

# FRACTURE MECHANICAL CHARACTERIZATION OF SEMICRYSTALLINE THERMOPLASTICS

H.H. Kausch, Ch. Grein, Ph. Béguelin, R. Gensler

Département des Matériaux, Ecole Polytechnique Fédérale de Lausanne (EPFL)  
CH 1015 – Lausanne

## ABSTRACT

The different modes of fracture of a (semi-crystalline) polymer are determined by the competition between different *deformation and damage mechanisms*. Their molecular and structural origins and their effect on fracture toughness are discussed using rubber-modified polypropylene (PP/EPR) as main example. Toughness has been assessed using the J-Integral, the Essential Work of Fracture (EWF) and the Linear Elastic Fracture Mechanics (LEFM) concept with plastic zone correction. For relatively ductile, strain-rate sensitive materials the first two methods gave ambiguous results whereas unique values of toughness  $K_{\text{eff}}$  and strain energy release rate  $G_{\text{eff}}$  were obtained from properly corrected LEFM data. As an additional advantage the latter approach can be used in a wide range of strain rates extending from slow creep to impact loading (at 7m/s) thus permitting the study of brittle-ductile transitions, often the most sensitive property to characterize the impact performance of a polymer [1].

## KEYWORDS

Toughness, semi-crystalline polymers, molecular mechanisms, plastic zone correction, strain-rate sensitive materials, ductile-brittle transitions, impact performance.

## INTRODUCTION

High stiffness and fracture toughness are still among the most important mechanical properties. The deformation and fracture behavior of semi-crystalline thermoplastics is strongly influenced by structural features from three different levels of organization: by *molecular configuration* (chain length, tacticity), the physical *structure of the crystal lamellae*, and by their *heterogeneous, frequently spherulitic morphology*. In addition the state of stress (presence of modifier particles, sample geometry) and the rate of loading play an important role. In order to direct the development of these attractive materials and to optimize their application reliable methods of physical and *continuous* mechanical characterization are needed. By *continuous* we understand a method, which works with identical specimen geometry in wide range of strains, strain rates and temperatures.

In this presentation we will mainly deal with polypropylene (PP), which shows an extraordinary breadth of fracture phenomena (*brittle fracture* through unstable rapid crack propagation, *slow creep crack* growth, crazing or macroscopically homogeneous deformation leading to *plastic instability*). The mode of fracture is largely determined by the competition between stress transfer onto backbone chains and the intensity of the different relaxation mechanisms, including segmental slip and disentanglement, void formation and chain scission. The inherent ductility and low glass transition temperature,  $T_g$ , of PP give rise to strongly rate dependent *local* plasticity effects, which have to be taken into consideration for a quantitative evaluation of toughness. In the following we will briefly indicate the molecular and structural origins of the different *deformation and damage mechanisms*. Their effect on fracture toughness will then be assessed using three methods (J-Integral, EWF, LFM).

## **DEFORMATION AND DAMAGE MECHANISMS AND THEIR EFFECT ON FRACTURE BEHAVIOR**

Semi-crystalline polymers are highly heterogeneous on a molecular and microscopic scale. The smallest building-blocks considered here are aggregates of crystal lamellae connected by amorphous regions. These latter consist of a network of non-extended entangled chains, dangling chain ends and/or loops, and more or less taut tie-molecules. When a spherulitic sample is strained, local strains within a lamellar stack will vary considerably, depending on the local Young's modulus, the relative orientation of the lamellar stack with respect to the principal stress direction and the modes of stress relaxation available to a given volume. Above  $T_g$  the amorphous regions will account for most of the elastic and anelastic deformation. The regions oriented perpendicular to an applied (uniaxial) stress will initially mainly deform by interlamellar separation.

Evidently, the difference between the crystalline and amorphous moduli and the resulting strain concentration become relatively small at  $T \ll T_g$ . Crack extension in this temperature range occurs by rapid straining and failure of the material ahead of the crack tip following the *plane of least resistance*, i.e. generally through and along the amorphous interlayers. Tie chains are stretched and broken rather than pulled out. Thus, plastic deformation of the bulk material is relatively limited and crack resistance is well quantified by the critical strain energy release rate  $G_{Ic}$  (or by the critical stress intensity factor  $K_{Ic}$ ) using the standard methods of *Linear Elastic Fracture Mechanics* [2, 3].

