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Fracture of high-density polyethylene used for bleach bottles

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Abstract

High-density polyethylene (HDPE) can be blow-molded and used for the production of bottles for aggressive products. These products can interact both chemically and physically with the polymer constituting these containers, leading to a decrease in the performance of the material and undermining the structural integrity of the component.

A fracture mechanics approach was adopted to evaluate the Environmental Stress Cracking Resistance (ESCR) of two HDPE commercial grades used for bleach containers; two different solutions, with and without sodium hypochlorite (the main ingredient of commercial bleach solutions), were considered as aggressive environments. Size effects were studied using different test configurations and loading histories in air. The correlation between the stress intensity factor and the initiation time was found. A clear effect of the aggressive solutions on the fracture resistance of the two HDPEs was observed, irrespective of the presence of sodium hypochlorite; the effect therefore has to be ascribed to other bleach components.

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Keywords: Polyethylene; Environmental Stress Cracking; Fracture mechanics; Bleach

1. Introduction

High-density polyethylene (HDPE) is a polymer widely used for packaging applications, such as bottles for household detergents. One of these products is bleach, an alkaline aqueous solution of sodium hypochlorite, which can also contain perfumes and surfactants.

Once filled with the product, these containers are packed on pallets, which in turn are stacked one on top of the other. The containers at the bottom may be subjected to very high mechanical stresses due to the weight of the

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surmounting bottles, even for a long time (i.e. several months); this mainly occurs before the shipment to the distributors, in the manufacturing facility, and before the display of the product on the retailer's shelves. The presence of bleach can cause accelerated craze formation, leading to bottle failures in shorter times and with lower loads than in absence of such an active environment. This phenomenon, known in the scientific literature as Environmental Stress Cracking (ESC), is related to a mainly physical interaction between a given substance and the polymer. The main effect of the fluid is to promote Slow Crack Growth (SCG) by being absorbed at craze, developing in close proximity of an existing defect, reducing the local strength by a plasticization. The diffusion of the active environment results in an easier disentanglement of the molecules making up the craze fibrils. This phenomenon affects craze initiation, its growth and the subsequent crack initiation and propagation leading to the failure of the material.

The ESC phenomenon has been widely studied in the literature. Altstaedt et al. (2004) used a fatigue crack growth approach to analyze the behavior of HIPS in contact with sunflower oil. On HDPE, Kurelec et al. (2005) found a correlation between Environmental Stress Cracking Resistance (ESCR) and strain hardening modulus; Men et al. (2004) and Munaro and Akcelrud (2008) reached good results considering the mobility of the amorphous phase as a main indicator for ESCR; Cazenave et al. (2006) showed that Natural Draw Ratio (NDR) and Stepwise Isothermal Segregation (SIS) could be adopted for predicting ESCR.

Williams and Marshall (1975) obtained good results applying from Linear Elastic Fracture Mechanics (LEFM); this approach, also followed by Moskala (1998), Rink et al. (2003), Andena et al. (2013) and a few others, was adopted also in this work to study ESC of two commercial HDPE grades used for bleach bottles.

The composition of commercial bleach is such that chemical interaction with HDPE (e.g. oxidation) could occur, as reported by Hassinen et al. (2003) and Castillo Montes et al. (2004). However, preliminary tests showed that chemical interaction between HDPE and bleach occurring within six month of exposure to the product has a negligible effect on the material's mechanical properties; therefore, in this work ESC was investigated independently and only the results obtained from fracture tests are reported. Before considering the effect of the environment, the fracture behavior in air of the two HDPEs and relevant size effects were investigated.

2. Experimental

2.1. Materials and sample preparation

Two blow-molding HDPE grades (HDPE-MONO and HDPE-BI), characterized by different molecular weight distribution, were considered.

6 mm and 11 mm thick plates were manufactured via compression molding using the following procedure:

- HDPE pellets were heated at 190°C for 5 minutes
- A pressure of about 20 bar was applied for 5 minutes; temperature was kept constant at 190°C
- A pressure of about 40 bar was applied for 5 minutes; temperature was kept constant at 190°C
- Mold and samples were cooled down to room temperature with a water cooling system

Plates were subsequently thermally treated at 130°C for 40 minutes in order to reduce thermal stresses in the material.

