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In situ AFM investigation of slow crack propagation mechanisms in a glassy polymer

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Abstract

A novel experimental technique based on *in situ* AFM monitoring of the mechanisms of damage and the strain fields associated to the slow steady-state propagation of a fracture in glassy polymers is presented. This micron-scale investigation is complemented by optical measurements of the sample deformation up to the millimetric macroscopic scale of the sample in order to assess the proper crack driving conditions. These multi-scale observations provide important insights towards the modeling of the fracture toughness of glassy polymers and its relationship with the macromolecular structure and non-linear rheological properties. This novel technique is first tested on a standard PMMA thermoplastic in order to both evaluate its performance and the richness of this new kind of observations. Although the fracture propagation in PMMA is well known to proceed through crazing in the bulk of the samples, our observations provide a clear description and quantitative evaluation of a change of fracture mechanism towards shear yielding fracture accompanied by local necking close to the free surface of the sample, which can be explained by the local change of stress triaxiality. Moreover, this primary surface necking mechanism is shown to be accompanied by a network of secondary grooves that can be related to surface crazes propagating towards the interior of the sample. This overall scenario is validated by post-mortem fractographic investigations by scanning electron microscopy.

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1. Introduction

Glassy polymers are widespread in technical and structural applications since the 30's due to their excellent mechanical properties, combined with low mass density and ease of implementation. Although their elastic moduli and yield strength are lower than other structural materials such as glasses or metals, glassy polymers possess a relatively high fracture toughness. This results from a combination of plastic deformation and the occurrence of several localization mechanisms such as crazing and shear banding (Donald and Kramer, 1982). Extensive studies have been devoted to the modeling of the relation between the mechanical properties and the material composition and microstructure. Their main aim was combining contributions from both macroscopic constitutive laws, mesoscale damage mechanisms and molecular issues (Williams, 1984; Brown, 1991; Réthoré and Estevez, 2013; Halary *et al.*, 2011).

Although glassy polymers (i.e. with a glass transition temperature well above ambient temperature) can belong to different families with different macromolecular structures such as thermoplastics, thermosets and semicrystalline polymers, their macroscopic mechanical properties are qualitatively quite similar up to yield condition. These materials have a typical elastic modulus of $E \approx 1$ GPa, a yield strength of about $\sigma_y \approx 100$ MPa, and a fracture toughness of about $K_c \approx 1$ MPa $\sqrt{\text{m}}$. The size of the inelastic process zone at the crack tip is thus of the order of magnitude of the Dugdale length:

$$\ell_D = \chi \frac{K_c^2}{\sigma_y^2} \approx 15 \div 40 \mu\text{m}$$

where χ ranges between $1/2\pi \simeq 0.16$ and $\pi/8 \simeq 0.39$ depending on the choice of a circular (McClintock and Irwin, 1964) or elongated (Dugdale, 1960) process zone.

It is thus possible to use the tools of Linear Elastic Fracture Mechanics (LEFM) on typical laboratory fracture specimens of centimeter size. Although the materials of this class share similar properties on scales larger than ℓ_D , the nature of the inelastic processes occurring in the process zone can be very different depending on the nature and structure of the macromolecular network, which results in a very different large strain behaviour. The kinetics of crack propagation can also

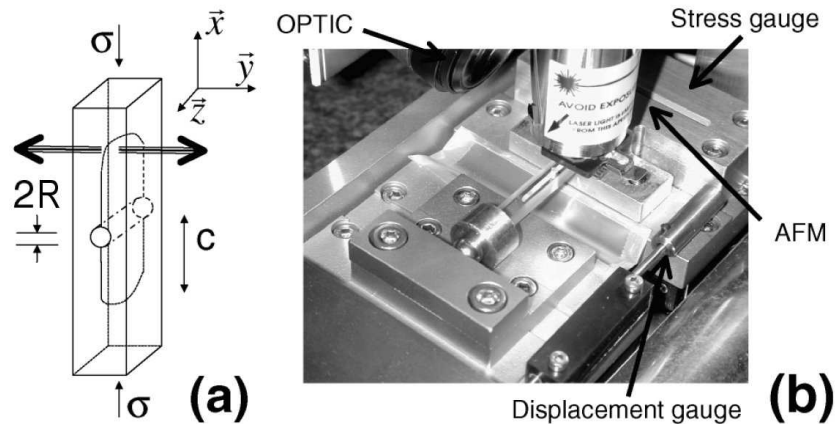


Figure 1: Experimental setup: (a) Sketch of the DCDC geometry; (b) picture of the experiment, including the DCDC sample on a loading stage under the AFM probe.

23 be very variable, changing from very stable steady-state crack propagation over a
 24 wide range of velocities in thermoplastics to jerky stick-slip fracture propagation
 25 in thermosets. Understanding and engineering the toughness of these polymers
 26 relies on the ability of describing and modeling the bulk deformation and energy
 27 dissipation mechanisms at the process zone scale, which is micrometric in size.
 28 This makes Atomic Force Microscopy (AFM) *in situ* investigations an ideal tool.