More extensive anelastic and/or plastic deformation is observed if the drawing process also involves the crystalline regions. *Homogeneous, ductile* deformation through lamellar shear is favored by intense stress transfer between crystal lamellae through strong, well-entangled amorphous regions and a large concentration of tie-molecules. These parameters also increase  $K_{Ic}$ . On the other hand, low molecular weight and rigid crystal lamellae favor heterogeneous, localized deformation leading to craze-like features and brittle fracture [4]. However, the mode of fracture is not an inherent property of a given material, it depends strongly on temperature, time scale and state of stress. For an unmodified high molecular weight polypropylene (PP) it changes as a function of loading rate  $v$  from full shear yielding ( $v < 1$  mm/s) to small scale yielding and multiple crazing (10 mm/s – 1m/s) and to formation of a single crack ( $v > 2$  m/s) [5]. The time scale is evidently shifted with molecular weight and temperature (see below).

## **FRACTURE MECHANICAL CHARACTERIZATION**

### ***Essential Work of Fracture (EWF)***

The EWF concept is based on the assumption that the total work of fracture,  $W_{tot}$ , is dissipated in two distinct regions at the crack tip, in the so-called process zone or inner fracture zone ( $W_e$ ), and in an outer plastic zone ( $W_p$ ). A test protocol has been developed by the European Structural Integrity Society (ESIS) [3]. The specific work of fracture,  $w_{tot}$ , is obtained by normalizing  $W_{tot}$  with the fracture surface  $A = \ell \cdot t$  (given by the sample thickness,  $t$ , and the so-called ligament length  $\ell$ ):

$$w_{tot} = w_e + \beta w_p \ell \quad (1)$$

The quantity  $w_e$  is referred to as the specific essential work of fracture (in  $\text{kJ/m}^2$ ) and the parameter  $w_p$  is called the specific non-essential or plastic work of fracture (in  $\text{MJ/m}^3$ ). A plot of  $w_{tot}$  versus the ligament length results in a straight line, which intersects the ordinate at  $w_e = 9.05 \text{ kJ/m}^2$  (EWF plot, Figure 1i). An analysis of the stress-strain curve (Figure 1 ii) shows that the energy values obtained for crack initiation and for propagation, both contain contributions to  $w_e$  and  $w_p$ . Thus, despite the linearity of the EWF plot, there is a notable ambiguity concerning the *fracture energy*. It should be noted, however, that the term  $\beta w_p$  gives a rather sensitive account of the capacity for plastic deformation, thus indicating the effects of e.g. aging much earlier than the yield stress [5].

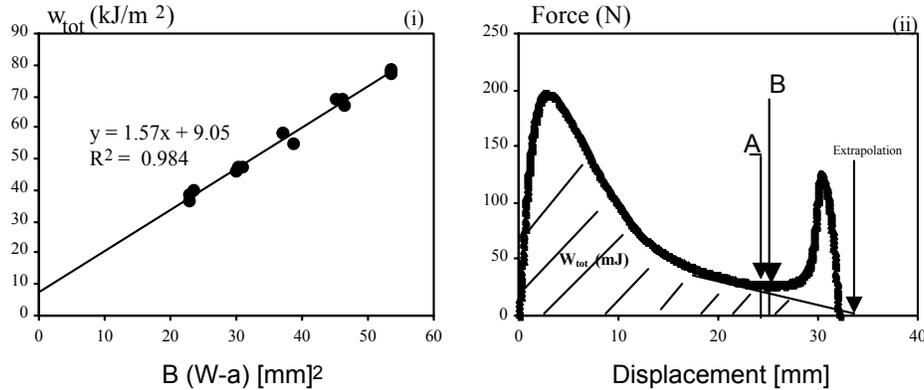


Figure 1: EWF plot (i) and stress-strain curve (ii) of a ductile polymer ( $\beta$ -PP/ 15 vol.% EPR) [1]. Two possible criteria for the determination of  $W_{tot}$  are indicated, a fixed displacement (A) and the minimum of force (B).

