Ductile to brittle transition concept on fracture behavior of poly(vinylidene fluoride) / poly(methyl methacrylate) blends

Lucien Laiarinandrasana[1,*], Yannick Nziakou[2], Jean-Louis Halary[2]

[1] Centre des Matériaux CNRS UMR 7633, Mines ParisTech, Evry Cedex 91003, France
[2] SIMM-Lab. UPMC/CNRS/ESPCI UMR 7615, ESPCI ParsTech, Paris Cedex 05 75231, France
* Corresponding author: Lucien.Laiarinandrasana@mines-paristech.fr

Abstract The fracture behavior of blends of poly(ninylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) was investigated by gradually increasing the PVDF content. The study focuses on semi-crystalline blends. The trends of net stress versus crack opening displacement curves were analyzed. From these plots, two fracture energies were defined: the fracture energy to crack initiation corresponding to the area under the curve up to the maximum net stress and the fracture energy to crack propagation considering the last part of the curve where the load continuously decreases. Fracture surface inspections confirmed typical semi-crystalline polymer features. Critical values of the degree of crystallinity corresponding to brittle to ductile transition were determined, depending on the selected fracture energy.

Keywords Blends, Poly(methyl methacrylate), Poly(vinylidene fluoride), Fracture toughness, Brittle to Ductile transition

1. Introduction

Mechanical parameters at failure are key factors to assess the durability of engineering components. For structural polymeric materials, fracture toughness is often characterized by the impact strength (Charpy or Izod tests). These are dynamic tests, accurate for brittle failure characterization. They might be inappropriate when the material exhibits significant ductility. Theoretically, fracture mechanics approaches suggest a methodology to define fracture toughness, whatever the mechanical response of the material. Whereas comprehensive research has been carried out for years on metallic materials concerning the equivalence between impact strength and fracture toughness, there is no such amount of work on polymers. Some attempts were made in this way but failed because, for instance, of the difficulty to fulfill requested plane strain conditions. Nevertheless, impact strength or toughness of polymeric materials was currently plotted as a function of the test temperature, in order to find a ductile to brittle transition temperature. The essential motivation of such a plot is to check whether the modification of the material process actually leads to an improvement of the toughness or the impact strength, by shifting the brittle to ductile transition temperature away from in-service temperature.

The present contribution focuses on blends of poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA). Indeed, in recent years, PMMA/PVDF blends got a renewal of interest with studies aiming at assessing their mechanical response. In terms of processing, they exhibited a transition from miscible amorphous to semi-crystalline structures. At room temperature and for approximately the same given crosshead speed, PMMA is basically brittle and neat PVDF exhibits ductile failure. By gradually increasing the PVDF content, toughening effects were evidenced according to a given fracture mechanics parameter based on fracture energy. The motivation here is then to determine a critical degree of crystallinity able to characterize the transition between brittle (low fracture energy) and ductile (high fracture energy) failures, for the same test conditions (room temperature/ crosshead speed). It was demonstrated that depending on the fracture energy definition,

corresponding to either fracture toughness or impact strength, the value of this critical degree of crystallinity was changed.

2. Experimental procedure

2.1. Materials - Specimen

The PVDF/PMMA blends were prepared from the homopolymers PVDF Kynar® 721 and PMMA Oroglas® V825, both provided by the company Arkema France. Blending was achieved by co-precipitation from a homogeneous solution [1]. Depending on the fraction of PVDF, either amorphous or semi-crystalline blends were produced. Typically, the blends remain amorphous when their PVDF content is less than about 50 wt%. In the following, blend identification was based on weight composition. For instance, %F = 20 or F/M 20:80 deals with a blend containing 20 wt. per cent of PVDF and 80 wt. per cent of PMMA. Of course, blend composition influenced the values of the glass transition temperature. Moreover, the presence of amorphous PVDF segments constrained by the crystallites was evidenced in the crystalline blends [1].

Table 1. Blends characteristics

Sample	%F	T_g (°C)	χ (%)
M	0	110	0
F/M 20:80	20	85	0
F/M 30:70	30	77	0
F/M 40:60	40	58	0
F/M 50:50	50	66	14
F/M 60:40	60	54	19
F/M 70:30	70	45	27
F/M 80:20	80	54	36
F/M 90:10	90	53	45
F	100	-40	55

Table 1 recalls the main characteristics of the blends under study, namely overall wt percentage of PVDF, %F, glass transition temperature, T_g and the degree of crystallinity, χ.