29 An adequate description of the deformation mechanisms requires the obser-
 30 vation of a well conditioned steady-state propagating fracture. This allows the
 31 energy flow to be coherently defined from the macroscopic scale of the loading
 32 stage down to the ultimate molecular failure scale. This novel technique exploits
 33 the combination of an AFM (Bruker ICON, Santa Barbara, USA) with a very
 34 stable and compact *in situ* loading configuration (Fig. 1) based on the Double
 35 Cleavage Drilled Compression (DCDC) sample (Janssen 1974) and a very stiff
 36 and compact loading stage (Deben Microtest, Woolpit, UK). The macroscopic na-
 37 ture of the sample and its excellent stability allow obtaining a well defined mode
 38 I loading and a very straight crack path. This allows for a very stable steady-state
 39 fracture propagation in materials where the fracture toughness K_c can be expressed
 40 as an increasing function of the crack propagation velocity v , such as thermoplas-
 41 tic glassy polymers. The two main constraints arising in this local probe investiga-
 42 tion are (1) that crack propagation is limited to slow velocities (between pm/s and
 43 nm/s) and (2) that observations are limited to the free surface of the sample. This
 44 technique was initially developed and extensively studied on more brittle materi-

45 als such as oxide glasses (Janssen, 1974; He *et al.*, 1995; Pallares *et al.*, 2009).
46 It has already provided enlightening information on the nanoscale mechanisms of
47 stress-corrosion during sub-critical crack propagation (Ciccotti, 2009; Pallares *et al.*,
48 *et al.*, 2015), including the relevance of crack tip plasticity (Han *et al.*, 2010), stress
49 induced ion exchange processes (Célarié *et al.*, 2007) and capillary condensation
50 in the crack tip cavity (Grimaldi *et al.*, 2008; Pallares *et al.*, 2011). An extension
51 of this technique is presented here for glassy polymers, where the use of DCDC
52 samples has been until recently hampered due to the difficulty of preventing buck-
53 ling and plastic yielding of the sample, which is loaded in compression (Plaisted
54 *et al.*, 2006).

55 The present study is focused on the study of PMMA since its mechanical and
56 fracture properties have been widely characterized. Slow crack propagation in
57 PMMA at ambient conditions has long been known to be dominated by crazing
58 on a micrometric region close to the crack tip. This consists of nanometric fibrils
59 being nucleated and drawn across the crack lips and providing extensive energy
60 dissipation and crack propagation resistance (Doll, 1983; Kramer, 1983). How-
61 ever, while the crazing mechanism is well established in the bulk of the sample,
62 i.e. in the center of the crack front, where the plane-strain condition induces a high
63 degree of stress triaxiality¹, its occurrence at the free surface of the sample is ques-
64 tionable due to the local reduction of the hydrostatic stress (Argon and Hannoosh,
65 1977; Kramer, 1983; Si *et al.*, 2005). Our *in situ* AFM observations at the free
66 surface of the sample show evidence of a transition in the fracture mechanism to-
67 wards shear yielding in a surface layer of about 10 μm thickness. While the large 4
68 mm thickness of the sample allows the experimental investigation of this interest-
69 ing change of mechanism in a well conditioned mechanical loading, this boundary
70 effect can become very important for understanding fracture propagation in thin
71 samples of few tens of μm thickness.

72 The manuscript is organized as follows. Section 2 reports the developments
73 of the DCDC technique required to obtain a well conditioned steady-state crack
74 propagation in glassy polymers. Section 3 reports the optical measurements re-
75 quired to characterize both the crack propagation kinetics and the strategy adopted
76 to estimate the stress intensity factor for partially yielding samples. Section 4 re-
77 ports the in-situ AFM investigation of the strain fields in a 40 μm wide region
78 progressively crossed by the process zone. The observed main necking region

¹Stress triaxiality is defined as $\psi = \sigma_m/\sigma_d$, where σ_m is the hydrostatic stress and σ_d is the equivalent Von Mises stress, which represents the shear stress (Lemaitre and Chaboche, 1990).

79 and secondary grooves are discussed and interpreted in terms of past knowledge
 80 on the physics and mechanics of inelastic processes occurring in the process zone
 81 for PMMA. Section 5 provides an overview of the potential of this novel investi-
 82 gation technique on a thermoset polymer. Section 6 drives the conclusions con-
 83 cerning both the novel experimental technique and the interesting observations on
 84 the surface features of fracture propagation in PMMA.

85 **2. Development of the DCDC technique for glassy polymers**

86 *2.1. Classic fracture mechanics of the DCDC sample for brittle samples*

87 The DCDC sample was initially developed by Janssen (1974) to study slow
 88 fracture in silicate glasses, which possess very high values for both Young mod-
 89 ulus $E \approx 70$ GPa and yield strength $\sigma_y \approx 10$ GPa. The sample (Fig. 1a) consists
 90 of a prism of dimensions $2L \times 2w \times 2t$ (corresponding to x, y, z directions) with
 91 a cylindrical cross hole of radius R drilled through the specimen thickness $2t$.
 92 The sample is loaded with a compressive force F , and thus a compressive stress
 93 $\sigma = F/4wt$ applied to the two opposite faces. This induces a tensile stress at the
 94 two poles of the central hole aligned with the sample loading direction. During
 95 the test in stiff and hard materials like glass, two symmetric cracks of length c
 96 are spontaneously nucleated at the crown of the central hole. The two cracks then
 97 propagate in opposite directions along the midplane of the sample (direction x
 98 in the $x - z$ plane), driven by the mode I opening induced at the crack tip.

99 In these very brittle materials the sample deformation is essentially linear elas-
 100 tic. The stress intensity factor has been derived by several authors via finite ele-
 101 ment simulations (Janssen, 1974; Michalske *et al.*, 1993; He *et al.*, 1995; Pallares
 102 *et al.*, 2009). When the crack tip is at a sufficient distance ($> w$) from the central
 103 hole and the sample ends, the mode I stress intensity factor can be expressed in
 104 the general form:

$$K_I = \sigma \sqrt{R} f\left(\frac{c}{R}, \frac{w}{R}\right) \quad (1)$$

105 where f is a decreasing function of the crack length c and the sample width w .
 106 Several different analytical approximations have been proposed for the function f
 107 by the authors cited above. Crack propagation is thus very stable at both imposed
 108 load and imposed displacement ($dK_I/dc < 0$). Moreover, the DCDC configuration
 109 presents an excellent directional stability of the straight crack propagation. This
 110 is due to the strongly negative values the T stress induced at the crack tip by the
 111 applied compression (Fett *et al.*, 2005).