In order to evaluate size effects Single Edge Notched (tested in three point bending configuration, SENB) and Double Cantilever Beam (DCB) specimens were prepared with varying thickness B , ligament length $W-a$ and relative crack depth a/W and tested to evaluate their apparent fracture toughness K_{IC} (in the following the subscript I referring to mode I fracture will be omitted). Specimens were grooved with a V profile on both sides in order to guide crack propagation in the notch plane; specimen dimensions are shown in Fig. 1. Notches were made via automated "chisel-wise" cutting, obtaining a final notch root radius lower than 10 μm . A series of SENB blunt notched samples were also prepared using a circular profile blade with 1 mm radius; these specimens were necessary to detect the initiation point in creep test (see next section). All the test performed for the evaluation of the size effects were performed on an Instron 1185R5800 electro-mechanical dynamometer at a constant displacement rate of 10 mm/min and in standard condition (23°C and 50% RH).

SENB fracture tests were also performed at 60°C at different constant displacement rates and at various constant loads (creep), in three point bending and four point bending configurations respectively. Specimen deflection was measured from the crosshead displacement or (in the case of creep tests) at the loading points, using a linear variable displacement transducer (LVDT).

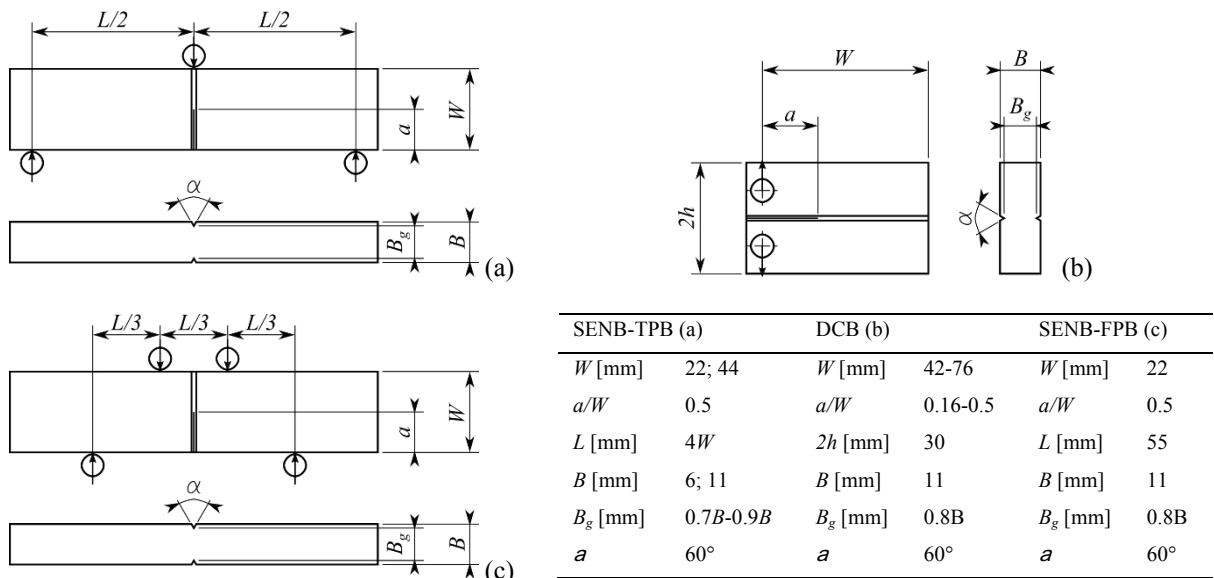


Fig. 1 – Specimen geometries and nominal dimensions. (a) SENB in three point bending configuration tested at constant displacement rate; (b) DCB tested in tension at constant displacement rate; (c) SENB in four point bending configuration tested at constant load (creep). Specimen tested at constant displacement rate were manufactured with varying thickness, ligament length and relative crack depth to study the size effect.