The blends were compression-molded in the form of 5 mm-thick sheets. Then, single edge notch bending (SENB) specimens were machined out of the sheets. Their characteristic dimensions were kept constant: thickness T = 5 mm, width W = 12 mm, crack depth a = 5 mm (thus a/W = 0.42), length L = 70 mm, span S = 50 mm. The pre-crack was machined with a notch root radius of approximately 250 µm.

2.2. Fracture energy measurements

Fracture tests on SENB specimen were carried out at room temperature on an Inströn testing machine with a constant crosshead speed of 0.5 $mm.s^{-1}$ for all tests. For the sake of reproducibility, all tests were repeated twice. The load F, the notch opening displacement δ and the crosshead displacement were recorded as a function of the running time. The net stress (σ_{net}) is defined as the

load F divided by the area of the initial net section: T (W –a).

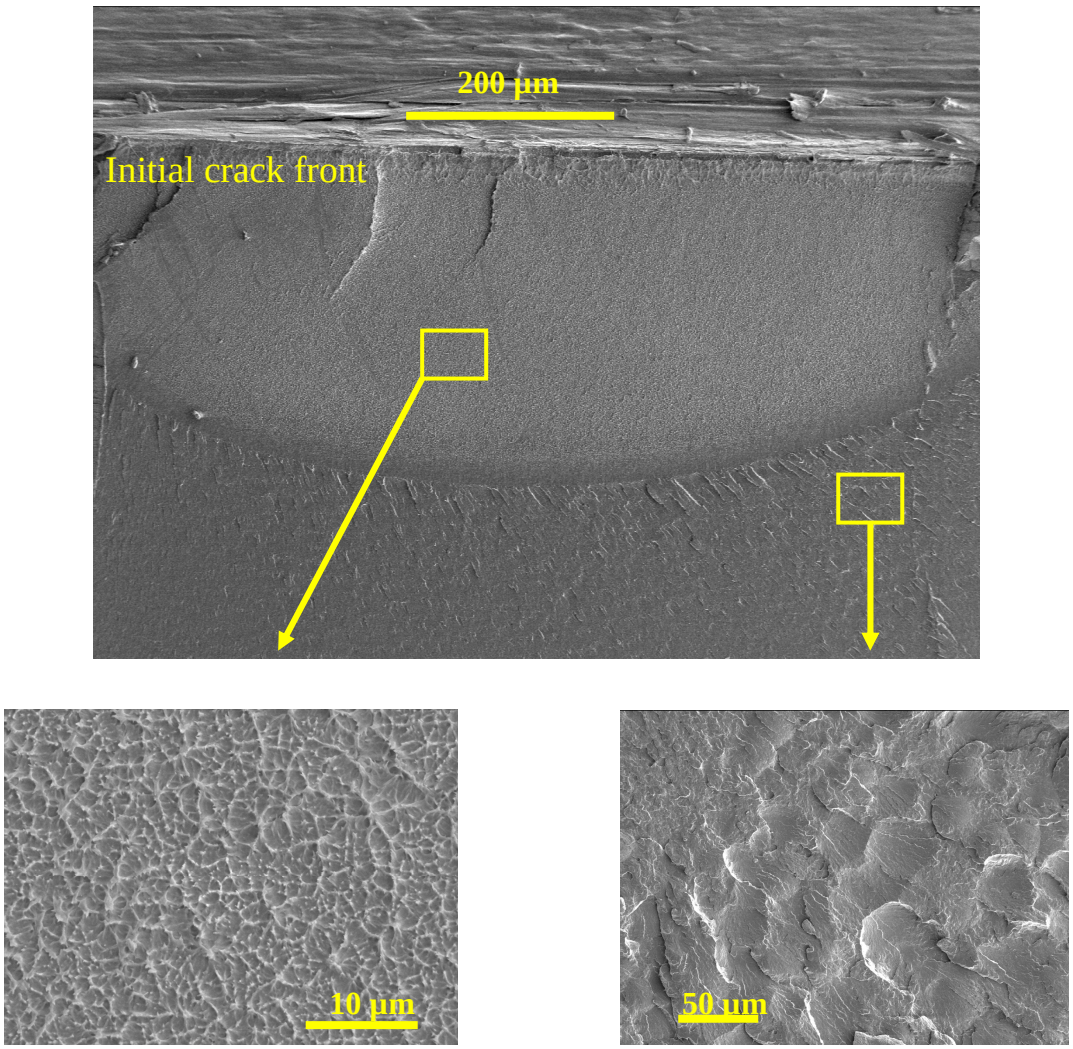


Figure 1. Typical features of semi-crystalline fracture surfaces for 50 ≤ %F ≤ 80