### ***J-Integral***

The J-integral concept has proven its usefulness for a variety of polymers. It relates the dissipated energy  $J$  to the crack advance  $\Delta a$ .  $J$  can be calculated for a cracked sample from:

$$J = \frac{\eta U}{B(W-a)} \quad (2)$$

where  $U$  is the surface under the stress-strain curve,  $B$  specimen thickness, and  $(W-a)$  the effective ligament length. The factor  $\eta$  depends on sample geometry [3]. Figure 2 represents the results of a multiple specimen test [1]. The method is not only *laborious* because of the large number of specimens (which could be avoided by the single-specimen J-integral method [3]) but it is also *ambiguous* because of the difficulties to determine  $\Delta a$  with sufficient precision in a non-transparent, tough material.

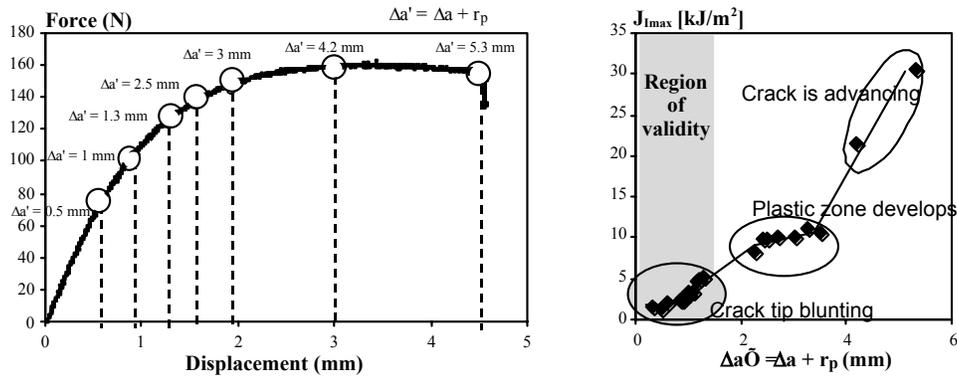


Figure 2 (3.11): Multiple specimen J-integral test on  $\alpha$ -PP/ 15 vol.% EPR,  $a/W = 0.5$ , tested at room temperature and at a displacement rate of  $v = 0.001$  m/s [1]

### Linear elastic fracture mechanics (LEFM) analysis with plastic zone correction

From LEFM one derives for a compact tension (CT) specimen a stress intensity factor  $K_I$ :

$$K_I = f(a/W) \frac{F_{\max}}{B\sqrt{W}} \quad (3)$$

where  $F_{\max}$  is the maximum force applied to the specimen and  $f(a/W)$  a correction function, which depends on sample geometry and is tabulated [6]. In the range of validity of LEFM  $K_I$  corresponds to  $K_{Ic}$  and a plot of  $F_{\max}$  over  $BW^{1/2}/f$  should give a straight line through the origin. If the criteria of LEFM are not met, an *apparent*  $K_{I\max}$  is obtained from Eqn. 3 (Figure 3i, bottom curve). In that case  $K_{I\max}$  will depend on sample and crack geometry as for instance on  $a/W$  (Figure 3ii). The main reason for such dependence is generally the presence of a small *confined plastic zone*  $r_p$  at the crack tip. In the classical models by Irwin [Irwin] for an elasto-plastic material and Dugdale [Dugdale] this has been taken into account by substituting the crack length  $a$  by  $a_{\text{eff}} = a + r_p$ . The size of  $r_p$  is derived from respectively a *yield* or a *line zone* criterion [2]. For a rubber modified polymer Gensler [5] has used a *volume strain* cri-

terion. Grein [1] uses a different procedure to correct for confined plasticity, she proposes to determine  $r_p$  by numerical iteration in such a way that all data of a corrected plot  $F_{\max}$  over  $BW^{1/2}/f(a_{\text{eff}})$  fall on a line through the origin (Figure 3i, upper curve). The *apparent*  $K$  obtained for a ductile ( $\beta$ -crystalline)

