Macromol. Symp. **2004**, *217*, 307-316

Thermo-Oxidative Degradation during Creep Crack Growth of PE-HD Grades as Assessed by FT-IR Spectroscopy

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Summary: Creep crack growth experiments under static loads were done with two polyethylene high density (PE-HD) types stabilised in two different ways. The degree of oxidation at the cracks was estimated by CO-numbers measured with FT-IR spectroscopy. The CO-number is the ratio of the peak of oxidation products at approx. 1720 cm^{-1} to an inherent PE-HD-peak at 2020 cm^{-1} and represents a direct measure for oxidative damage. Higher CO-numbers could be measured near the crack surfaces. However, this phenomenon could only be found in the low crack growth rate regime, where sufficient time is available for oxidation processes to take place. Moreover, local ageing decreases very quickly in some distance away from the crack path. A direct influence of different stabiliser systems on the degree of these local ageing processes could not be found.

Keywords: ageing; creep crack growth; FT-IR; poly(ethylene) (PE)

Introduction

It is generally accepted that the rate of chemical reactions in solid polymers may change significantly under the influence of external or internal stresses.[1] On the one hand, this may be due to substantial changes in the structural and physical parameters of a polymer under the action of mechanical stresses (molecular conformation, free volume increase, changes in the permeability of low-molecular mass substances, etc.). On the other hand, stress may directly affect the reactivity of deformed macromolecules, thereby altering the effective activation energies for chemical reactions.

The accelerating effects of mechanical stresses on oxidative ageing processes were first observed with rubber [2] and designated by the authors as mechanical-chemical ageing. Popov and co-workers[1] and Terselius and co-workers[3] reported effects of stresses on chemical ageing also for

DOI: 10.1002/masy.200451327

other polymers, primarily for poly(ethylene) (PE) and poly(propylene) (PP).

A modification of activation energies of chemical reactions by stresses was proposed in a quantitative form originally by Zhurkov[4] and Bueche[5]. For a stressed polymer, the time to failure is given by an Arrhenius-type expression as:

$$\tau = A \cdot \exp\left(\frac{\Delta G - B \cdot \sigma}{R \cdot T}\right) \qquad (1)$$

where ΔG is the energy barrier (activation energy), σ is the applied stress, R is the gas constant, T the absolute temperature and A and B (frequently referred to as activation volume) are constants.

Systematic investigations of the effect of stresses on the thermo-oxidative ageing behaviour of polymers were performed so far mainly in long-term tests on pipes, which were internally pressurised at temperatures from 60 to 120 °C covering a time period of up to 20 years[6, 7]. These tests were performed mainly with polyolefins and focused on the characterisation of “global” ageing phenomena. Nevertheless, it was recognised by at least some authors that oxidation often originates locally at highly degraded “oxidation spots“ (i.e., heterogeneous initiation of oxidation).[8-10]

Hence, although molecular and morphological variations caused by ageing processes are accepted as important mechanisms which may affect long-term failure of polymers, very few investigations so far have addressed the potential for enhanced local crack tip ageing.[10-13] The hypothesis of local crack tip ageing caused by the simultaneous influence of high stresses, time and thermo-oxidative environments in the immediate crack tip region (see Fig.1) has been proposed by the authors before.[10-12] They could show that the use of different stabilisers influences creep crack growth (CCG) rates in polymers. Stabilisers delay the auto-oxidation and degradation of a polymer. Hence, they should also be effective near the tip of a growing crack and thus influence the development of local ageing processes and CCG rates corresponding to their individual performance.

In this work the above mentioned hypothesis on local crack tip ageing should be verified by characterising the state of the oxidation at cracks. FT-IR spectroscopy was used to identify carbonyl groups, which may be formed during very localised ageing processes in the immediate environment of slowly growing cracks in different grades of PE-HD and differently stabilised PE-HD types under static loads.

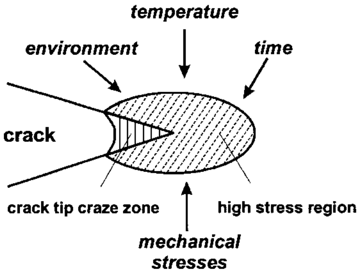


Figure 1. Schematic illustration of the crack tip region in PE-HD along with parameters controlling local crack tip ageing.