112 The toughness of materials presenting sub-critical crack propagation is char-
 113 acterized by a $K_{Ic}(v)$ with positive slope as a function of the velocity v up to a
 114 critical velocity v_c where crack propagation undergoes an instability towards dy-
 115 namic propagation. When using the DCDC sample to study sub-critical propaga-
 116 tion with a constant applied displacement, the crack progressively slows down as
 117 a consequence of the increase of the crack length. This allows to progressively
 118 reach very slow velocities without any activation of the loading stage. At the
 119 very low crack propagation velocities required by AFM observations (below 10
 120 nm/s = 36 $\mu\text{m/h}$), the variations of the crack length c , and consequently of K_I , are
 121 very weak. A steady-state propagation in very pure asymptotic mode I loading
 122 ($K_{II}/K_I \leq 5\%$) can thus be observed over conveniently long *in situ* investigations
 123 : a few days or weeks depending on the crack propagation velocity.

124 2.2. Crack initiation for glassy polymers and geometrical optimization

125 The application of the DCDC configuration to glassy polymers implies sev-
 126 eral issues since these materials are less stiff ($E \approx 1$ GPa) and less hard ($\sigma_y \approx 100$
 127 MPa) than silicate glasses. Moreover they present a slow viscoelastic relaxation
 128 at macroscopic scale. These materials are not brittle enough to provide a sponta-
 129 neous crack initiation from the central hole. Even when the two cracks are well es-
 130 tablished, their steady-state propagation should be attained while limiting as much
 131 as possible the buckling and yielding of the sample at macroscopic scale. Last,
 132 but not least, the estimation of the stress intensity factor acting at the crack tip
 133 is made considerably more difficult by the occurrence of stress relaxation, larger
 134 deformations and plastic yield due to the shear stress concentration in the region
 135 of the central hole.

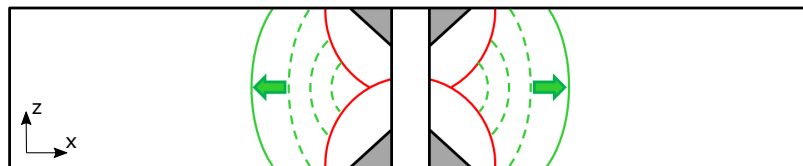


Figure 2: Two step initiation of the DCDC cracks in glassy polymers. The indented triangular blades (grey) induce the pop-in of the two penny shape cracks (red). The loading of the DCDC sample induces the development of the two parabolic propagating cracks (green).

136 The crack initiation was implemented with the help of an instrumented razor
 137 blade (Nziakou, 2015) by developing the techniques proposed by Idonije *et al.*
 138 (1993) and Plaisted *et al.* (2006). In a first step, two sharp triangular blades were

139 indented at each side of the central hole up to obtaining pop-in of two penny shape
140 cracks that merge in the middle of the sample (in red in Fig. 2). In a second step
141 the DCDC sample is preloaded in its standard configuration in order to obtain the
142 full coalescence of the penny cracks. This leads to the development of the two
143 typical DCDC cracks with parabolic crack front (in green in Fig. 2).

144 In order to minimize buckling and yielding during crack propagation while
145 preserving the small sample dimension required by our *in situ* AFM investigation,
146 the scaling of Eq. (1) allows to optimize the sample dimensions. PMMA has a
147 similar toughness K_{Ic} to glass, but lower values for the stiffness and yield strength.
148 Eq. (1) suggests that the K_I/σ ratio can be increased by increasing the radius R
149 of the central hole. To preserve the scaling of eq. (1), the sample width $2w$ and
150 the crack length c should also be increased in a proportional way. The sample
151 thickness $2t$ is not implied in eq. (1), so we used the maximum value allowed by
152 our loading stage. The sample dimensions selected for the present investigation
153 are $2L = 45$ mm, $2w = 7.2$ mm, $2t = 4.95$ mm and $R = 1.2$ mm. The stable
154 propagation of very straight cracks with slow velocities in the desired range for
155 AFM investigation was achieved, presenting steady-state conditions over several
156 days.

157 2.3. Strategies of evaluation of K_I for glassy polymers

158 The rest of this section is dedicated to the discussion of the evaluation of K_I on
159 DCDC samples made of glassy polymers by treating in an independent way the
160 occurrence at the macroscopic scale of stress relaxation, finite strain and plastic
161 yield of the sample.

162 2.3.1. Macroscopic stress relaxation

163 In the case where macroscopic stress relaxation is the only issue, the relax-
164 ation following the initial loading of the sample up to a fixed displacement can be
165 treated by considering an elastic modulus $E(t)$ that weakly diminishes with time.
166 In this case, equation (1) can be used for the calculation of K_I from a direct mea-
167 surement of the applied force F (Marshall *et al.*, 1974). From a practical point of
168 view, for very slow propagating cracks, this can lead to a progressive reduction of
169 K_I (and thus of the crack velocity) even when the variation of the crack length is
170 not appreciable on a macroscopic scale.

171 2.3.2. Large strain in DCDC samples

172 Since the values of K_I for crack propagation in silicate and polymer glasses
173 are quite similar, while the elastic modulus of glassy polymers is about 100 times

174 smaller, the strain field and the associated displacements are 100 times larger. In
175 particular, the compressive displacement applied to the sample is about 1 mm and
176 the crack opening at the intersection with the central hole can reach 1 mm, which
177 leads to an appreciable deformation of our samples (cf. Fig. 3), and makes the
178 use of the linear equation (1) questionable. An alternative modeling has been pro-
179 posed by Plaisted *et al.* (2006) based on the elastic buckling of the two beams
180 surrounding the full crack length (outward buckling in direction y in Fig. 3). This
181 model results in K_I values that are proportional on the applied stress σ , but inde-
182 pendent of the crack length c . While the predicted values of K_I are comparable
183 to those given by eq. (1) for short cracks, they are larger for longer cracks. This
184 model was tested by Plaisted *et al.* (2006) on crack arrest tests on PMMA, but it
185 does not provide consistent values in our steady-state tests, and remains question-
186 able since both relaxation and yielding are neglected.