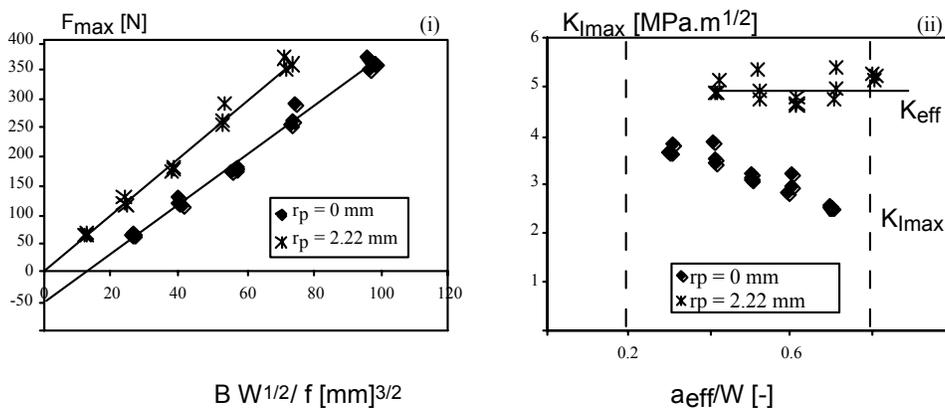


Figure 3: (i) Determination of the size  $r_p$  of the plastic zone by an iteration procedure (see text); (ii) evolution of  $K_{\text{eff}}$  of an unmodified  $\beta$ -PP as a function of  $a_{\text{eff}}/W$  [1]

material without correction decreases with  $a/W$ , whereas  $K_{\text{eff}}$  vs.  $a_{\text{eff}}/W$  is constant thus giving credit to the applied procedure (Fig. 3ii) [1].

### APPLICATION: TOUGHNESS AS A FONCTION OF LOADING RATE (DUCTILE-BRITTLE TRANSITIONS)

A major advantage of the corrected LEFM method is its applicability in a wide range of strains and strain rates, which permits a homogeneous characterization of ductile-brittle transitions and a convenient comparison of different blends, the principal aim of this investigation. The development of  $r_p$ ,  $K_{\text{Imax}}$  and  $K_{\text{eff}}$  in an  $\alpha$ -PP/ 15 vol.% EPR with rate of displacement  $v$  is indicated in Figure 4. The transition from ductile to brittle fracture occurs between 0.4 m/s (which corresponds to the maximum of  $K_{\text{eff}}$ ) and 0.7 m/s (where the tenacity decreases notably). A microstructural analysis shows that in ductile fracture three regions ahead of the crack tip can be identified where respectively particle cavitation, interlamellar cavitation leading to craze formation, and large scale matrix plastic deformation dominate. In brittle fracture a single crack propagates with no signs of rubber cavitation or crazing visible [1]. These observations confirm that energy dissipation is triggered by rubber particle cavitation, which contributes to relax the *unfavorable* tri-axial state of stress. Cavitation in itself does not dissipate much energy; for efficient toughening it is essential that the matrix be capable to engage large strains by crystal plastic deformation. The notable influence of the presence of cavitating particles and of matrix ductility are brought out by comparing the fracture behavior of different PP-resins.

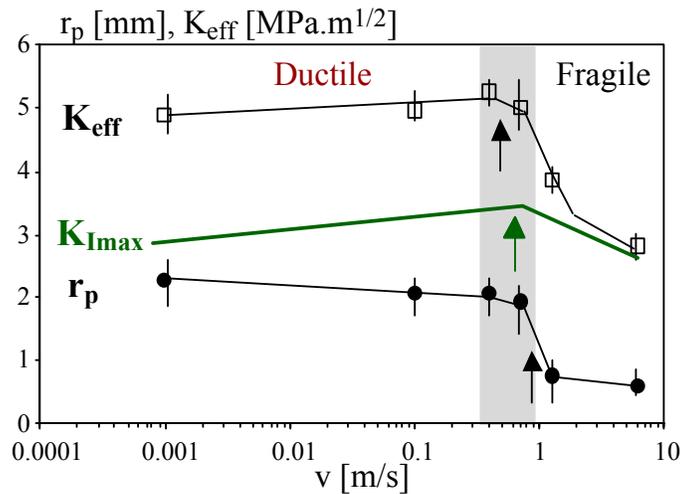


Figure 4: Development of  $r_p$ ,  $K_{\text{Imax}}$  and  $K_{\text{eff}}$  of an  $\alpha$ -PP/ 15 vol.% EPR with rate of displacement  $v$  [1]

