long term mechanical behavior, but processing is more and more difficult as the chain length increases, and, above a certain limit, the increase in polymer strength would be largely counterbalanced by the build-up of heterogeneities capable to play a very disfavorable stress concentration effect. In the same way, high crystallinity ratios would be favorable because they increase the yield stress, but they disfavor ductility. This is the reason why medium density linear polyethylene is generally chosen. In these polymers, a small quantity of comonomers such as butene, hexene or octene, is added to ethylene to introduce some disorder in the chain and then limit crystallinity in a more or less controlled way. The need for such compromises leads to the reasonable assumption that, for linear polyethylene, there is a limited potential of durability increase from the optimization of molar mass distribution and chain microstructure. Any change of these characteristics will eventually shift the ductile-brittle transition towards longer times, but not suppress it.

If the slow brittle crack growth is due to disentanglement by chain crawling [3], crazing [2] and/or creep [4], then cross-linking could make a large increase in durability improvement because it is expected to inhibit or at least limit all the above processes. Indeed, this effect could be counterbalanced by some disfavorable effect of cross-linking on crystallization, but comparative studies of short term mechanical properties on peroxide, silane or radiochemically cross-linked polyethylenes (XPE), indicate that they keep acceptable modulus and yield stress values [5].

If, in contrast, the ductile-brittle transition is associated to polymer oxidation [6, 7] then one sees no reason, a priori, for a positive effect of cross-linking

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on durability. On the contrary, at least in peroxide or irradiation processes, one could expect some disfavorable effect due to stabilizer over-consumption during processing.

Is or not cross-linking a solution to increase polyethylene pipe durability? Despite the existence of theoretical reasons and encouraging experimental data on short term properties, allowing to envisage optimistically its choice, there is, to our knowledge, only two published articles on this subject [8, 9].

The aim of this article is to report the results of about 20 years of pressure testing at various temperatures ranging from 20 to 120°C, on cross-linked polyethylene pipes (16 samples of various origins with distinct cross-linking processes). They will be compared to uncross-linked samples (6 samples differing also by their origin).

2. Experimental

2.1. Materials

The chosen materials are listed in Table I.

The diameters and thickness of the chosen pipes are linked by the following equation:

$$S = \frac{D - e}{2e},$$

with $S = 5$, D: outside diameter and e: minimum thickness.

2.2. Pressure testing

Pressure tests were performed according to the French Standard NF EN 921. The hoop stress σ was calculated from pressure P using the simplified Lamé relationship:

$$\sigma = P\frac{D - e}{2e} \qquad (1)$$

where D is the outer diameter and e the wall thickness. Thickness measurements are made on several points of the tube and the minimum value is used in the above relationship.

Pressure is regulated at $-1/+2\%$ during the whole test duration. Failure is detected from the pressure drop [10].

The fluid under pressure into the pipe is always water. The pipes are immersed in water for temperatures lower or equal than 80°C and placed in ventilated ovens for temperatures higher than 80°C. The temperatures are regulated at ±1°C for temperature lower or equal than 80°C and at $-1/+3$°C for temperature above 80°C.

TABLE I Origin of pipes under study

Linear polyethylene crosslink method	Number producer	Number samples
Engel (peroxydic)	7	13
Silane	3	5
Irradiated	3	5
Unknown	2	3

3. Results

The results obtained on uncross-linked PE and cross-linked PE pipes are summarized in respectively Fig. 1 and Fig. 2. Globally it can be observed that the sample to sample scatter is lower than the difference due to a 20°C temperature change so that it can be considered that the curves are representative of the polymer families under study. The relative homogeneity of these latter is not surprising if one recalls that all the samples under study satisfy the requirements of the French standard NF T 54-085 “Plastics—Cross-linked polyethylene pipes for pipelines under pressure—Specifications”.

The difference between PE and XPE appears very clearly. A change of kinetic regime is observed only in PE. The slope $\Delta\sigma/\Delta \log t$ increases by a factor of 5 to 10 after an exposure time t_c varying from about 3500 hours at 40°C to about 100 hours at 80°C. This change which corresponds to the well known ductile-brittle transition is not observed in the timescale under study ($t \leq 10^5$ hours) at temperatures $T \leq 120$°C for XPE. It cannot be deduced however that brittle failure does not exist in XPE, in fact it can be observed at long times but without a change of kinetic regime. Ductile and brittle facture can be distinguished, as in uncross-linked PE, by a local ballooning in the former and a slit-like crack in the latter.