187 2.3.3. *Local strategy to handle plastic yielding in DCDC samples*

188 If the plastic yielding was limited to the the process zone of micrometric size
189 close to the crack tip, small scale yielding conditions would allow the use of
190 LEFM and eq. (1) for the calculation of K_I on our centimeter sized DCDC sam-
191 ples. However, in the case of a plastic yield on a more macroscopic region the non-
192 linear structural response of the DCDC sample should be evaluated by a different
193 elasto-plastic modeling. Due to the stress concentration induced by the presence
194 of the central hole, both the plastic yield and large strains remain confined in the
195 two ligaments around the central hole, as confirmed by empirical considerations
196 on our DCDC samples (cf. Fig. 3). The effect of a plastic yielding of the ligaments
197 around the central hole would lead to almost constant bending moments applied
198 to each of the elastic dual cantilever systems, and thus to an equation for K_I that is
199 once again almost independent on the crack length (Hutchinson and Suo, 1992).
200 Based on these considerations, we derive here a technique for the estimation of
201 K_I based on a local measurement of the crack opening profile $u_y(X)$ over an inter-
202 mediate scale range where the material response is neither affected by crack tip
203 inelastic processes nor by the plastic yield around the hole. LEFM solutions are
204 thus applicable to evaluate the value of K_I applied to the process zone from these
205 intermediates scale measurements.

206 In a previous work (Pallares *et al.*, 2009) it was shown by finite element sim-
207 ulation that for an elastic DCDC sample, the crack opening profile $u_y(X)$ over a
208 distance from the crack tip less than the specimen half-width ($X < 0.85w$) can
209 be written in terms of a Williams expansion with invariant coefficients for all the

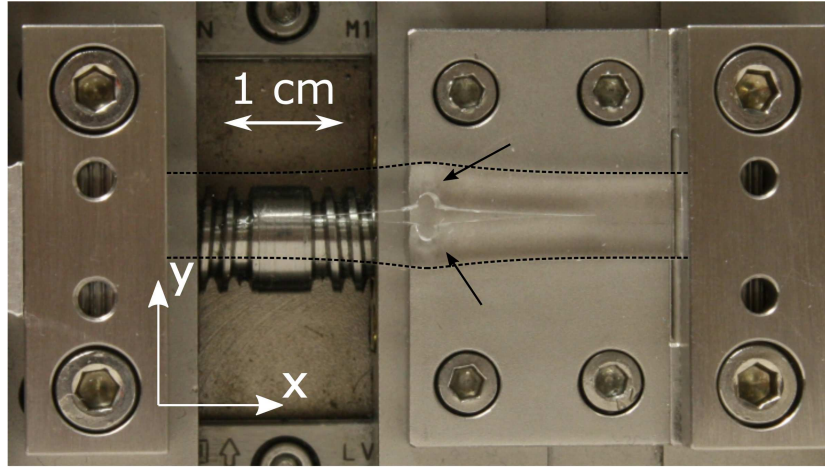


Figure 3: PMMA DCDC sample under load. The black arrows indicate local large strain regions close to the central hole.

210 specimen geometries and crack lengths analyzed:

$$u_y(X) = p \sqrt{X} \left(1 + 1.319 \left(\frac{X}{w} \right) + 0.515 \left(\frac{X}{w} \right)^2 \right) \quad (2)$$

211

$$p = \frac{K_I}{E'} \sqrt{\frac{8}{\pi}} \quad (3)$$

212 where $E' = E/(1 - \nu^2)$ because plane-strain conditions are dominant in our speci-
 213 men. Since the region of validity of this expression (2 mm here) remains elastic in
 214 our PMMA specimens, we can extend its application to our experiments for eval-
 215 uating the stress intensity factor from the crack opening displacement measured
 216 in this intermediate region. In the presence of a significant stress relaxation, the
 217 evaluation of K_I from the crack opening profile would require a suited evaluation
 218 of the relaxation modulus $E(t)$.

219 Since the relative importance of stress relaxation, finite strain and plastic yield
 220 can change between different glassy polymers, the choice of the appropriate method
 221 for the estimation of K_I should be evaluated and discussed in each case. In the
 222 present paper the application to PMMA will be discussed in detail based on our
 223 experimental results and on the comparison with values reported in the literature.

224 3. Crack propagation results of PMMA samples

225 This section will be devoted to the application of the techniques developed to
226 obtain a controlled crack propagation in DCDC samples made of PMMA, and to
227 perform an appropriate evaluation of the corresponding values of K_I . The mea-
228 sured $K_{Ic}(v)$ curve is then validated against measurements available in the litera-
229 ture for similar grades of PMMA.

230 3.1. Material properties and crack propagation kinetics

231 The material used is a commercial grade of PMMA with very low additive
232 content. The glass transition temperature is $T_g = 122^\circ\text{C}$ as measured by Differ-
233 ential Scanning Calorimetry (DSC), the average molecular weight is $M_w = 1200$
234 kg/mol with polydispersity 1.7 as measured by Gel Permeation Chromatography
235 (GPC), the density is $\rho = 1180 \text{ kg/m}^3$ after Nziakou (2015).