Following fracture mechanics theory [2], the energy release rate G can be expressed as:

$$G = f(a/W)\, U \qquad (1)$$

where $f(a/W)$ is a function of the crack depth ratio and the specimen geometry; U the area under the load versus δ plot. Here both a/W and specimen geometry were kept constant so G was assumed to be proportional to the area under σ_{net} versus δ. Note that this area is homogeneous to an energy density and can be directly calculated from experimental data. In the following, it will be integrated and split into two fracture energies: E_i during the loading path up to the maximum σ_{net} and E_p corresponding to the consecutive decrease in σ_{net}. For brittle fracture $E_p = 0$, E_i is therefore related to the critical energy release rate. It is representative of the toughness of the material. For the general case where $E_p \neq 0$, the total fracture energy $E_t = E_i + E_p$ can be linked to the Charpy impact fracture strength [3-5] but adapted here to quasi-static loading of the specimen. Both E_i and E_t will then be considered here to follow the toughness improvement according to the PVDF content.

3. Results

3.1. Fractography

In Table 1, the degree of crystallinity χ is zero for %F ranging from 0 to 50. Additionally, T_g values were "stabilized" for %F ≥ 50. As already mentioned, the blends were considered as semi-crystalline when their PVDF content was more than 50 wt%. By examining fracture surfaces of broken SENB specimens (fig.1), it was demonstrated that typical semi-crystalline features were identified on blends corresponding to 50 ≤ %F ≤ 80. Accordingly, investigations focused on blends for which %F ≥ 50, *that is* 14% ≤ χ ≤ 55%. Indeed, to better assess the transition between brittle (low fracture energy) and ductile (high fracture energy) fractures, the failure mechanisms should be ensured to be the same. Moreover, since T_g does not vary so much for semi-crystalline blends and since all tests were carried out the room temperature, the degree of crystallinity χ was selected as the relevant parameter allowing for the characterization of this transition.