The ESCR of the two HDPEs was also evaluated performing creep tests: in this case, specimens were placed in flexible polyethylene bags filled with two solutions:

- Sol. A: an aqueous solution of sodium hypochlorite, sodium hydroxide, sodium carbonate, surfactants and perfume;
- Sol. B: a solution analogous to Sol.A, in which sodium hypochlorite is replaced with water

Compression molded 1 mm thick plates were also produced (using the same procedure adopted for the thicker ones) and “type 5 dumb-bell specimens” were obtained using a die cutter according to ISO 527-3. Tensile tests were performed at 23°C and at 60°C at a constant displacement rate of 10 mm/min; a conventional value of the yield stress was identified as the maximum of the stress-strain curve. At least three specimens for each condition (material and temperature) were tested.

2.2. Fracture data analysis

For SENB samples tested in three point bending configuration, the stress intensity factor K was calculated as indicated by Anderson (1995):

$$K = Y \frac{P}{B\sqrt{W}} \quad (1)$$

in which P is the load and Y is the relative shape factor. The formation of rim films near the crack tip during the tests prevented in most cases a reliable determination of crack initiation by visual means. On some instances optical detection could be performed and crack initiation was found to occur very close to the maximum of the load-displacement curve; the latter was therefore selected as the crack initiation point for all tests.

For DCB samples, the Kanninen solution reported by Stam (1996) was used to evaluate K :

$$K = 2\sqrt{3} \frac{Pa}{B^* h^{3/2}} \left(1 + 0.64 \frac{h}{a} \right) \quad (2)$$

in which B^* is the effective thickness that, in case of DCB samples, can be calculated using the formula proposed by Machida (1997):

$$B^* = \sqrt{B \cdot B_g} \quad (3)$$

In this case, no rim filming was observed at the crack tip: crack initiation was then visually detected by recording the tests with a high-resolution camera.

For SENB specimens tested in four point bending configuration under constant load, K was calculated according to the equation:

$$K = Y \frac{PL\sqrt{\pi a}}{B^* W^2} \quad (4)$$

in which the shape factor for pure bending was adopted as reported in Rooke and Cartwright (1976). The effective thickness for SENB specimens in four point bending configuration can be calculated as reported by Andena et al. (2013):

$$B^* = B^{0.263} B_g^{0.737} \quad (5)$$

In order to identify initiation time during a creep test, the approach proposed by Andena et al. (2013) was adopted. Specimen compliance C is defined as the displacement recorded by the LVDT divided for the applied load, was considered.

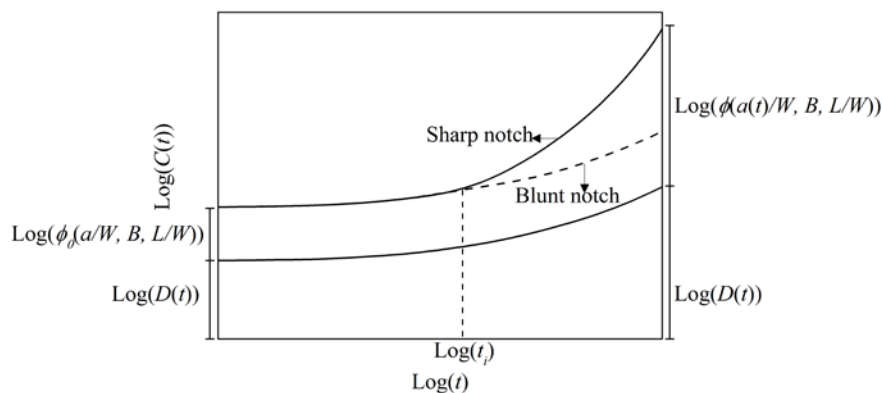


Fig. 2 - Sketch of the relation between specimen compliance and time during a creep test. $\text{Log}(C)$ can be considered as the sum of two contribution: the logarithm of material creep compliance $D(t)$, and the logarithm of the geometrical factor $\phi(a(t)/W)$; this term remains equal to $\text{Log}(\phi_0(a/W))$ until crack initiation at time t_i .

