

Fracture of polymers @ PolyEngLab

Introduction

The Polymer Engineering Lab (PolyEngLab) research group of Politecnico di Milano has been studying long-term fracture of viscoelastic materials since its foundation. During the '90s it developed a robust framework based on the application of Fracture Mechanics, following pseudo- or visco-elastic approaches which were exploited to characterize the fracture behaviour of polymeric materials as a function of time and temperature. The same approach has been more recently extended to the study of fracture occurring in aggressive environments (Environmental Stress Cracking, ESC).

Theoretical background

It is well known that the onset of fracture phenomena is associated to the presence of material defects of various origin (geometrical irregularities, notches, inclusions, compositional variations). These defects bring about stress concentrations, which allow the stresses arising from external loads to locally exceed the material resistance to fracture initiation and its subsequent propagation.

In its most simple implementation, Fracture Mechanics (FM) relies on the evaluation of a parameter known as the Stress Intensity Factor, K , which embraces at the same time defect size and applied external loads. For elastic materials, under any given loading condition or geometrical configuration, fracture occurs once K attains a critical value corresponding to the intrinsic material toughness, K_C

$$K = K_C \quad (1)$$

The viscoelastic nature of polymeric materials, strictly associated to the well-known creep and relaxation phenomena occurring at low deformations, also plays an important role when it comes to fracture. Fracture can initiate long after the initial application of the mechanical load, with this characteristic initiation time, t_i , depending on the intensity of the load itself. This evidence can be described by simple models such as the one reported in Equation 2:

$$t_i = B \cdot K^{-p} \quad (2)$$

The higher the applied K , the shorter will be the time require to observe fracture initiation; but for any given load, sooner or later fracture will occur. This phenomenon is known as slow crack growth. A similar relation can be obtained to describe the speed of crack propagation, \dot{a} , after initiation took place:

$$\dot{a} = A \cdot K^q \quad (3)$$

The parameters appearing in Equations 2-3 are characteristic properties of a material, and they are influenced by external variables which thus modify its fracture resistance.

A very important one is temperature, whose relationship with viscoelastic phenomena is well-established. In particular, time-temperature superposition schemes can also be applied to FM data to generate master curves which allow to describe the material behaviour over a much broader range, compared to the available experimental window. It is quite common to conduct accelerated FM tests at high temperature, and then use the underlying theory to quantitatively predict long-term behaviour at room temperature.

Applications of Fracture Mechanics

The use of Fracture Mechanics to characterize the fracture behaviour of polymeric materials offers a few essential advantages:

- By providing geometry-independent material parameters, FM allows the quantification of the intrinsic fracture resistance of different materials on small-scale laboratory specimens, without the need to actually produce components made of these materials
- The richness of the description of fracture phenomena based on K vs. t_i and K vs. \dot{a} relationships can give precious insight about the fracture mechanisms active under different conditions (e.g. ductile to brittle transition) and their association with relevant structural

features of the material (e.g. molecular weight distribution, crystallinity...)

- Once these parameters have been evaluated and the typical defect size associated with a given material / production process is assessed, FM data can be used to predict the service life of any component under whatever loading or environmental (e.g. temperature) conditions it is going to endure in the field.

An example is shown in Figure 1, reporting a comparison between the propagation behaviour of two isotactic polybutenes. The curves clearly demonstrate the superior toughness offered by PB2 with respect to PB1, as well as the region in which a transition from stable to partially unstable crack propagation (consistent with the appearance of fracture surfaces) is observed. These data were fed into a numerical model to predict the expected lifetime of polybutene pipes. This information was extracted from laboratory tests lasting at most a couple of hours, as opposed to 1-2 years required for conventional pressurized pipe testing.

