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THERMOANALYTICAL STUDY OF AN AGED XLPE-PIPE

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SUMMARY

A high quality pipe made of XLPE (Engel method) for industrial applications was used for the study of the material deterioration process upon accelerated aging. A sample aged at 110°C while submitted to an hydrostatic pressure of 0.53 MPa, giving a hoop stress of 2.66 MPa, was studied by means of Thermal Analysis, Density, and Gel Content measurements. The effects of aging are compared to a reference unexposed sample and the experimental results are discussed in terms of annealing effects, free volume and structural relaxation processes.

INTRODUCTION

High quality crosslinked polyethylene (XLPE) for industrial applications are materials that, despite of advanced techniques and rigorous process control during manufacturing, present some structural inhomogenties. In the production process, the high density polyethylene raw material (Lupolen 5261-Z) is treated with a peroxide (Engel method). Peroxide homolytic dissociation throughout alkoxy radicals, reacts, in the polymeric environment, forming polymeric macroradicals which carries an unpaired electron on an inner member of the chain. These macroradicals in turn crosslink throughout the building of tetrafunctional bridges in a recombination reaction (ref. 1). This seemingly straightforward chemical reaction is obviously very sensitive to the thermodynamic conditions during the manufacturing process. Besides, the mixing of the raw materials and the pipe forming conditions as well as additives present in the system, will also affect the final material quality and homogeneity. Thus, processing conditions affect the basic assumption that there is a perfect random distribution of intermolecular crosslinks homogeneously distributed throughout the material (ref. 2).

During the manufacturing process, the XLPE-pipe is formed and then rapidly cooled from the melt with water. This thermal quench results in not only a different chemical activity throughout the pipe wall, but also results in structural changes at the molecular level. From the structural point of view, molecules rearrange themselves in randomly oriented stacks of parallel lamellae with no or low macroscopic orientation which can be regarded as incipient spherulitic embrios. The stacking of several lamellae, parallely

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ordered, produces local orientations that are normally regarded as a paracrystalline microstructure (ref. 3). This process evolves from the melt, and therefore it can be affected by the rapid cooling at the external surface of the pipe, leading, for example, to a higher degree of amorphicity.

Additionally the chemically activated crosslinking of the peroxide treated raw HDPE (density of about 0.95 gcm^{-3}) leads to a reduction of density as the crosslinking evolves. This in turn obstructs the development of further crystallization of the resulting XLPE. The processing conditions of the HDPE raw material, and the cooling rate after the pipe forming process, are such that they can result in an inhomogeneous crosslinking, crystallinity, density, etc. This should be reflected in local fluctuations of material properties in the XLPE-pipes. These kinds of inhomogeneities should, in turn, affect the aging behaviour of the material.

The aim of the present research was to study the distribution of some experimental parameters throughout the pipe wall, in a comparative study in order to gain insight into the understanding of aging processes of XLPE.

EXPERIMENTAL

High quality XLPE-pipe with an overall diameter of 110 mm and a nominal thickness of 10.0 mm, were aged in an oven with circulating air at $110 \pm 2^{o}C$. The pipes were submitted to 0.53 MPa hydrostatic pressure giving a hoop stress of 2.66 MPa. A sample that failed after 17.136 hours was chosen for the purpose of the present comparative study with respect to a reference, unexposed pipe.

The aged sample shows a rupture with a multiple brittle microfracture that was initiated at the internal wall side. That type of failure has been proven to be typical of final chemical deterioration of aged polymers. This typical rupture mechanism has been classified as Stage III in the experimental study of long term testin of plastic pipes for industrial use (ref. 4).

The present study comprises of Thermal Analysis, Density, and Gel Content (crossliking degree) measurements throughout the pipe wall. The measurements were done on a number of samples that was considered enough to have a representative distribution of the measured paremeters throughout the pipe wall.

THERMAL ANALYSIS

A Mettler thermoanalytical instrument with a cryogenic DSC measurement cell was used to study the glass transition temperature of samples selected from both reference and aged XLPE-pipes. The glass transition temperature of XLPE in the present work, is the temperature at the enthalpic change that can be determined in XLPE at about 153 K (usually refere as $-120^{o}C$ transition).