The specimen compliance $C(t)$ can be expressed as the product of the material compliance $D(t)$ and a geometrical factor ϕ which is a function of specimen dimensions and length (Fig. 2) which can be calculated from the shape factor Y :

$$C(t) = \phi \left(\frac{a(t)}{W}, B, \frac{L}{W} \right) \cdot D(t) \tag{6}$$

Performing a test on a blunt specimen, for which crack length remains unchanged during the whole test, the creep compliance $D(t)$ can be determined from equation (6).

In a test with a sharp notch since $D(t)$ is known, $\phi(a(t)/W, B, L/W)$ can be determined from the experimental compliance using equation (6). Up to crack initiation, for a given specimen, this geometrical factor is constant (ϕ_0), thus:

$$\frac{\phi \left(\frac{a(t)}{W} \right)}{\phi_0} = 1 \tag{7}$$

Accordingly, crack initiation time t_i was identified as the time for which (7) is no more satisfied.

3. Results and discussion

3.1. Size effects

To properly select specimen dimensions, a study on the size effects was first conducted at 23°C: the effects of sample thickness and ligament length on fracture toughness are reported in Fig. 3 and Fig. 4 respectively. K_{Ic} turns out to be independent of sample dimensions in the range of thickness and ligament length examined; SENB specimen with $W=22$ mm, $B=11$ mm, $B_g=0.8B$ were adopted to study the fracture behavior in air and the ESCR of the two materials. Tests were performed at 60°C at different constant displacement rate and different applied load (creep); the results obtained at a constant displacement rate of 10 mm/min are also reported in Fig. 3 and Fig. 4.

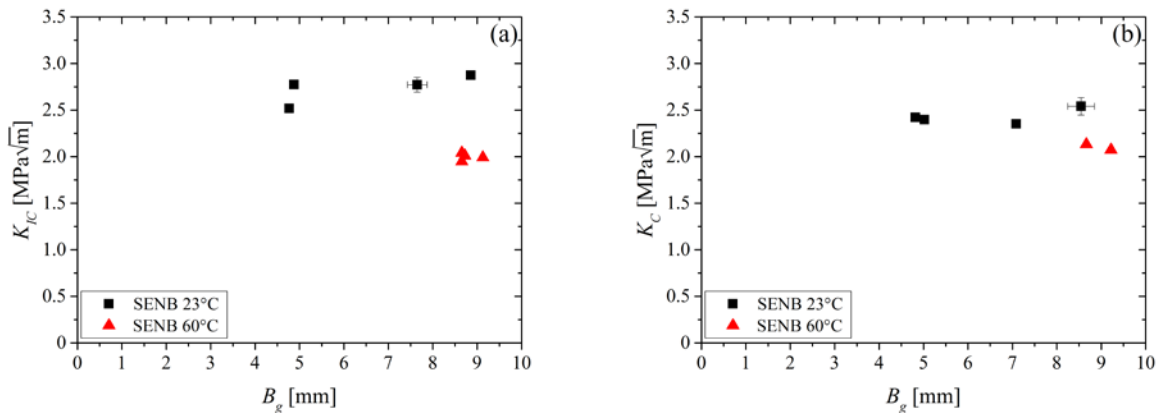


Fig. 3 - Effect of specimen thickness on fracture toughness. (a) HDPE-MONO; (b) HDPE-BI. For specimens having nominal dimensions of $B=11$ mm and $B_g=0.8B$, average values are reported with error bars representing standard deviation over at least 4 samples.