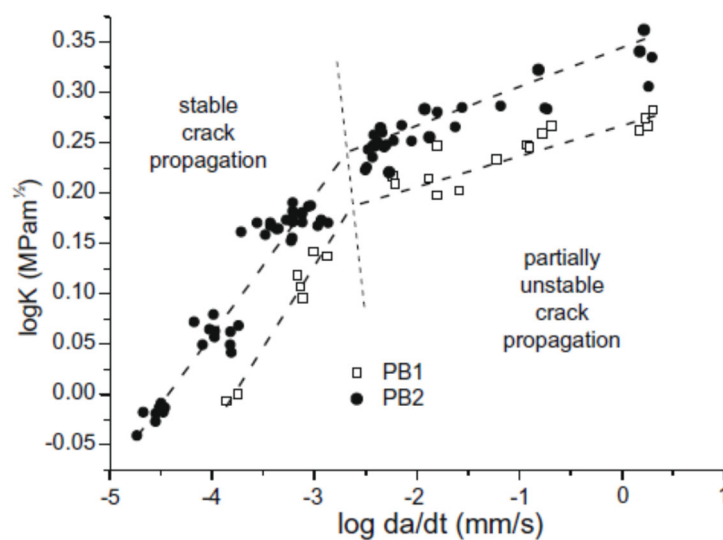


Figure 1. Master propagation curves at 23°C for two isotactic polybutenes, highlighting the transition between stable and unstable crack propagation [1].

Environmental Stress Cracking (ESC)

It is well known that the simultaneous presence of mechanical stress and specific chemical agents can significantly reduce the fracture resistance of many polymeric materials. This phenomenon is called Environmental Stress Cracking (ESC) and is deemed responsible for a significant share of failures in polymeric components worldwide. ESC agents do not chemically attack the material, instead facilitating fracture because of a pure acceleration of the same phenomena occurring during slow crack growth in air.

This observation prompted the application of the same FM approach described above to ESC phenomena. Experimental setups (with ad-hoc environmental tanks or bags) were developed, allowing the execution of FM tests in presence of selected active environments with the option of maintaining temperature control.

Successful applications include the case of amorphous high-impact polystyrene (HIPS) and sunflower oil, reported in [2], in which the method was employed to demonstrate its ability to discriminate a general-purpose HIPS grade from a variant specifically designed to resist ESC. As can be seen from Figure 2, there is a huge effect of the environment, with a reduction of t_f of a few orders of magnitude when the materials are tested in presence of oil. The general-purpose grade (HIPS B) performs better in air but it is way more sensitive to the environment when compared with the ESC resistant variant (HIPS A): for the relatively low loads encountered during real-life applications the latter actually exhibits a significantly higher resistance to fracture.

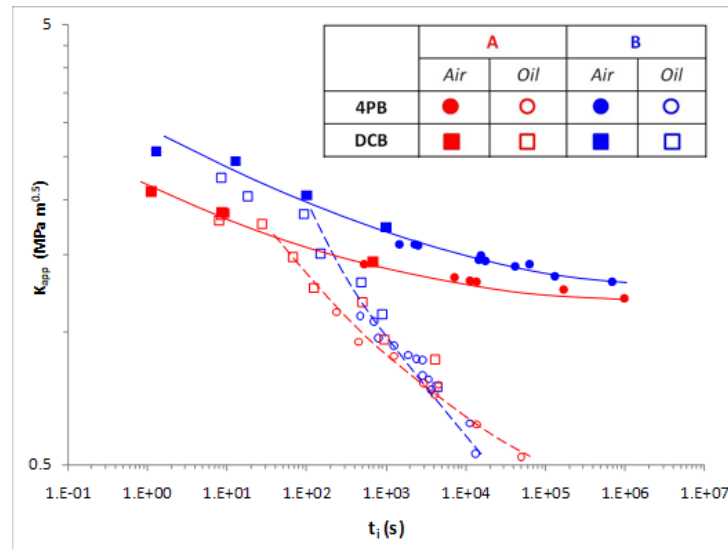


Figure 2. Master initiation curves at 23°C for two HIPS, in air and environment (sunflower oil) [2].

The data in Figure 2 were obtained using two different testing configurations and loading histories, demonstrating once again the robustness of the FM approach.

The latter has been also applied also to study ESCR of semicrystalline polymers, with the specific case of high-density polyethylene used for bleach containers detailed in [3-4]. The two elements of novelty of these research works are the application of time-temperature superposition and plane stress conditions to the study of ESC.