Samples were cut from the inside, the middle and the outside of the pipe wall in the form of a disk with a diameter of about 5 mm and a thickness of 0.5 mm. DSC analysis was also performed on the same set of samples from room temperature up to 523 K. The DSC results, the change in the specific heat at T_g, and the glass transition temperature, are given in Table 1.

The measurements at the glass transition were performed by first cooling the sample to liquid nitrogen temperature (77 K), and then heating them at rate of 10.0 K/min, up to the room temperature. The entalpic changes in the thermogram at the glass transition temperature were registered and, based on the shift in the base line, the change in the heat capacity and the transition temperature were calculated.

The T_g results for the aged sample can be discussed in terms of the well known relationship (ref. 5).

$$T_g = T_{gm} - K/M_m \tag{1}$$

In eqn. (1), K is a constant, M_m is the average value for the molecular weight, and T_{gm} is the limiting T_g at high molecular weight. Although an average molecular weight for XLPE, and consequently T_{gm}, can not be unambiguosly deffined, eqn. (1) would be used in the present case as a rather empiric relation. The M_m value may be considered as representative of the polymer molar mass. Defining $T_{ge} = T_{gm} - T_g$, it can be demonstrated that the ratio of the T_{ge} for the aged sample to the unexposed sample is inversely proportional to the respective molar masses, providing that the constant K is unaffected upon aging.

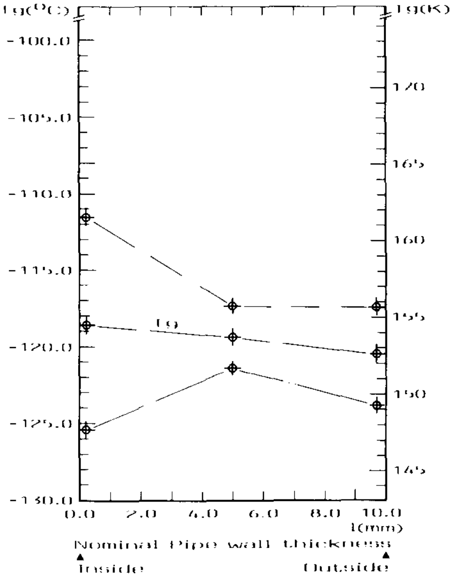
$$T_{ge}(\text{aged})/T_{ge}(\text{ref.}) = M_m(\text{ref})/M_m(\text{aged}) \tag{2}$$

With this relationship, the relative change in the molar mass upon aging can be estimated. The calculation indicates that at the inside of the aged pipe, the M_m is reduced to 97.7% of the original value, while at the middle the reduction is only to 99.4%.

The glass transition at the outside of the aged pipe was not found on the first scan, however, a second scan showed a transition that could be evaluated. This experimental result is affected by the thermal cycling, and thus cannot be used in the same manner for the discussion. Nevertheless, since the thermal cycling is known to introduce a shift in Tg towards higher values, this result can still be used in eqn. (2) to calculate a ratio that provide with an indication of a molar mass change. The calculated ratio for the outside of the pipe shows, indeed, a rather high value for the molar mass reduction, a reduction to 93.7% of the original value, while a reasonable value should be around 99%.

On the other side, the expected molecular reacommodation of the amorphous part of XLPE on aging, can also be a reason for the observed change in T_g

(ref. 6). This entanglement will result in a free volume reduction and therefore in T_g changes. In addition, changes in the degree of crystallinity should also affect the values of T_g throughout the pipe wall. Consequently, the calculated relative changes in the molar mass may be overestimated.