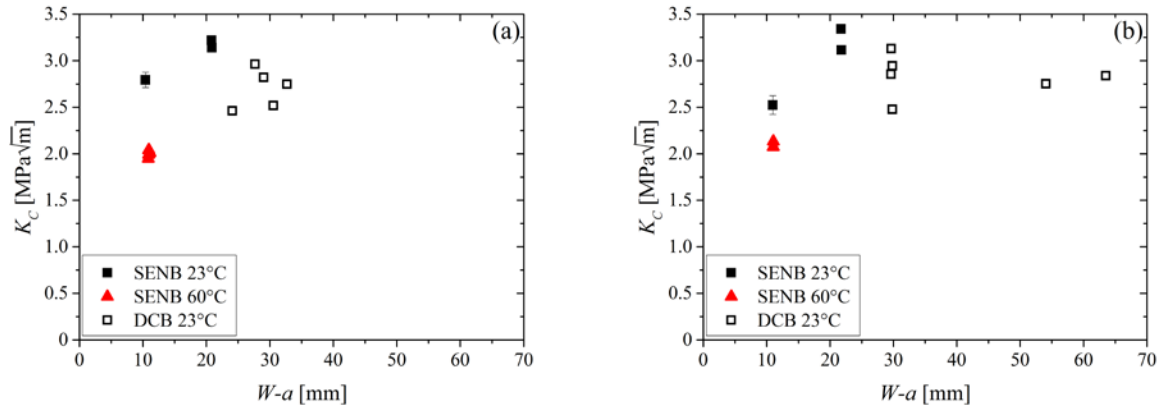


Fig. 4 - Ligament length effect on fracture toughness. (a) HDPE-MONO; (b) HDPE-BI. For specimens having nominal dimensions of $W = 22$ mm, average values are reported with error bars representing standard deviation over at least 5 samples.

Table 1 reports the yield stress, the fracture toughness and the plastic zone extent r_p of the two materials measured at 23°C and 60°C. r_p was evaluated according to the formula proposed by Irwin (1961):

$$r_p = \frac{1}{3\pi} \left(\frac{K_{IC}}{\sigma_y} \right)^2 \quad (8)$$

Both at 23°C and at 60°C the plastic zone is small with respect to thickness and ligament length.

Table 1 - Yield stress, fracture toughness and plastic zone extent at 23 and 60°C. Average and standard deviation values are reported; at least three specimen were tested for each condition.

Temperature [°C]	Yield stress [MPa]		Fracture toughness [MPa m ^{1/2}]		Plastic zone extent [mm]	
	HDPE-MONO	HDPE-BI	HDPE-MONO	HDPE-BI	HDPE-MONO	HDPE-BI
23	23.0±0.6	24.6±0.3	2.8±0.2	2.7±0.3	1.6±0.2	1.3±0.3
60	13.0±0.3	13.3±0.2	2.1±0.04	2.0±0.06	2.8±0.2	2.4±0.2

3.2. Fracture behavior and ESC resistance

Fig. 5 shows the results obtained from fracture tests conducted in air and in the two active environments.

Considering the results obtained from tests in air it can be seen that data obtained from constant displacement rate and creep tests fall on a single curve indicating that the K vs. t_i correlation does not depend on the loading history. The expected decreasing trend of K_C vs. t_i is observed; however, a change in slope is visible between 10^2 and 10^3 s, more evident for HDPE-BI. By looking at fracture surfaces of the samples whose data lies within the two regions, a clearly distinct visual appearance can be observed (Fig. 6). Indeed, for high loads (and correspondingly short initiation times) a rough surface was found, while for low levels of load (and longer initiation times) a smooth fracture surface was detected. These fracture surfaces seem to suggest that different fracture mechanisms are active at different loads, as previously reported by Andena et al. (2009): a high level of applied K is required to promote the micro-ductile crack propagation observed in Fig. 6(a).

Considering the tests in the active environment, it is very clear that both solutions promote a significantly faster initiation of the crack growth. It also seems that the two solutions have the same effect on the fracture behavior of the two materials. As a consequence, it would seem that sodium hypochlorite is not responsible for the reduction in

fracture initiation time of the two HDPEs. This decrease is more evident for relatively larger times (and correspondingly relatively low applied K); if fracture phenomena occur faster, the aggressive solutions have not enough time to interact with the polymer and negatively affect its resistance to fracture. A critical interaction time, t_i^* , can therefore be identified, as reported by Andena et al. (2013). According to the available data, t_i^* amounts to only a few minutes for HDPE-MONO but to a significantly larger value of a few hours for HDPE-BI.