236 During our experimental campaign we could obtain a successful crack initia-
237 tion and well conditioned steady-state crack propagation over four different sam-
238 ples of PMMA. The quality of the crack propagation was assessed by evaluating
239 the degree of symmetry of the crack along each of the three symmetry axes of
240 the DCDC sample: weak deviation ($y < 100 \mu\text{m}$) of the crack plane from the
241 mid plane (xz), small difference in length between the two propagating cracks
242 ($\Delta c < 100 \mu\text{m}$), good centering and weak tilt of the parabolic crack fronts (the
243 position where the green fronts in Fig. 2 intersect the two external surfaces should
244 not differ more than $100 \mu\text{m}$). This latest point is a very sensitive test against
245 the occurrence of buckling in a direction y perpendicular to the loading direction
246 x . Despite the optimization of the sample dimensions, a close inspection of our
247 loaded DCDC samples reveals the presence of macroscopic bulk plastic yield-
248 ing in the region of the central hole, with an extension limited to the millimetric
249 size of the hole (cf. Fig. 3). Crack propagation was performed at ambient condi-
250 tions ($T = 23 \pm 2^\circ\text{C}$, $RH = 35 \pm 10\%$). By applying forces ranging between
251 900 and 1200 N (± 4 N) crack propagation velocities were spanned over a large
252 range (10^{-10} m/s to 10^{-5} m/s) measured by combining *in situ* AFM and optical
253 microscopy observations (cf. Fig. 4). Each sample provided a very large amount
254 of measurements over the available range of crack length c between 4 and 12 mm.

255 3.2. Evaluation of K_I for PMMA samples

256 In light of the macroscopic yield region observed in the neighborhood of the
257 central hole (cf. Fig. 3), K_I was estimated using the local strategy presented in
258 section 2.3.3, based on the measurement of the crack opening profiles. Since the

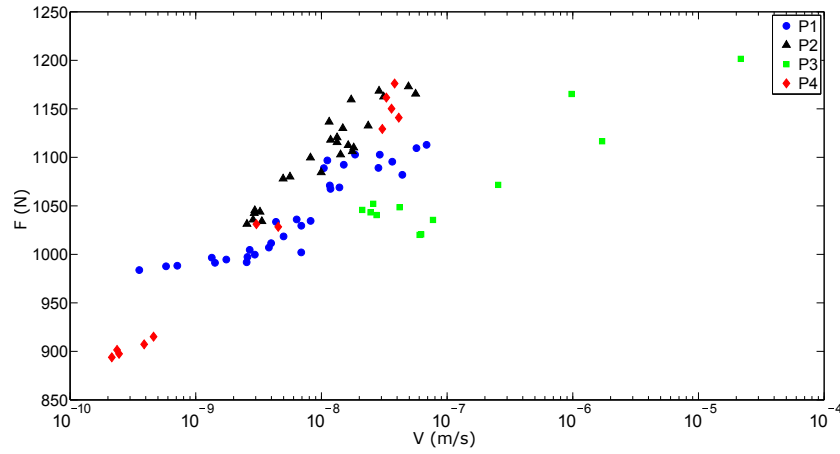


Figure 4: Measurements of the crack velocities and applied forces for the four different samples (named in the legend). Most measurements of crack velocities are performed by optical microscopy on series of $140\ \mu\text{m}$ sized images. The velocities below $5 \cdot 10^{-9}\ \text{m/s}$ are measured by AFM on series of 40 or $10\ \mu\text{m}$ wide images.

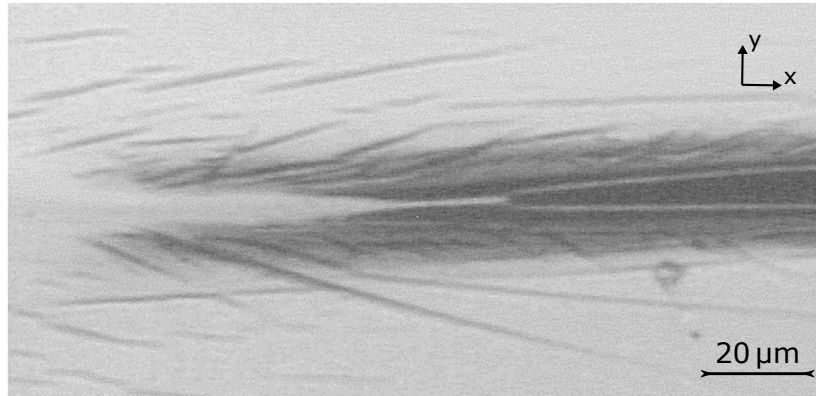


Figure 5: Neighborhood of the crack tip imaged by light reflection. The crack propagates towards the left of the image (x direction). The crack opening profile in the right of the picture is identified by the bright line surrounding the black crack cavity. The elongated dark and bright regions surrounding and extending the crack cavity represent an extended necking region as confirmed by AFM measurements in section 4.2. The dark lateral portions represent strongly tilted side walls where the incident light is reflected out of the camera objective, while the bright regions represent flat zones that cause direct light reflection into the camera objective. The gray tilted lines represent secondary surface grooves as confirmed by AFM measurements in section 4.3. A full movie corresponding to several hours of steady state propagation can be found in the supplementary information (SI).

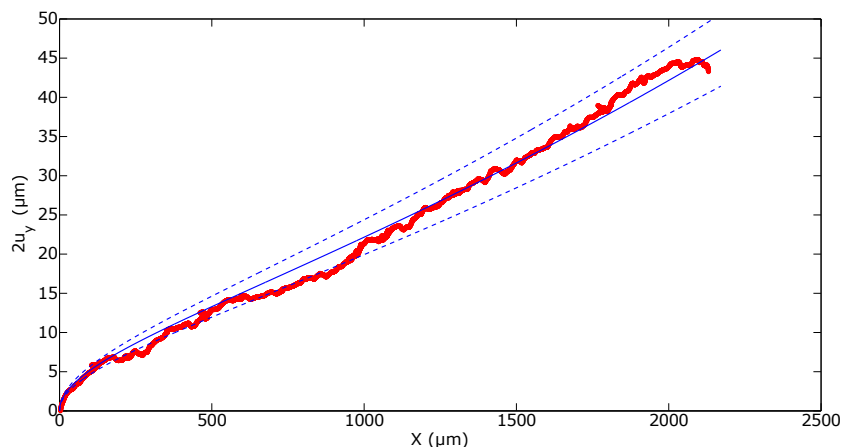


Figure 6: Crack opening profile measured by optical microscopy (red line), calculated as the vertical distance $2u_y$ between the two bright lines surrounding the black crack cavity in Fig. 5 as a function of the distance X from the crack tip. The blue line represents the least square linear fit through eq. (2) and the blue dashed lines represent a $\pm 10\%$ variation on the fitted parameter p .