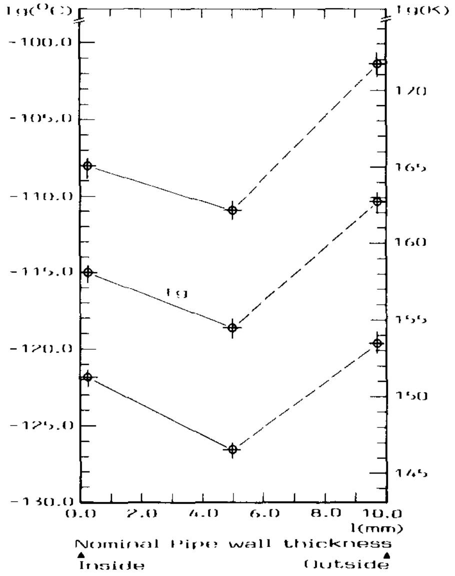


Fig. 1. (left) The glass transition temperature at the inside, the middle, and the outside of the pipe for the unexposed reference sample. The results above and below the T_g values represent the temperature width of the transition.
Fig. 2. (right)^{g}The glass transition temperature at the inside , the middle and the outside of the aged sample after 17.136 hours at 110°C and a hoop stress of 2.66 MPa. The T_g at the outside of the pipe were obtained at the second scan and therefore this^{g}result is affected by thermal relaxation.

DSC results, at the same sample positions, are presented in Table 1. DSC scans were obtained with the same equipment at a heating rate of 10.0 K/min, and evaluated by the computerized unit. It can be noted that the temperature for the onset of exothermal entalpic change at oxidation, T_{ox}, shows a homogeneous distribution throughout the unexposed pipe wall, while the aged sample shows a drastic drop of T_{ox} at both the outside and the inside pipe wall sides. The endothermal melting phase transition, T_m, is also homogeneous throughout the reference material, while in aged samples it shows higher values at both sides of the pipe wall. The relative change in (gravimetric) crystallinity is similarly distributed for both reference and aged samples, however, the aged sample shows an increase in the relative percent change by about 23%. The increase of crystallinity experienced by the aged samples, may also cause an increase in T_g (ref. 7). These results are consistent since they correlate well with the deterioration shown by the aged pipe, at both the internal and external surface. It is evident that several competing effects are taking place during aging. The possibility of uncoupling these effects for a better understanding of the aging process (ref. 8), is far beyond the scope of the present work.

TABLE 1

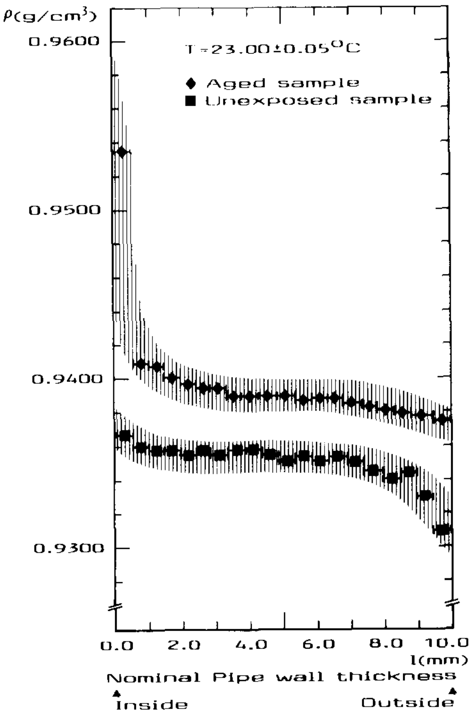
Summary of thermoanalytical results for both the reference material and the aged sample. Results at the internal surface, in the middle, and at the external side of the pipe wall are presented.

Parameter	Position	Reference sample	Aged sample
Temperature for the Onset of Oxidation			
T_{ox}	Inside	217.8 °C	183.0 °C
	Middle	224.4 °C	218.0 °C
	Outside	223.0 °C	198.5 °C
Melting Temperature			
T_m	Inside	129.8 °C	135.8 °C
	Middle	130.2 °C	131.2 °C
	Outside	130.0 °C	133.8 °C
Relative Cristallynity			
κ	Inside	49.5 %	59.8 %
	Middle	48.8 %	59.8 %
	Outside	47.0 %	59.5 %
Glass Transition Temperature			
T_g	Inside	- 118.6 °C	- 115.0 °C
	Middle	- 119.5 °C	- 118.6 °C
	Outside	- 120.6 °C	(- 110.4 °C)*
Change in the Specific Heat			
Δc_p	Inside	0.175 J/gK	0.196 J/gK
	Middle	0.127 J/gK	0.149 J/gK
	Outside	0.064 J/gK	(0.266 J/gK)*

* These values were obtained at a second run, therefore they are affected by thermal relaxation.