Experimental

Materials

All investigations in this study were performed with the base polymers (i.e. before compounding and thus without standard additives) of two commercial grade PE-HD compounds (Borealis AG, Linz, A; designated as PE-HD 1 and PE-HD 2). Some characteristic material properties are summarised in Table 1.

With these base polymers two formulations containing different stabiliser systems and stabiliser concentrations were produced. To formulation S 0.1 % of a sulphur containing secondary antioxidant (Santonox R; Monsanto, B) was added. The formulation K2 contained 0.2 % of a mixture of a primary and secondary antioxidant (Irganox B 225, Ciba Specialty Chemicals, Basle, CH). All material formulations were compression moulded into plaques with a nominal thickness of 12 mm.

Table 1. Characteristic properties of the PE-HD base polymers (ρ: density, M_W: weight average molecular mass, E: youngs's modulus, σ_y: yield strength).

Material	ρ (ISO 1183)	M_w	$E^{*)}$ (ISO 527)	$\sigma_y{}^{*)}$ (ISO 527)
	g/cm^3	kg/mol	N/mm^2	N/mm^2
PE-HD 1	0.964	80	1600	32
PE-HD 2	0.959	320	1450	31

$^{*)}$ 23 °C, 50 % r. H.

Test Methods

Creep crack growth tests

The crack growth experiments under static loads were performed at 80 °C with specimens of the compact-type (CT) in distilled water (dissolved oxygen content at 80 °C: $1{,}5 \cdot 10^{-3}$ g/100g) in a test apparatus designed and constructed at the Institute of Materials Science and Testing of Plastics (University of Leoben, Austria).[10] A schematic drawing of the test set-up is shown in Figure 2. The specimens were loaded with dead weights, and values of the crack length were measured with a travelling microscope at a magnification of 30X as a function of time at the specimen's lateral surface.

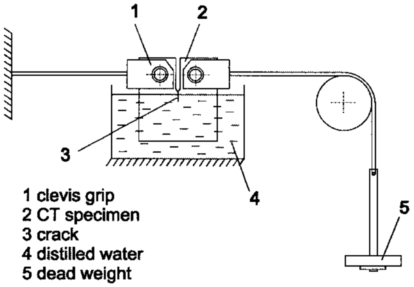


Figure 2. Schematic drawing of the test apparatus for crack growth under static loads.

According to linear elastic fracture mechanics (LEFM) principles, the growth rates of the cracks under static loads are governed by the applied stress intensity factor K_I (index I stands for opening mode or pure tensile loading conditions), which describes the local crack tip stress and strain field. Using this concept, CCG rates were then plotted as function of K_I, that was calculated according to the following expression [14]:

$$K_I = \frac{F}{B \cdot \sqrt{W}} \cdot f\left(\frac{a}{W}\right) \tag{2}$$

where F is the applied load, B the specimen thickness, W the specimen width and a the crack length; f(a/W) is a non-dimensional correction function that accounts for the specimen configuration, geometry and the loading conditions.

The crack growth rates da/dt were calculated by a method analogous to that proposed in ASTM E647-93 for the determination of fatigue crack growth. Further details as to the test apparatus and the test and data reduction procedure are described elsewhere.[15]

Infrared spectroscopy

To identify the existence of carbonyl groups which may be formed during oxidation, a FT-IR microscope (Perkin Elmer Spectrum One combined with an AutoImage FTIR microscope, Überlingen, D) was used. Thin films (thickness approx. 150 µm) were cut from the specimens normal to the crack opening with a microtome cutter. These films were placed in the microscope and the spectra were collected in transmission at 16 scans per point and a resolution of 1 cm^{-1}. The individual carbonyl groups formed during oxidation were identified by their specific absorption bands in the spectrum (acid groups at 1705 cm^{-1}, ketone groups at 1715 cm^{-1}, aldehyde and ester groups in the region of 1735 to 1740 cm^{-1}).

Line-scans were carried out leading from the crack surface into the bulk of the specimens with a regular distance of 10 µm between the scanning points (see Fig.3.). As an aperture a rectangle with a dimension of 10x200 $µm^2$ was used, the long side normal to the line-scan direction. For the map scans an aperture size of 20 x 20 $µm^2$ was used. The distance of the grid points was 10 µm in direction of the x- as well as the y-axes.