259 sample width is $2w = (7.2 \pm 0.1)$ mm, the crack opening profiles $u_y(X)$ were
 260 measured over the region of validity $X < 2$ mm of the Williams expansion (Eq. 2)
 261 starting at the crack tip. Because of the very small crack opening ($< 100 \mu\text{m}$) the
 262 measurement was performed by combining several overlapped optical microscope
 263 images of $140 \mu\text{m}$ width of the free surface of the sample, such as the one in
 264 Fig. 5. The crack opening profile was measured by detecting the position of the
 265 bright line surrounding the open crack. A calibration of this observable against
 266 AFM measurements over the accessible region of $300 \mu\text{m}$ from the crack tip (cf.
 267 Nziakou, 2015) allowed to obtain accurate crack opening profiles such as the one
 268 plotted in Fig. 6. The obtained profiles are well described by the fit through the
 269 Williams expansion of Eq. (2) (blue line in Fig. 6), which has a single adjustable
 270 parameter p related to its opening. The precision on the measurement of p can be
 271 estimated to be $\pm 10\%$. This is due to the limited resolution of the optical images,
 272 which are perturbed by the presence of the extended damaged zone at the surface
 273 of the DCDC sample. Since the expected variations of K_{Ic} for PMMA over the
 274 measured slow velocity range is very weak (cf. data from Doll, 1983, reported in
 275 Fig. 7), the precision of the local crack opening technique reveals to be insufficient
 276 for an accurate measurement of the dependence of K_{Ic} on v .

277 On the other hand, the resolution of the force measurements is clearly higher
 278 (± 4 N) and their correlation with the velocity measurements is clearly apparent,
 279 as observed in Fig. 4. The choice was made to use a hybrid approach to take

280 the best party of all available measurements: (1) using the measured crack open-
281 ing profiles to set the average value of K_I during all our experiments on the four
282 PMMA samples reported in Fig. 7 and (2) using the force measurements in order
283 to estimate the slope of the $K_{Ic}(v)$ curves reported in Fig. 7. The assumption of
284 the proportionality between K_I and F is consistent with both the arguments of
285 Plaisted *et al.* (2006) and Hutchinson and Suo (1992) that support a weak or van-
286 ishing dependence of K_I over the crack length c due to large strain and yield near
287 the central hole of the sample.

288 In order to relate the average measured opening $\langle p \rangle = (4.8 \pm 0.5) \cdot 10^{-4} \text{ m}^{1/2}$
289 to the average stress intensity factor $\langle K_I \rangle$ through Eq. (3), an appropriate value
290 of the elastic modulus has to be estimated. Since our crack propagation tests are
291 very slow and cover several days, it is appropriate to chose the relaxed modulus of
292 PMMA at ambient temperature. This can be estimated by the Dynamic Mechan-
293 ical Analysis (DMA) measurement at 1 Hz ($E = 2.4 \pm 0.2 \text{ GPa}$, $\nu = 0.35 \pm 0.03$,
294 according to Nziakou, 2015) since most of the β relaxation of PMMA occurs at
295 higher frequencies in the 100 Hz range and further long term relaxation can be
296 estimated to less than 10% (Halary, 2011). The average stress intensity factor ob-
297 tained through eq. (3) is $\langle K_{Ic} \rangle = (0.8 \pm 0.1) \text{ MPa m}^{1/2}$. The $K_{Ic}(v)$ curve plotted
298 in Fig. 7 is thus obtained by renormalizing the force data in Fig. 4 by the relation
299 $K_{Ic} = F(\langle K_{Ic} \rangle / \langle F \rangle)$, where $\langle F \rangle = (1000 \pm 100) \text{ N}$ is the average value of
300 the measured force over the same set of data. The $K_{Ic}(v)$ data from the literature
301 are also plotted to show the good consistency within the expected 10% accuracy.

302 The precision of the technique should be improved in the future for providing
303 more accurate measurements of the $K_{Ic}(v)$ curves of glassy polymers, which only
304 present weak velocity dependence at ambient temperature. However, the main
305 purpose of this section is to prove that we can robustly obtain a well conditioned
306 steady-state slow crack propagation regime and to control the crack propagation
307 over several orders of magnitude of velocity. This insures the good conditions for
308 the *in situ* AFM investigations presented in the next section.

309 4. AFM investigation

310 4.1. Evaluation of the strain fields in the process zone

311 4.1.1. Qualitative observation of the AFM data

312 Optical microscopy (cf. Fig. 5 and movie in SI) revealed that steady-state crack
313 propagation is accompanied by a whole range of localized damage processes at
314 the free surface of the sample, extending over a large neighborhood of the crack
315 tip. To get a more accurate observation of the process zone and of this secondary

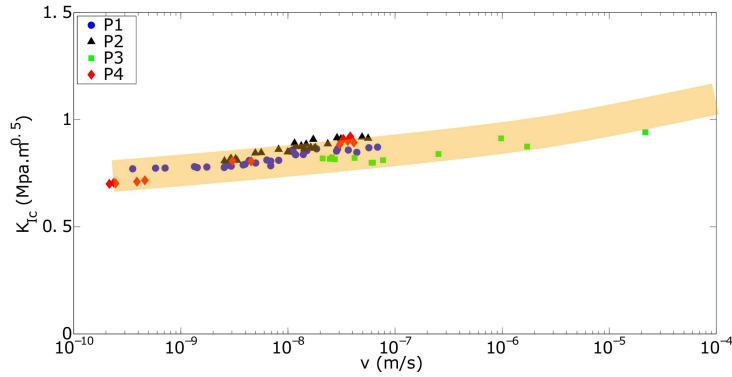


Figure 7: $K_{Ic}(v)$ data for PMMA obtained by the present technique compared with data from Doll (1983), within the estimated 10% accuracy (orange band).