DENSITY MEASUREMENTS

The density, of the samples was determined at a temperature of 23.00 ± 0.05°C by the column gradient density method (ASTM D1505-85 or British Standard B.S. 2782-70, Method 509B, and B.S. 3715-64). The column, a Davenport Ltd. (London) instrument, using a mixture of ethanol and distilled water, was calibrated for the density range 0.92 to 0.98 gcm^{-3}. Due to careful degassing of the mixture and the long term stability of the final sample positioning in the column, the density measurements are believed to accurate to ± 0.00005 gcm^{-3}. The samples were cut in form of disks with an average weight of 8.4 mg and 7.9 mg for the reference and aged samples respectively. The disks were obtained from cylindrical samples cut through the pipe wall. The samples were about 0.5 mm thick, giving thus a good representation of the density distribution throughout the pipe wall thickness (10.0 mm nominal thickness). The experimental results shows good reproducibility upon verification.



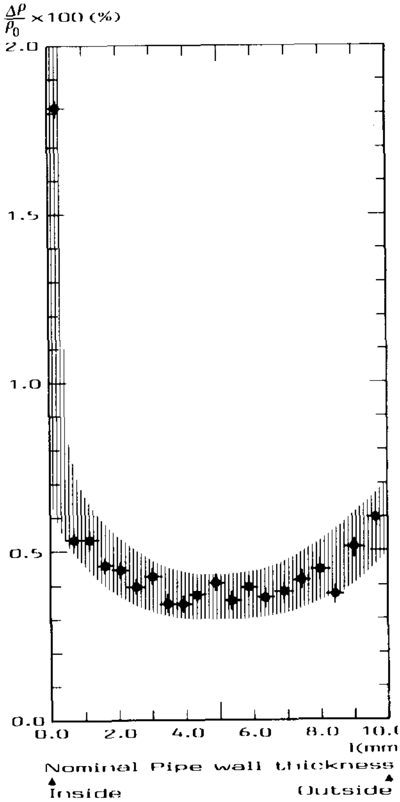


Fig. 3. (left) Density distribution throughout the pipe wall for both the reference and the aged sample. The results were obtained by the density gradien column method at 23.00±0.05°C. Fig. 4. (right) Differential reduced density change in percentage, throughout the pipe wall thickness.

The results of density measurements are shown in Fig. 3, and were obtained for one set of samples for each material category. Fig. 4 shows the reduced differential change in the density upon ageing. This change is a measurement of the degree of compactation of the material due to the long term exposure of the pipe to a high hydrostatic pressure under isothermal aging.

The reference unexposed material shows two major interesting features. First, the density values show a somewhat higher spread compare to the aged sample. Secondly, the density values show a profile with lower densities toward the outside of the pipe. This scattered density distribution throughout the reference material is believed to be related to an inhomogeneous formation of the PEX material during the processing of the pipe.

The aged sample shows a lower spread of density values throughout the pipe wall and also a much lower density difference between the outside of the pipe and the bulk of the material. However, towards the inside of the pipe, there appears a large increase in density. In addition, the total density distribution has been shifted towards higher values upon aging.

The shift of the density of the aged sample towards higher values can be discussed in terms of the relative density change, Fig. 2. Voids and intermolecular cavities, that result during manufacturing, can be described by the free-volume fraction $f = (V-V(T,t))/V$, where V is the specific volume, and $V(T,t)$ is a function of temperature and time. Molecular mobility, free-volume fraction and thermal activation are related. The relationship is known as the Doolittle approximation, and is given in the following equation (ref. 9).

$$\ln M = A - B/f \qquad (3)$$

This expression shows that the molecular mobility M clearly decreases with the increasing degree of packing, or the reduction of the free-volume f. In eqn. (3) A and B are constants. The free-volume fraction f is related to the glass transition temperature, T_g, through the following relationship (ref. 9).

$$f(T) = f_g + \Delta\alpha(T - T_g) \qquad (4)$$

Where f_g denotes the free-volume fraction at T_g, and $\Delta\alpha$ the difference between the (cubical) thermal expansivities above and below T_g.

Using eqn. (4), a first estimation of the relative change in the free volume at the internal pipe wall side, gives a result of 2.5%, base on the assumption that the thermal expansivities do not change significantly upon aging. The same calculation for the T_g values at the middle of the pipe gives a relative change of 0.6%. These results, compared to the relative density change (Fig. 4) are consistent, although somewhat high. This can be due to the raise in the degree of cristallynity. The assumption of a unaffected thermal expansivity of XLPE with aging call for further investigations.