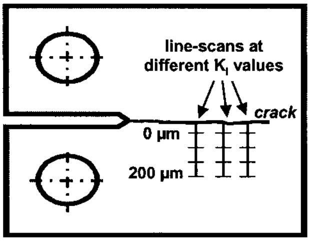


Figure 3. Schematic illustration illustrating the way the FT-IR line-scans were taken in the measurements.

According to DIN 53383, the degree of oxidative degradation can be evaluated with the help of the CO-number. The CO-number is the ratio of the absorbance band at 1718 cm^{-1} (carbonyl group absorbance) to the inherent absorbance band of PE-HD at 2020 cm^{-1} (C-H bond absorbance). In this work the sum of the carbonyl peak areas of the acid, ketone, aldehyde and ester groups instead of the height of the absorbance band at 1718 cm^{-1} was used to calculate the CO-number.

Results

In Fig. 4 the distribution of the CO-numbers (map-scan) along the path of a crack in PE-HD 1/K2 is shown. It is obvious that only in the immediate environment of the crack the CO numbers and the extent of ageing resp. are enhanced. In the bulk material, away from the crack, no signs of global ageing are visible. Therefore the degree of oxidation at the cracks was investigated more precisely with the help of line-scans. In Fig. 5a and 6a the CCG behaviour of the two investigated PE-HD types both equipped with stabiliser formulation K2 is shown. In Fig. 5b and 6b the corresponding CO-numbers as a function of distance from the crack surface at places of different K_I values and different CCG rates resp. are presented in comparison to measurements on the specimen's lateral surfaces as reference. With both materials it could be shown that the CO-numbers and the extent of ageing resp. are enhanced near the crack surface, but only about 50 µm deep in the bulk of the material no differences in the CO-numbers to the reference lateral surface could be detected. A very interesting aspect is, that the highest CO-numbers could be found at places at the crack surface that correspond to low K_I values and low CCG rates resp.. As the time scale for local ageing is reduced at high crack speeds, the CO-numbers decrease till they are in the range of the reference spot at the specimen's lateral surface.

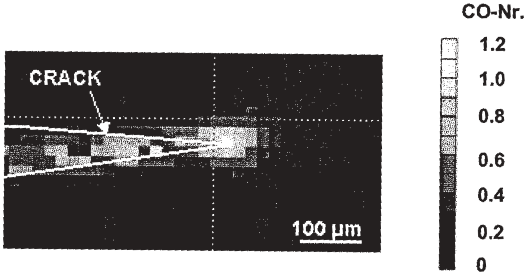
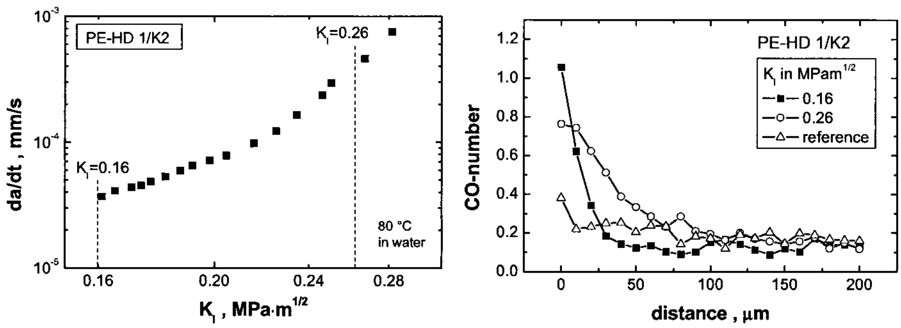
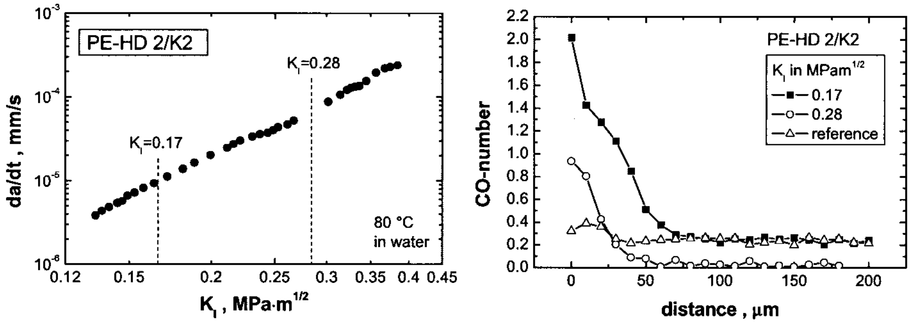


Figure 4. Distribution of CO-numbers in the immediate environment of a crack in PE-HD 1/K2.