3.2. Mechanical parameters

3.2.1. Net stress versus δ curves

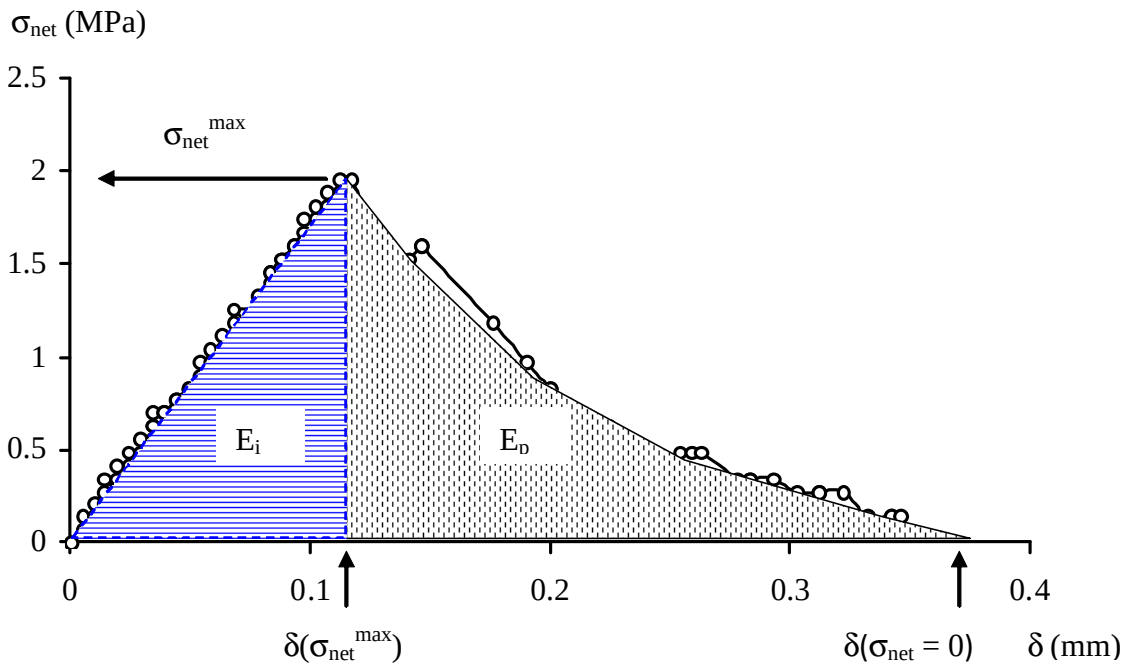


Figure 2. Typical net stress versus opening displacement curve for %F = 50.

The main mechanical parameters were derived from the curve of net stress versus the opening displacement δ as illustrated in fig.2. The definitions of σ_{net}^{max}, $\delta(\sigma_{net}^{max})$ and $\delta(\sigma_{net} = 0)$ were clearly indicated. Moreover, two specific steps could be distinguished in this plot: i) the loading stage (up to maximum net stress), where the crack is supposed to be stationary at the initial value of a/W = 0.42. This part is concerned with "crack initiation" process and therefore to E_i; ii) the crack

growth stage, characterized by the decrease of net stress, related then to E_p.

3.2.2. Maximum net stress

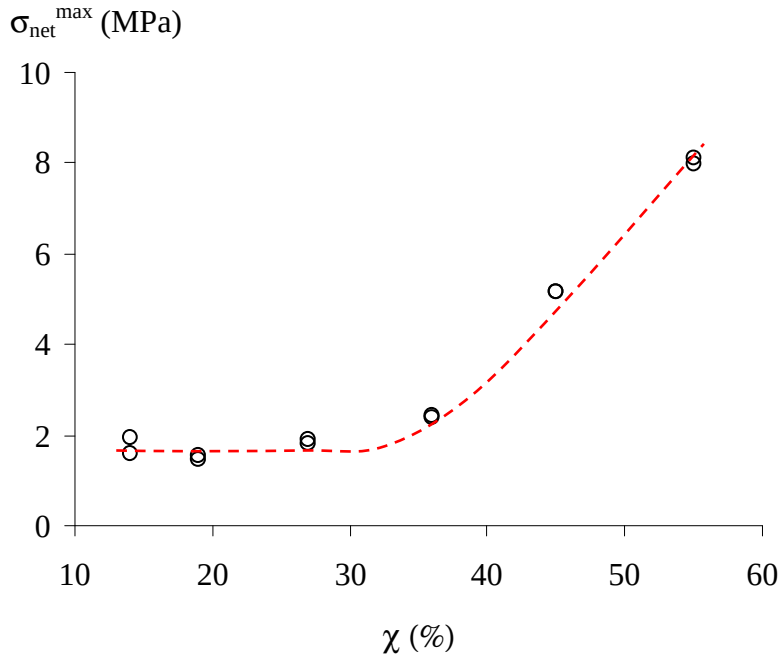


Figure 3. σ_{net}^{max} as a function of the degree of crystallinity χ (%)

The maximum values of the net stress (σ_{net}^{max}) were plotted as a function of χ (%) in fig.3. A continuous increase in σ_{net}^{max} is observed, slightly between 14% and 35% then significantly for the last values of the degree of crystallinity. Moreover, excellent reproducibility of (σ_{net}^{max}) values could be noticed.

3.2.3. Opening displacements: $\delta(\sigma_{net}^{max})$ and $\delta(\sigma_{net} = 0)$

Fig.4 displays the crack opening displacements δ corresponding to respectively, $\sigma_{net} = 0$ at the complete failure of the specimens (first Y-axis) and σ_{net}^{max} (second Y-axis). The same trend as in fig.3 is observed for $\delta(\sigma_{net}^{max})$. This similarity indicates that during the loading step, the net stress versus δ curve was quasi-linear.

Instead, the evolution of $\delta(\sigma_{net} = 0)$ versus χ (first Y-axis) exhibited a jump between 20% and 30%. Actually, this jump was essentially due to the propagation stage where additional deformation of the crack tip (blunting) was observed. For $\chi \geq 35\%$ a saturation of $\delta(\sigma_{net} = 0)$ value was observed.