The relative density change after 17.136 hours aging at 110^{0}C, as illustrated in Fig. 4, shows a densification of about 0.4% on average for the bulk. Towards the outside of the pipe, values of about 0.6% for the relative densification are most likely due to the high values for the initial free volume fraction of the material due to the rapid cooling after the pipe forming equipment. The value of the relative density change at the internal pipe wall side, about 1.8%, is not only due to the free volume fraction changes, but also to structural changes. Electron microscopy studies, (ref. 10), reveal the onset of a thin layer of degraded, oxidized polymer as a common feature of aged polymer pipes. The texture of this layer, at fracture surface, shows little or any fibril structure, indicating a different molecular configuration. A high density, close packed structure is develop, where oxidized molecules and segmentation process onsets upon ageing, with a resulting weakness that allows for microcracks and failure initiation.

GEL CONTENT

The Gel Content of the samples, an indirect measurement of the degree of crosslinking, was determined by the ASTM D2765-68 standard method. The method used decahydronaphthalyn (Dekalin) as the solvent with 1% addition of (2.2-Methylen-bis-(4-methyl-6-tert-buthylphenol)), an antioxidant.

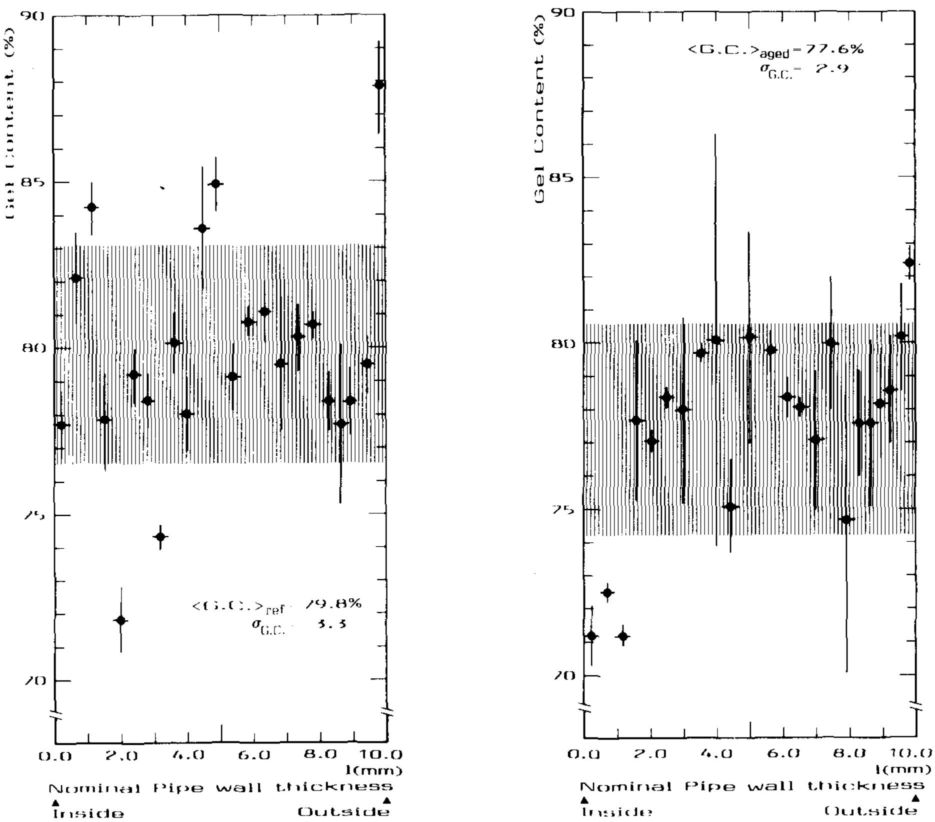


Fig. 5. (left) Gel Content of the unexposed reference XLPE material obtained by the method described in ASTM D2765-68. The shaded area indicates the variance around the mean value. Fig. 6. (right) Gel Content of the aged sample of XLPE, after 17 136 h, exposed to an hydrostatic pressure resulting in a hoop stress of 2.62 MPa, and a temperature of 110°C.