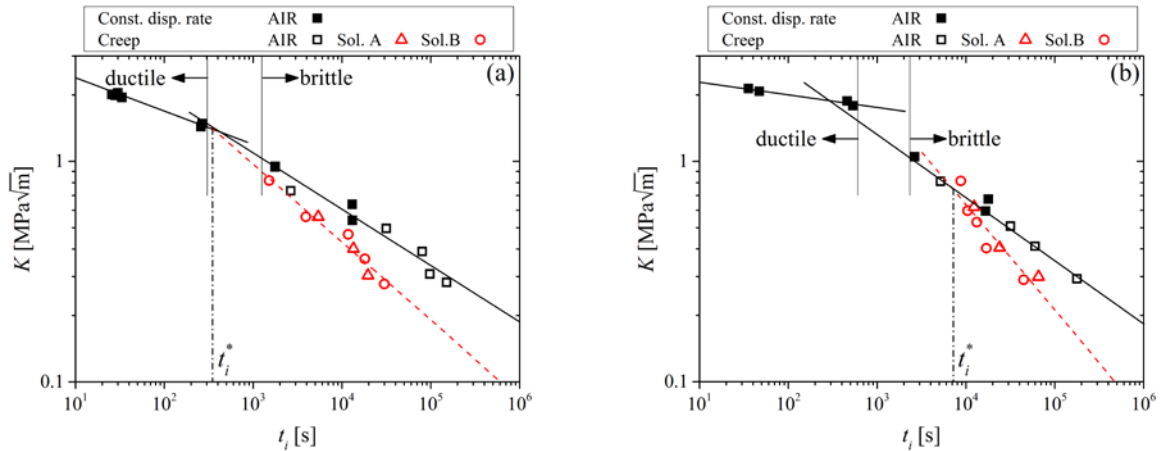


Fig. 5 - Applied stress intensity factor vs. initiation time plot; results in air and active environments. (a) HDPE-MONO; (b) HDPE-BI. Continuous lines represent a linear fit of in-air data in the regions corresponding to the two fracture mechanisms described in Fig. 4; dashed lines are a fit of all data in solutions A and B. Vertical continuous lines qualitatively indicate the regions in which ductile and brittle failure mode occurred; vertical dash-dotted lines represent the minimum interaction time t_i^* required to observe ESC.

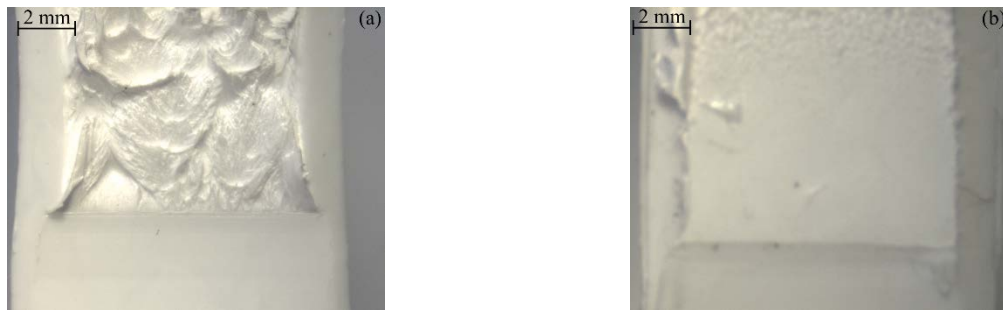


Fig. 6 - Fracture surface of two HDPE-BI samples. (a) ductile failure; (b) brittle failure. Similar surfaces were observed for HDPE-MONO.

4. Conclusions

A study of the fracture behavior of two HDPEs used for the production of bleach bottles was conducted using a LEFM approach. The ESCR of the two materials was determined by comparing results of fracture tests performed in air and in an active environment.