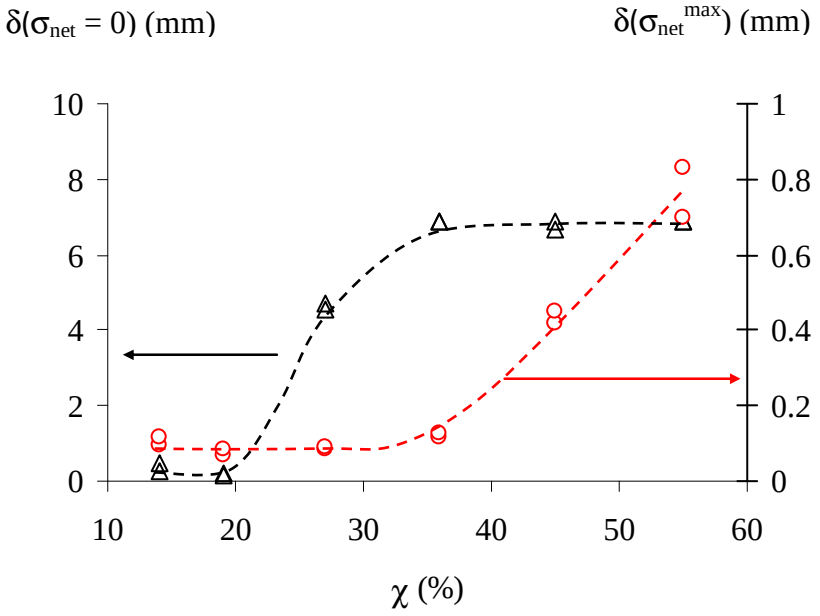


Figure 4. $\delta(\sigma_{net}^{max})$ and $\delta(\sigma_{net} = 0)$ as a function of the degree of crystallinity χ (%)

3.2.3. Fracture energies E_i and E_t

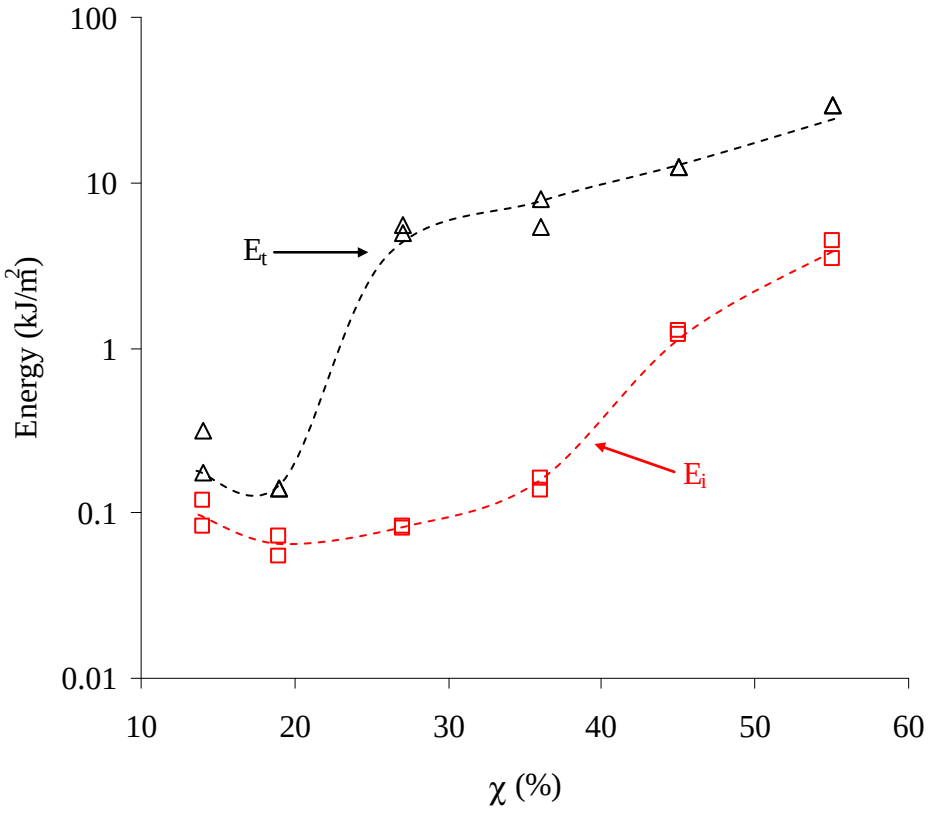


Figure 5. Fracture energies plotted as a function of the degree of crystallinity χ (%)