Samples were selected throughout the pipe wall in order to obtain a representative distribution of the gel content. Two sets of measurements were performed and the average value are presented in Fig. 5 for the unexposed reference sample, and in Fig 6 for the aged sample.

The reference XLPE material shows an average gel Content of 79.8% with a standard deviation of 3.3. The average value for the Gel Content of the aged sample was 77.6%, and the standard deviation 2.9. The relevant result from this study is that the crosslinking degree of the aged sample shows a relative percent reduction of 2.8%, and a relative homogenization in the ditribution of measured values throughout the pipe wall after aging (about 18.2% better).

It is worth noticing that the aged sample shows lower Gel Content values at the internal pipe wall side, with respect to the resulting average value for the total cross section of the reference sample (about 10.8% compared to a total reduction of only 2.8% in the average). This is an indication that a molar mass reduction of the XLPE due to chain scissions, will result in a reduced thermal stability and mechanical strength of the material, (ref. 11), and consequently of the long term with standability at technical applications, (ref. 4). This result is in agreement with the absence of fibril structure at the internal surface layer, as demonstrated in SEM studies of the rupture surface of several XLPE qualities at various degrees of ageing (ref. 10).

Obviously, the changes upon aging in the gel constent, and consequently in the degree of crosslinking, can be discusen in terms of the glass temperature changes. However, exhaustive termoanalytical studies are in progress in order to have a more detailed experimental support.

DISCUSSION

Thermal Analysis results show that in general, it seems to be more than a single kinetic deterioration process during the long term aging test of XLPE pipes. The density increase shown by the sample upon aging can apparently be increased by two different routes. Either by means of an increase of crystallinity at a slow crystallization rate during the initial physical aging or, by a free volume relaxation leading to a partially compressed amorphous phase. In both cases the density will increase (and consequenlty the elastic modulus and the microhardness, (ref. 12).

The Gel Content reduction as a consequence of aging is assumed to be due to a slow chain scission process. Although a higher degree of changes were expected in boths the inside and outside of the pipe wall, it should be remembered that the method itself is not accurate enough for a more quantitative analysis.

It seems to be possible to argue in favour of multiple cooperative deterioration processes at different chemical kinetics, where the posibility of uncoupling the various mechanism would demand long and careful studies at several acceleration ageing rates.

The present study shows the relationship between the thermoanalytical parameters, density and Gel Content, as usefull parameters in the qualitative description of the effect of aging upon XLPE. Attempts at quantitative evaluation, made clear the need for further insigth on the consequences of deterioration processes at molecular level, so that correlations between different parameters may be calculated.

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REFERENCES

1 R. Rado, Int. Pol. Sc & Tech., 3(8) (1976) T/107.
2 A. Charlesby, J. Polym. Sci, 11 (1953) 513.
3 J. Martinez Salazar and F.J. Balta Calleja, J. Cryst. Growth, 48 (1980) 283.
4 M. Ifwarson and P. Eriksson, Kunststoffe, 76(3) (1986) 245.
5 T.G. Fox and P.J. Flory, J. Appl. Phys., 21(1985) 581.
6 E.A. Turi, Thermal Characterization of polymeric Materials, Academic Press, New York, 1981, pp. 248-251.
7 E.A. Turi, Ibid, pp. 254-255.
8 E.A. Turi, Ibid, pp. 290-291.
9 L.C.E. Struik, Physical Aging in Amorphous Polymers and Other Materials, Elsevier, Amsterdam, 1978.
10 F.J. Balta Calleja, J. Martinez Salazar, H. Cackovic and J. Loboda-Cackovic, J. Mater. Sci., 16(1981) 739.
11 T.G. Fox and S. Loshaek, J. Polymer Sci, 15(1955) 371.
12 P. Eriksson and M. Ifwarson, Kunststoffe, 76(6) (1986) 512.
13 Ch. Hall, Polymer Materials, Macmillan Press Ltd, London, 1981, pp. 128-131.
14 F.J. Balta-Calleja, D.R. Rueda, J. Garcia-Pena, F.P. Wolf and V.H. Karl, J Mat. Sci, 21(1986) 1139.