316 damage zone occurring at the free surface of the DCDC sample (cf. Fig. 1), AFM
 317 images of $40 \times 40 \mu\text{m}^2$ size were acquired in contact mode² in the crack tip region
 318 providing topographic images such as shown in Fig. 8. The height resolution
 319 of 0.2 nm is very small in front of the height variations in the crack tip region,
 320 which approach the maximum height range of $7 \mu\text{m}$ achievable on a single AFM
 321 image. The lateral resolution is generally provided by the size of AFM tip, which
 322 is nominally of 10 nm, but it can quickly be worn to a few tens of nm during
 323 imaging. However in our $40 \mu\text{m}$ wide images (512×512 pixels²), it is limited by
 324 the 78 nm size of the pixels.

325 On the one hand, the black region surrounding the crack tip in the optical

²An AFM image is obtained by scanning a cantilever provided with a very sharp tip over a series of parallel lines that progressively form an image. When imaging in contact mode the AFM is in molecular repulsive contact with the sample surface and the deflection of the cantilever is measured to estimate the applied force. During the scan of each line, a feedback loop acts on the vertical position of the AFM head in order to keep the deflection of the cantilever constant to a given set point (Binnig and Quate, 1986). The resulting vertical position of the head during the scan is used to form a height image, which is essentially a topographic image, provided the sample is stiff enough like PMMA. A second kind of image is also provided by recording the error signal of the feedback loop, i.e. the difference between the measured deflection signal and its setpoint value. In case of perfect imaging this error image should be flat and close to zero. On a practical point of view, this image contains both the instrumental noise (0.2 nm) and a signal which is closely related to the derivative of the height image along the scanning direction. These images are particularly useful to highlight fine surface imperfections while getting rid of smooth height variations.

326 images (cf. Fig. 5) can be seen as resulting from an extended “necking” of the
327 free surface of the sample (a few micrometer deep), inside which a sharp crack
328 tip is propagating. On the other hand, the network of secondary dark lines that
329 were apparent on the optical images can be clearly interpreted as a series of minor
330 surface grooves of very shallow depth and small width superimposed to the main
331 necking region. Note that the very fine lines that can be distinguished on the AFM
332 images are surface scratches due to polishing of the sample surface prior to the
333 mechanical test.

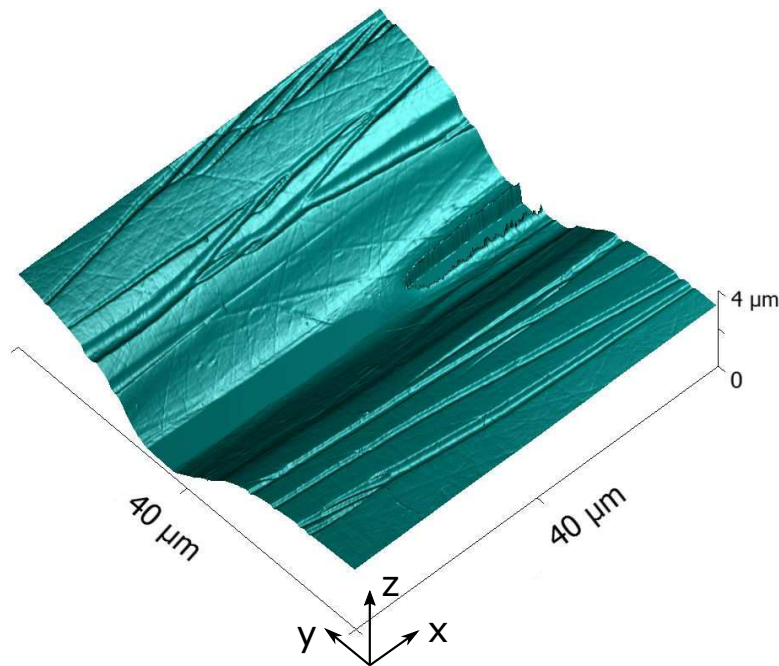


Figure 8: 3D representation of the topography of the crack tip region ($40 \times 40 \mu\text{m}^2$) measured by AFM at the free surface of the sample. Note that the aspect ratio of the vertical axis is exaggerated by a factor 2 for better appreciating the topography of the necking region.

334 The optical measurements reveal that the surface necking region at the free sur-
335 face of the sample extends about $300 \mu\text{m}$ ahead of the observed crack tip, which
336 is significantly larger than the typical $30\text{-}40 \mu\text{m}$ size generally observed for the
337 craze region in the middle of the sample (Doll, 1983). However, an enhancement
338 and potential modification of the mechanisms of crack plasticity at the free sur-
339 face should be expected (Kramer, 1983). In order to proceed to a more systematic
340 characterization of this extended process zone region over its whole size, we po-