According to Figs 1 and 2, the stress-lifetime relationship in ductile regime for PE and in the

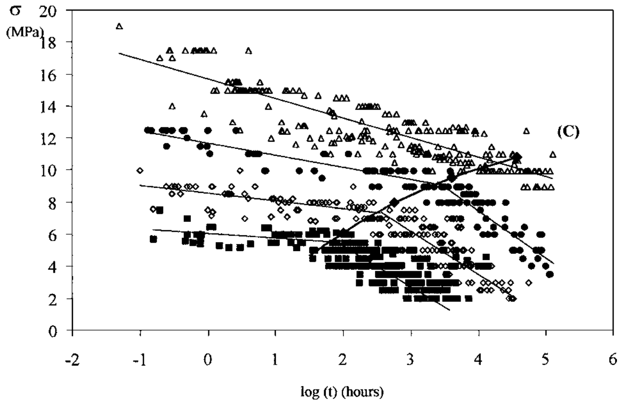

Figure 1 Stress–time to failure for uncrosslinked PE pipes. (►) 20°C; (►) 40°C; (►) 60°C; (►) 80°C.

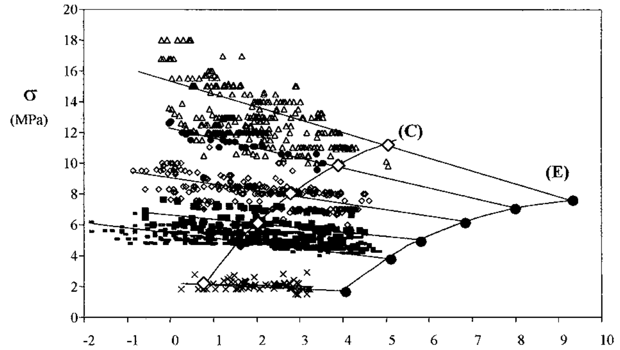

Figure 2 Stress–time to failure for crosslinked PE pipes. The curve (C) is the envelope of ductile–brittle transition points of PE. The curve (E) corresponds to oxidation embrittlement times (►) 20°C; (►) 40°C; (►) 60°C; (►) 80°C, (–) 95°C, (×) 120°C.

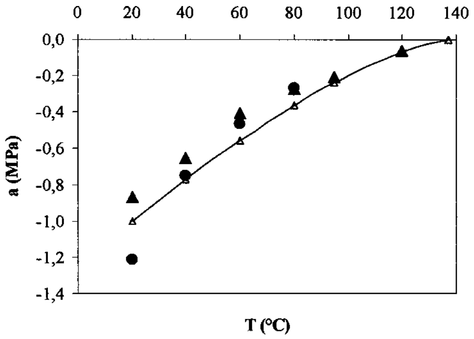

Figure 3 Parameter a versus temperature. (●) linear PE; (▲) XPE. The curve corresponds to: $a = 1.27 \times 10^{-3}\ (T_M - T)^{1.4}$.

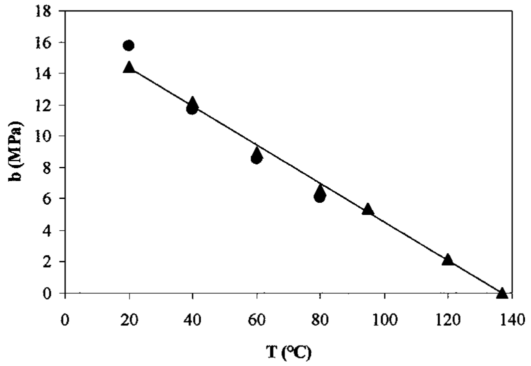

Figure 4 Parameter b versus temperature. (●) linear PE; (▲) XPE.

unique kinetic regime for XPE can be expressed as follows:

$$\sigma = b + a \log t \qquad (2)$$

The values of a and b, determined by linear regression, were plotted against temperature, for both sample families, in respectively Figs 3 and 4. These curves call for the following comments: The values of a and b are similar, within experimental incertitude, for PE and XPE, except eventually at 20°C but the especially high scatter, at this temperature (Figs 1 and 2), does not allow to conclude definitively about a significant difference between both families (in ductile regime for PE).

The envelope of transition points observed for PE constitutes therefore a boundary between the domain where PE and XPE behave quite similarly and the domain where XPE displays clearly a higher durability than PE. The coordinates of transition points experimentally determined at 40, 60, and 80°C, are given in Table II. The time values seem to obey Arrhenius law:

$$t_C = t_{C0} \exp(Q/RT) \qquad (3)$$

With $\ln t_{C0} = -24.2$ and $Q = 84.6\ \mathrm{kJ \cdot mol^{-1}}$.