(a) (b)

Figure 5. (a) Creep crack growth behaviour of PE-HD 1/K2 at 80 °C in water; (b) CO-numbers as a function of distance from the crack surface at different K_I values in PE-HD 1/K2 in comparison to the specimen's lateral surface as reference.



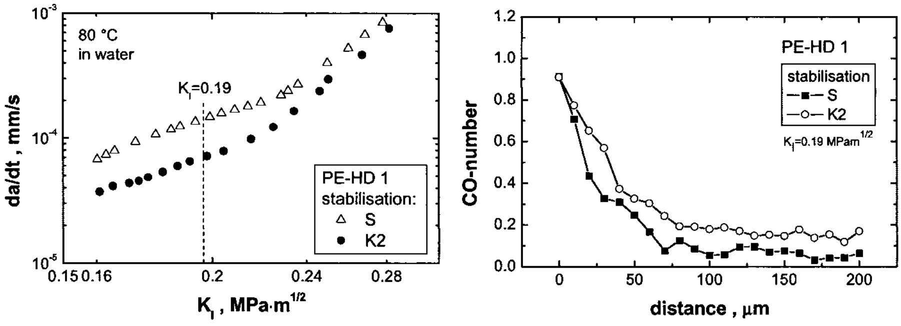
(a) (b)

Figure 6. (a) Creep crack growth behaviour of PE-HD 2/K2 at 80 °C in water; (b) CO-numbers as a function of distance from the crack surface at different K_I values in PE-HD 2/K2 in comparison to the specimen's lateral surface as reference.

If the CO-numbers of the specimens are compared in Fig. 5 and 6, it could be concluded that local ageing is pronounced in PE-HD 2. In plenty of different measurements, however, it was found that the scatter in the CO-numbers was rather big, so that no differentiation concerning the extent of local ageing between the two materials can be done.

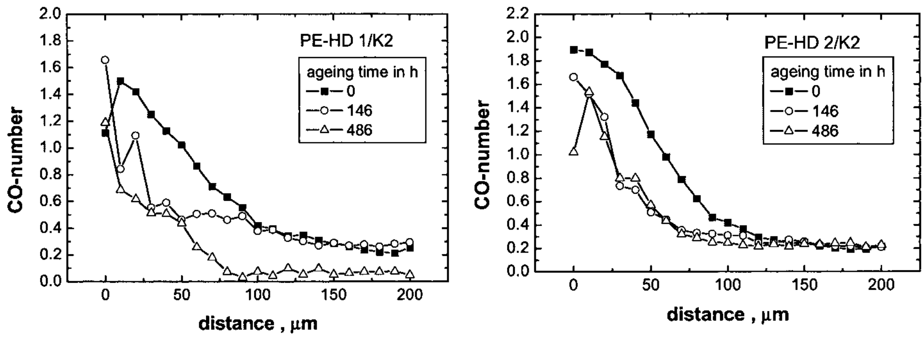
Special attention was given to describe the effects of different stabiliser systems on the CCG behaviour and the extent of local ageing. As the time scale for the CCG experiments with the two investigated materials was not more than 2 weeks any effects regarding the diffusivity of the stabilisers used could be neglected.[16] As demonstrated in Fig. 7a for material PE-HD 1 formulation S resulted in considerably higher crack growth rates than formulation K2 in the low creep crack speed region. Following [11, 12] this phenomenon was explained by the assumption that different stabilisers affect crack tip ageing processes leading to stabiliser dependent CCG rates in a given polymer. At higher crack speeds, where there is not enough time for local crack tip ageing processes, the CCG curves of the two formulations converge. The line-scans at an equal K_I value of 0.19 MPam$^{1/2}$ of the two differently stabilised formulations in Fig. 7b again show enhanced CO-numbers for both formulations at the crack surface. However, the expected differentiation in CO-numbers and in the extent of local ageing resp. could not be found.