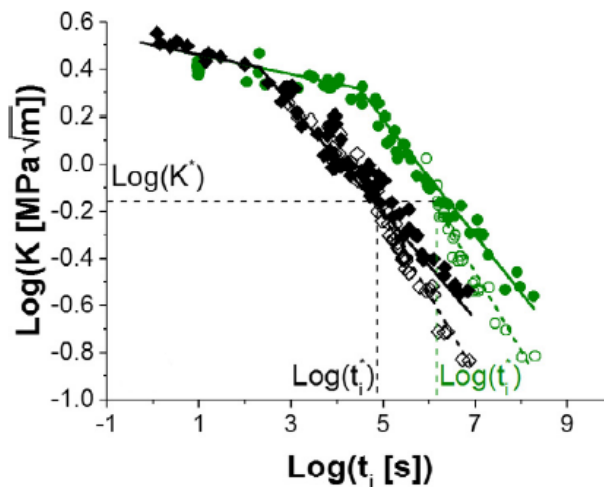


Figure 3. Master initiation curves at 23°C for two HDPE, in air and environment (detergent solution): black – monomodal HDPE; green – bimodal HDPE [3].

Figure 3 shows initiation data obtained at different temperatures, reduced on a single master curve at 23°C. Two HDPE materials are compared: they possess similar characteristics, except for a different molecular weight distribution (monomodal and bimodal). The bimodal grade is superior in terms of its stress cracking resistance, although the performance under ductile failure conditions (at high loads) is similar for the two materials. Different parts of the curve can be associated to the behaviour of either the crystalline or amorphous phase. The environment has a similar accelerating effect but because of the inherently superior fracture resistance of the bimodal material its critical interaction time, above which air and environment data diverge, is sensibly higher.

The Linear Elastic Fracture Mechanics (LEFM) approach so far adopted has been recently extended to Elasto-Plastic Fracture Mechanics (EPFM) in order to deal with situations like plane stress. This loading state, typical of thin products (such as blow-moulded bottles and thin sheets), is characterized

by extensive plastic deformations whose presence requires a more refined approach for proper evaluation of fracture properties. Yet the output of the analysis is very similar, provided a different fracture parameter (J-integral) is used to replace K . This has been done in [4] for the same monomodal HDPE + detergent system mentioned above, and results are detailed in Figure 4.

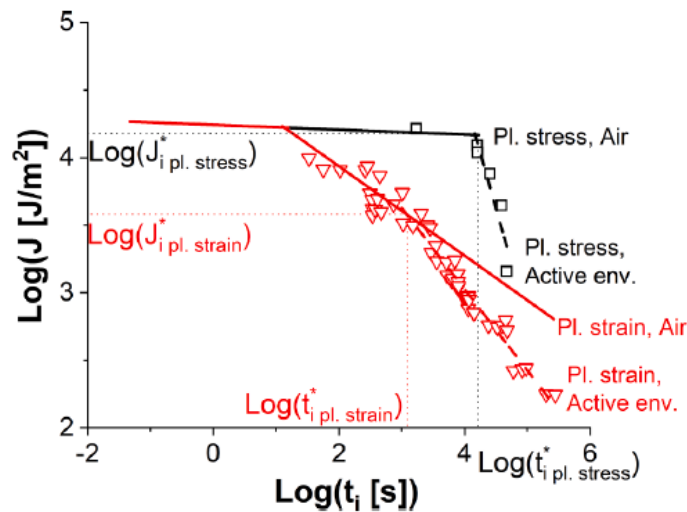


Figure 4. Master initiation curves at 60°C for monomodal HDPE, in air and environment (detergent solution), under different loading conditions: black – plane stress; red – plane strain [4].

The advantage of adopting plane-stress conditions for FM testing is that the material samples can be directly sourced from polymeric products, thus accounting for the modifications of the material structure and characteristics originated by the actual shaping process. Indeed, in [4] this approach was used to compare the relative performance of compression-moulded and blow-moulded parts.

Conclusions

Fracture Mechanics can be a very powerful tool to study the mechanical performance of polymeric materials. It is a versatile approach suitable for both material development and product design. It provides a clear explanation of the phenomena which eventually define products lifetime, especially considering its application with non-ambient conditions which could range from high temperature to the presence of aggressive environments. Its ability to finely detect changes in properties originating from modifications of the polymer structure (possibly related to the production process) can be of great help to material producers in driving the development of better solutions to existing industrial challenges.

Key references

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