The apparent activation energy value Q is very close to the one found by Brown and coworkers: 85.5 kJ · mol^{-1}.

Equation 3 was used to extrapolate t_C values at 20, 95, 110 and 120°C (Table II). The slope change cannot be clearly observed at 20°C owing to the short exposure duration in brittle regime ($t \leq 10^5$ hours against $t_C = 10^{4.5}$ hours for the transition time) and the high data scatter. Extrapolated t_C values above 80°C have only an indicative value since this temperature domain is very difficult to explore in the case of uncross-linked PE. The ductile-brittle boundary has been plotted in Fig. 2. It indicates clearly the stress-temperature domain in which XPE displays a better durability than PE.

TABLE II Parameters a and b against temperature

Temperature (°C)	a (MPa)	b (MPa)	$\alpha \times 10^5$ (MPa · K^{-1})	β (MPa · K^{-1})
20	−0.8685	14.4238	742	0.123
40	−0.6518	12.2145	672	0.126
60	−0.4087	8.9165	531	0.116
80	−0.2736	6.5832	480	0.115
95	−0.2044	5.4202	487	0.124
120	−0.0584	2.1740	343	0.128

4. Discussion

The main experimental fact is, no doubt, the absence of change in kinetic regime of failure, at least in the time interval under study. This fact constitutes an argument in favor of physical theories of this transition, for instance chain disentanglement in amorphous phase or crazing. Cross-linking is obviously expected to inhibit disentanglement and to disfavor crazing.

For certain authors, however, failure could be attributed to chain scission resulting from low temperature oxidation [6, 7]. It seems, here, difficult to explain the difference between PE and XPE in terms of difference in oxidative stability. As a matter of fact: (i) Thermal aging studies have clearly shown that XPE behaves qualitatively as PE: After an induction period, its ultimate properties decrease rapidly so that the end of induction period would correspond to a change in the kinetic regime of failure as in PE. The fact that this change was not observed in our results seems to indicate that oxidation is not the cause of failure in the conditions (σ, T) under study for XPE. (ii) Anyhow, it would be difficult to explain the difference between XPE and PE by the fact that the latter is less stable to oxidation than the former. On the contrary, there are many reasons to suppose that XPE is less stable than PE: The cross-linking process, at least in the cases of peroxide or radiation cure, is expected to induce some stabilizer over-consumption. Furthermore, cross-linking creates tertiary carbons which are well known to be more reactive, towards oxidation, than secondary ones. Unfortunately, oxidation induction times in the 20–120°C temperature range are not available for the materials under study. More generally, experimental data in the oxidative stability of XPE below melting point are very scarce, obviously because very long exposure times, typically more than one year, are needed. One disposes however of few results obtained on a radiation cured XPE stabilized by classical phenol–phosphite combination [11, 12], according which the time to embrittlement could obey Arrhenius law:

$$t_E = t_{EO} \exp(H_E/RT) \qquad (4)$$

With $\ln t_E = -24.45$ and $H_E = 116\ \mathrm{kJ \cdot mol^{-1}}$.

Lifetimes t_E have been calculated at the temperatures under consideration, and the corresponding points plotted in Fig. 2. Assuming that the XPE sample studied by Langlois *et al.* [9] is more or less representative of the average stability of cross-linked polyethylene, one could interpret the results as follows:

(i) In the whole stress and temperature range under study, the sample lifetime was always shorter than the time for oxidative embrittlement t_E: The materials perished always by a physical mechanism.

(ii) On a given straight-line $\sigma = a \log t + b$, for a given temperature, the point of abscissa t_E corresponds to a stress σ_E such as:

- If $\sigma > \sigma_E$, then, the equation $\sigma = a. \log t + b$ can be used to predict the time failure. This latter occurs by a physical mechanism:
- If $\sigma \leq \sigma_E$ than the time to failure is $t_F = t_E$ whatever the stress value, as a result of oxidation induced embrittlement. Thus the curves $\sigma = f$[log (time to rupture)] are expected to display a slope change at $t_F = t_E$, the slope of the brittle part being almost vertical.

The envelope of points E (σ_E, t_E) constitutes thus the ultimate boundary beyond which the equation $\sigma = a \log t + b$ may no longer be extrapolated and the material is no longer usable whatever the applied stress.

(iii) If t_L is the expected service life, for instance $t_L = 50$ years $= 10^{5.64}$ hours in France, then one can define a ceiling temperature T_L such as $t_L = t_E$ (Here, $T_L \sim 80°\mathrm{C}$ as shown in Fig. 2). It can be easily seen that:

- If $T > T_L$, then the time to embrittlement will always be shorter than the expected service life.
- If $T < T_L$, than the time to embrittlement will be longer than the expected service life, provided that $\sigma \leq \sigma_E$.