In order to prove that oxidative degradation took place at the crack tip during crack growth and not in the run of the tests when the free crack surface was subjected to the environment (distilled water at 80 °C), some cracked test specimens were tempered in water at a temperature of 80 °C for about 500 hours and possible changes in the distribution of the CO-numbers at a fixed position of the cracks were documented. It was found for both materials (see. Fig. 8) that additional ageing did not change the CO-numbers. So it was concluded, that the higher CO-numbers at the cracks are a result of the stress concentration in the immediate vicinity of the crack tip that acts to assist and accelerate the local thermo-oxidative degradation of the materials.



(a) (b)

Figure 7. Influence of stabilisation in PE-HD 1on (a) creep crack growth rates at 80 °C in water and on (b) CO-numbers as a function of distance from the crack surface at K_I= 0.19 MPam$^{1/2}$.



(a) (b)

Figure 8. Influence of ageing time at 80 °C in water on CO-numbers as a function of distance from the crack surface, (a) PE-HD 1; (b) PE-HD 2.

Conclusions

With the help of FT-IR spectroscopy a higher concentration of carbonyl groups and a higher degree of local ageing resp. could be identified along the path of cracks, that grew under static loading conditions in water at 80 °C. Hence, the hypothesis of local crack tip ageing [10, 11, 12] caused by the simultaneous influence of high stresses and thermo-oxidative environments on the immediate vicinity of a crack tip could be strengthened. However, this phenomenon could only be found in the low crack growth rate regime, where there is sufficient time for oxidation processes. Moreover, local ageing decreased very quickly in some distance away from the crack path. A direct influence of different stabiliser systems on the degree of these local ageing processes could not be found.

Acknowledgements

The research work of this paper was performed at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the K_{plus}-program of the Austrian Ministry of Traffic, Innovation and Technology with contributions by the University of Leoben. The PCCL is funded by the Austrian Government and the State Governments of Styria and Upper Austria.

[1] A. Popov, N. Rapoport, G. Zaikov, *"Oxidation of Stressed Polymers"*, Gordon & Breach, New York 1991.
[2] G. Scott, *Polym. Eng. Sci.* **1984**, *24*, 1007.
[3] B. Terselius, U. W. Gedde, J. F. Jansson, in *"Failure of Plastics"*, W. Brostow, R.D. Corneliussen, Eds., SPE Hanser, Munich 1973, p.273ff.
[4] S. N. Zhurkov, V. A. Zakrevskyi, V. E. Korsukov, A. F. Kuksenko, *J. Polym. Sci., A-2 Polym. Phys. Ed.* **1972**, *10*, 1509.
[5] F. Bueche, *J. Appl. Phys.* **1955**, *26*, 1133.
[6] G. Dörner, R. W. Lang, *3R international* **1997**, *11(36)*, 672.
[7] U. W. Gedde, J. Viebke, H. Leijström, M. Ifwarson, *Polym. Eng. Sci.* **1994**, *34(24)*, 1773.
[8] I. D. Skrypnyk, H. D. Hockstra, J. L. Spoormaker, Polym. Degrad. Stab. **1998**, 21.
[9] U. W. Gedde, M. Ifwarson, *Polym. Eng. Sci.* **1990**, *30*, 202.
[10] R. W. Lang, A. Stern, G. Dörner, *Die angew. Makrom. Chemie* **1997**, *247*, 131.
[11] G. Pinter, R.W. Lang, J. Appl. Polym. Sci. **2003**, 90, 3191.
[12] G. Pinter, R. W. Lang, *Plastics, Rubber and Composites* **2001**, *30(2)*, 94.
[13] C. T. Kelly, L. Tong, J. R. White, *J. Mater. Sci.* **1997**, *32*, 851.
[14] A. J. Kinloch, R. J. Young, *"Fracture Behaviour of Polymers"*. Applied Science Publishers Ltd., Barking 1983.
[15] A. Stern, M. Novotny, R. W. Lang, *Polym. Test.* **1998**, *17*, 403.
[16] H. Zweifel, "Stabilization of Polymeric Materials", Springer Verlag Berlin Heidelberg New York 1998.