When comparing blends of different composition it is useful to plot the rate of increase of  $K$  (determined from Eqn.3 by introducing  $dF/dt$ ) instead of  $v$ . This eliminates effects due to differences in sample compliance. A  $K$ -rate temperature diagram of the ductile-brittle transitions of three  $\alpha$ -PPs is compiled in Figure 5. It clearly shows the important rate sensitivity of PP (the fracture transition is shifted by 4 decades of  $K$ -rate over a temperature interval of 110 K), the dramatic toughening effect caused by the addition of the first 15% of rubber particles (the unmodified matrix at +60°C is brittle at loading rates larger than 0.1 MPa.m<sup>1/2</sup>s<sup>-1</sup>, whereas the transition jumps to 7000 MPa.m<sup>1/2</sup>s<sup>-1</sup> for the  $\alpha$ -15%), and the large difference between unmodified  $\alpha$ - and  $\beta$ -PP. The latter behavior is ascribed to the increased molecular mobility of the  $\beta$ -phase as evidenced by the fact that the  $\beta$ -transition of  $\beta$ -PP at +5 °C is much more intense than that of  $\alpha$ -PP [1]. Unfortunately this difference between  $\alpha$ - and  $\beta$ -PP is not maintained after modification with EPR.

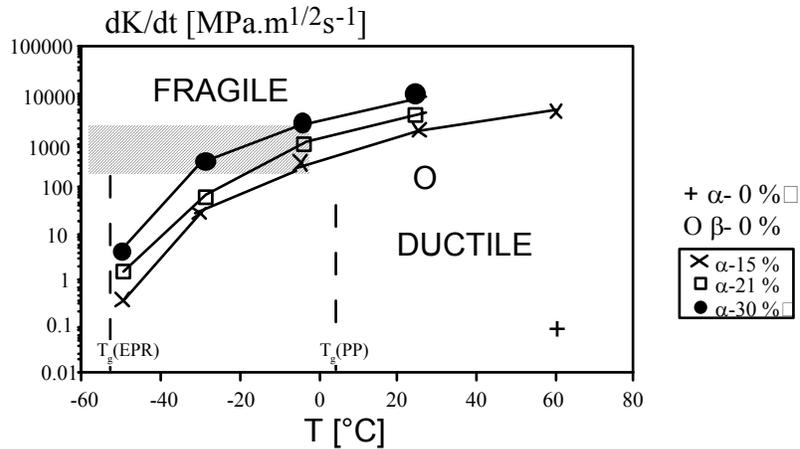


Figure 5: Ductile-brittle transitions of  $\alpha$ -PP filled with respectively 15, 21 and 30 vol% EPR as a function of temperature and of rate of increase of  $K$ . For comparison are also indicated the  $K$ -rates where the ductile-brittle transition of the pure resins  $\alpha$ -PP (+) and  $\beta$ -PP (O) occur.

## CONCLUSIONS

Three methods for a quantitative evaluation of fracture toughness have been compared using polypropylene (PP) as an example. Its inherent ductility (low glass transition temperature,  $T_g$ ) and strain hardening capacity give rise to large, strongly rate dependent local plasticity effects. We have shown that for such materials the J-Integral and the Essential Work of Fracture (EWF) concepts give ambiguous results. From the Linear Elastic Fracture Mechanics (LEFM) approach with plastic zone correction unique values of toughness  $K_{eff}$  and strain energy release rate  $G_{eff}$  are obtained. Thus one and the same approach can be used in a wide range of strain rates (from creep to impact loading) and fracture modes. The study of brittle-ductile transitions is a sensitive means to elucidate the toughening mechanisms of differently modified PPs and of the influences of the molecular, crystallographic and morphological structure on toughness.

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