Is the chosen thermal oxidation example really representative of the whole XPE family ? It appears a priori difficult to answer this question, however it is noteworthy that:

(i) No one of the 15 studied samples displayed a slope change of $(\sigma - \log t)$ curves in the temperature interval under study but at high temperature, the longer exposure times were not very far from the oxidation embrittlement time t_E (Fig. 2).

(ii) It seems thus that, generally, the oxidation embrittlement time is equal to or longer than the values found by Langlois *et al.* [9]. These latter can be thus used as in the above reasoning with an unknown security margin.

The use of Arrhenius law to extrapolate t_E values at low temperatures can be considered very speculative: there are many incertitudes concerning the rate determining process (propagation of the oxidation radical chain? stabilizer loss by evaporation or leaching? etc...). The research field remains largely open in this domain.

It is interesting to remark that both a and b parameters of the $(\sigma - \log t)$ relationship vary monotonically with temperature and tend towards zero when T tends towards the melting point $T_M = 137°\mathrm{C}$ (Table II, Figs 3 and 4). This dependence could be represented by:

$$a = (1.27 \pm 0.1) \times 10^{-3}(T_M - T)^{1.4}$$

And

$$b = (0.123 \pm 0.01)(T_M - T)$$

So that the (σ, T, t) relationships could be expressed by a single equation:

$$\sigma = -1.27 \times 10^{-3}(T_M - T)^{1.4} \log t + 0.123(T_M - T)$$
$$(t \text{ in hours}, \sigma \text{ in MPa})$$

This expression could be simplified using linear functions for a:

$$a \approx (0.006 \pm 0.001)(T_M - T) \qquad \text{for } T \leq 80°\mathrm{C}$$
$$a \approx (0.004 \pm 0.0006)(T_M - T) \qquad \text{for } T > 80°\mathrm{C}$$

The above equation would then become:

$$\sigma = \alpha(T_M - T)[\beta - \log t] \qquad (t \text{ in hours}, \sigma \text{in MPa})$$

with

$$\alpha = 6 \times 10^{-3} \text{ and } \beta = 20 \text{ at } T \leq 80°\mathrm{C}$$

and

$$\alpha = 4 \times 10^{-3} \text{ and } \beta = 30 \text{ at } T > 80°\mathrm{C}$$

5. Conclusion

The time to failure of various (16) XPE pipes has been determined for hoop stress values ranging from 2 to 18 MPa, in the 20–120°C temperature domain. The behavior of XPE was compared to the one of uncross-linked PE (6 samples of distinct origins). It appeared that, in the exposure conditions under consideration, XPE doesn't display the ductile-brittle transition observed in PE.

XPE and PE behave quite similarly on this side of this transition, i.e., in the ductile regime where the stress-temperature-time of failure relationships can be resumed by the following equation:

$$\sigma = \alpha(T_M - T)[\beta - \log t]$$

with

$$\alpha = 6 \times 10^{-3} \text{ and } \beta = 20 \text{ at } T \leq 80°\mathrm{C}$$

and

$$\alpha = 4 \times 10^{-3} \text{ and } \beta = 30 \text{ at } T > 80^{\circ}\text{C}$$

In the case of PE, the ductile—brittle transition coordinates are given by the following equation (in the t, T plane):

$$T_{\mathrm{C}} = t_{\mathrm{C}0} \exp(Q/RT)$$

with ln t_{C} (hours) $= -24.2$ and $Q = 81.6\ \mathrm{kJ \cdot mol^{-1}}$.

XPE can be used beyond this boundary, its working domain is only limited by oxidation, the coordinates of the corresponding boundary, tentatively determined from previously obtained results on a radiation cured PE, could be estimated using:

$$t_{\mathrm{E}} = t_{\mathrm{EO}} \exp(H_{\mathrm{E}}/RT)$$

with ln t_{EO} (hours) $= -26.45$ and $H_{\mathrm{E}} = 116\ \mathrm{kJ \cdot mol^{-1}}$

In fact, in the domain investigated here, (maximum lifetimes ranging typically from 10^3 hours (120°C) to 10^5 hours (20°C), the pipes failed always by a physical/mechanical mechanism obeying to the above kinetic equation.

It can be concluded that XPE performs generally better than PE in the domain comprised between the boundaries t_{C} and t_{E}. Lifetimes larger than 50 years can be reasonably expected for temperatures up to 80°C.

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