The behavior in air of the two materials showed that different fracture mechanisms may be active depending on the applied K : this was made evident by a change in the dependence of initiation time on applied K (more evident for the bimodal HDPE) and a markedly different aspect of the relevant fracture surfaces,

The fracture resistance in presence of two aggressive solutions was also characterized. A significant reduction of the initiation time t_i was observed for both materials, irrespective of the presence of sodium hypochlorite. This suggests

that other bleach components (as reported by Rink et al. (2003) and Cazenave et al. (2006)) are mainly responsible for ESC phenomena.

A characteristic interaction time, below which there is no effect of the environment, was determined for both materials; its value is significantly higher for the bimodal HDPE.

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References

- Altstaed, V., Keiter, S., Renner, M., Schlarb, A., 2004, Environmental stress cracking of polymers monitored by fatigue crack growth experiments, *Macromolecular Symposia*, 214, 31-46
- Andena, L., Rink, M., Frassine, R., Corrieri, R., 2009, A fracture mechanics approach for the prediction of the failure time of polybutene pipes, *Engineering Fracture Mechanics*, 76, 2666-2677
- Andena, L., Castellani, L., Castiglioni, A., Mendogni, A., Rink, M., Sacchetti, F., 2013, Determination of environmental stress cracking resistance of polymers: Effects of loading history and testing configuration, *Engineering Fracture Mechanics*, 101, 33-46
- Anderson, T.L., 1995, *Fracture Mechanics, Fundamentals and applications*, CRC Press, Boca Raton (Florida, U.S.A.)
- Castillo Montes, J., Cadoux, D., Creus, J., Touzain, S., Gaudichet-Maurin, E., Correc, O., 2012, Ageing of Polyethylene at raised temperature in contact with chlorinated sanitary hot water. Part I - Chemical aspects, *Polymer Degradation and Stability*, 97, 149-157
- Cazenave, J., Seguela, R., Sixou, B., Germain, Y., 2006, Short-term mechanical and structural approaches for the evaluation of polyethylene crack resistance, *Polymer*, 47, 3904-3914
- Hassinen, J., Lundbäck, M., Ifwarson, M., Gedde, U.W., 2004, Deterioration of polyethylene pipes exposed to chlorinated water, *Polymer Degradation and Stability*, 84, 261-267
- Irwin, G.R., 1961, Plastic zone near a crack and fracture toughness, *Sagamore Research Conference proceedings*, IV, 63-78
- Kurelec, L., Teeuwen, M., Schoffeleers, H., Deblieck, R., 2005, Strain hardening modulus as a measure of environmental stress crack resistance of high density polyethylene, *Polymer*, 46, 6369-6379
- Machida, K., 1997, JIC evaluation and effective thickness of thin specimens with and without side-grooves, *International Journal of Pressure Vessels and Piping*, 71, 181-188
- Men, Y.F., Rieger, J., Enderle, H.-F., Lilge, D., 2004, The mobility of the amorphous phase in polyethylene as a determining factor for slow crack growth, *The European Physical Journal E*, 15, 421-425
- Moskala, E.J., 1998, A fracture mechanics approach to environmental stress cracking in poly(ethyleneterephthalate), *Polymer*, 39, 675-680
- Munaro, M., Akcelrud, L., Polyethylene blends: A correlation study between morphology and environmental resistance, 2008, *Polymer Degradation and Stability*, 93, 43-49
- Rink, M., Frassine, R., Mariani, P., Carianni, G., 2003, Effect of detergent on crack initiation and propagation in polyethylenes, *Fracture of Polymers, Composites and Adhesives*, II, 103-114
- Rooke, D.P., Cartwright, D.J., 1976, *Compendium of stress intensity factors*, The Hillingdon Press, Uxbridge (Middlesex, U.K.)
- Stam, G., 1996, The stress intensity factor for grooved DCB specimens loaded by splitting forces, *International Journal of Fracture*, 76, 341-354
- Williams, J.G., Marshall, G.P., 1975, Environmental Crack and Craze Growth Phenomena in Polymers, *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Science*, 342, 55-77