Fig.5 displays the fracture energies E_i and E_t in a semi-logarithmic scale versus χ. For E_i, the trend was the same as that of σ_{net}^{max} and $\delta(\sigma_{net}^{max})$, whereas the jump of E_t between 20% and 30%

coincided to that of $\delta(\sigma_{net} = 0)$. Furthermore, fig.5 showed that at low values of fracture energy ($\chi \leq$ 20%), $E_t \approx 2E_i$. This was due to that E_i and E_p had approximately the same value. In the upper shelf of the fracture energy ($\chi > 40$) E_p was of higher order of magnitude than E_i.

4. Discussion

The effects of the PVDF content on the fracture energies were analyzed for %F ≥ 50 corresponding to $\chi \geq 14\%$. Depending on the selected fracture parameter, the observed gain in fracture energy may significantly differ in their absolute value (factor 10). Indeed, a jump in the total fracture energy E_t was clearly established whereas a smoother increase in E_i was evidenced at the same time. It should be recalled that E_t is representative of the Charpy impact strength. The "gain in toughness" observed for both parameters was shown to be of the same order of magnitude. In practice, the shape of E_t suggests that the degree of crystallinity corresponding to the brittle to ductile transition was estimated at about $\chi = 23\%$. Around this transition, E_t value drastically increased from 0.13 kJ/m^2 to 5.3kJ/m^2 (factor 40). It is to be noted that for higher values of χ, E_t was still growing from 5.3 kJ/m^2 to 29 kJ/m^2.

For the fracture toughness parameter E_i, a slight and progressive transition was observed at χ values ranging from 30% to 45%. In this χ range, E_i increased from 0.08 kJ/m^2 to 1.2 kJ/m^2 (factor 10).

5. Conclusion

Consideration of the blends of PVDF and PMMA all over the composition range proved to be a powerful tool to assess the characteristics that govern the fracture behavior of polymers. The amorphous blends (PMMA-rich materials) corresponding to PVDF content lower than 50% exhibited zero degree of crystallinity, low values of fracture energy and no particular pattern on their fracture surfaces. They were not taken under consideration in this work.

The PVDF-richer blends exhibited higher degrees of crystallinity $\chi \geq 14\%$. The fracture surfaces issued from tested SENB samples showed dimples characteristics of semi-crystalline polymers. Transitions from brittle to ductile fracture behavior of these semi-crystalline blends were identified, in terms of critical degree of crystallinity χ. The value of such a transition was found to depend on the fracture mechanics parameter: either the fracture toughness (fracture energy to crack initiation E_i) or the equivalent of the Charpy impact strength in quasi-static case (total fracture energy E_t).

The transition for E_i and E_t was estimated at $\chi \sim 38\%$ and $\chi = 23\%$, respectively. At these χ-transitions, E_i was found to increase from 0.08 kJ/m^2 to 1.2 kJ/m^2 (factor 10) whereas E_t jumped from 0.13 kJ/m^2 to 5.3kJ/m^2 (factor 40).

Acknowledgements

The authors would like to acknowledge Julie Heurtel (Mines ParisTech) for technical support.

References

[1] L. Laiarinandrasana, Y. Nziakou, J.L. Halary, Fracture behavior of amorphous and semi-crystalline blends of poly(vinylidene fluoride) and poly(methyl methacrylate). Journal of Polymer Science Part B: Polymer Physics, 50 (2012) 1740-1747.

[2] J.D. Landes, J.A. Begley, Fracture Analysis, STP 560. American Society for Testing Analysis. Philadelphia 1974, pp. 170-186.

[3] L.C.A. Folch, F.M. Burdekin, Application of coupled brittle–ductile model to study correlation between Charpy energy and fracture toughness values. Engineering Fracture Mechanics 63 (1999), 57-80.

[4] A. Rossol, C. Berdin, C. Prioul, Determination of the fracture toughness of a low alloy steel by the instrumented Charpy impact test. International Journal of Fracture, 115 (2002) 205-226

[5] B. Tanguy, C. Bouchet, S. Bugat, J. Besson, Local approach to fracture based prediction of the ΔT_{56J} and ΔT_{KIc100} shifts due to irradiation for an A508 pressure vessel steel. Engineering Fracture Mechanics 73 (2006) 191-206