341 sitioned the AFM scanning head in an initially unyielded region $300\ \mu\text{m}$ ahead of
342 a crack tip propagating at a few nm/s. A series of 150 AFM images of 40×40
343 μm^2 size (the largest scan size providing sufficient spatial resolution) was then
344 acquired every 15 minutes over a period of about 36 hours without moving the
345 scanning head position. The imaging ended after the crack tip had passed through
346 the imaging region and traveled $300\ \mu\text{m}$ ahead of it. Fig. 9 presents six of these im-
347 ages taken at different times during the propagation. The full movie can be found
348 in the supplementary information (SI). As detailed in footnote 2, the AFM height
349 images allow appreciating the real shape of the imaged surface, while the error
350 images provide flattened images that highlight fine surface features. During the
351 crack propagation, the main central necking gradually develops as a large valley
352 in front of the crack tip, about $20\ \mu\text{m}$ wide and $4\ \mu\text{m}$ deep. The secondary grooves
353 develop symmetrically on the two sides of the main necking and propagate for-
354 ward along with the region of first formation of the central necking (about 270
355 μm ahead of the crack tip). They thus appear to accommodate the surface stretch
356 that results along the banks of the main necking as its bed sinks down, as it will
357 be discussed in more details in section 4.3. It is worth noting that when explor-
358 ing the close neighborhood of the crack tip with small size high resolution AFM
359 images there is no clear evidence of fibrillar structures associated to crazing or to
360 other types of damage. However, this is not a strong proof because it is difficult
361 to ensure that the AFM tip doesn't wear to a radius comparable to the interfibril
362 spacing of about $30\ \text{nm}$.

363 Both the optical and AFM observations of the process zone region have been
364 repeated on the four PMMA samples presented in Fig. 7 and provided the same
365 kind of features. In the next two subsections we present a detailed analysis on the
366 sample P4 in order to extract more quantitative information on the strain fields.

367 *4.1.2. Characterization of the steady-state out-of-plane displacement field*

368 A progressive characterization of the plastic deformation field at different
369 scales is now discussed. The extreme stability of the steady-state propagation
370 of the crack in our experimental set up allowed to maintain a well conditioned
371 crack propagation over the 36 hours of measurements ($\langle V \rangle = 5 \pm 3\ \text{nm/s}$).

372 A great care was taken in reducing AFM drifts (less than $10\ \text{pm/s}$, correspond-
373 ing to $2\ \mu\text{m}$ drift over the three day measurements). All the images could thus be
374 recombined together to obtain a complete and accurate map of the out-of-plane
375 displacement field (direction z) of the free surface (Fig. 10) over a $640\ \mu\text{m}$ region
376 centered at the crack tip. This region contains both the full necking region in front

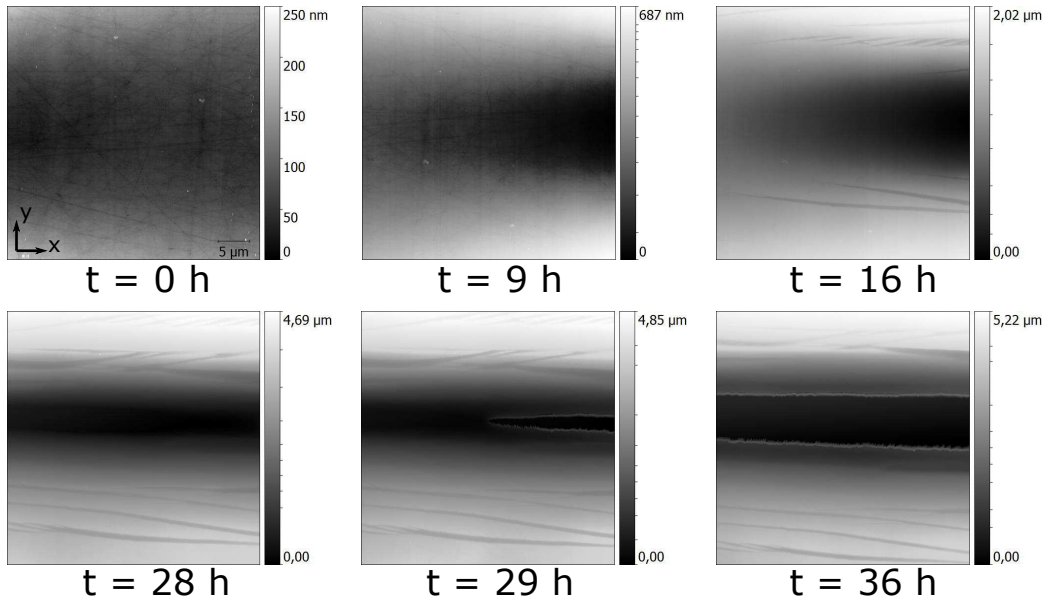


Figure 9: AFM topographical (height) images acquired at 6 different times t during the crack propagation. The full 150 frames movie is available in the SI.

377 of the crack tip and a portion of the crack opening profile.³ It is worth mentioning
 378 that because the initial surface was flat, this displacement field is also the mean
 379 topography in the reference frame of the crack tip. Since the large displacement
 380 field associated to the central necking is propagating along with the crack, the lat-
 381 eral grooves, which are stuck in the material reference frame after their formation,
 382 are averaged out by the reconstruction procedure.

383 The first important remark is that the depression of the free surface caused by
 384 the crack tip stresses has a very elongated shape, extended over $300 \mu\text{m}$ ahead
 385 of the crack tip and with a lateral span of only $20 \mu\text{m}$. This is very different

³The acquisition time of each AFM scan line (perpendicular to the crack axis) is combined with the measurement of the crack propagation velocity in order to determine precisely the distance X of the given line from the crack tip position. The full field reconstruction in Fig. 10 results from the juxtaposition of all the measured profiles. Each portion of the steady-state displacement field is thus measured several times on different images. More precisely, since the crack tip field moves in average of $4.5 \mu\text{m}$ in the x direction between two images, there is a 89% overlap between consecutive images. Each region of the steady-state displacement field is thus measured in average 8 to 9 different times, except near the boundaries of the image series, i.e. in the more distant regions from the crack tip.

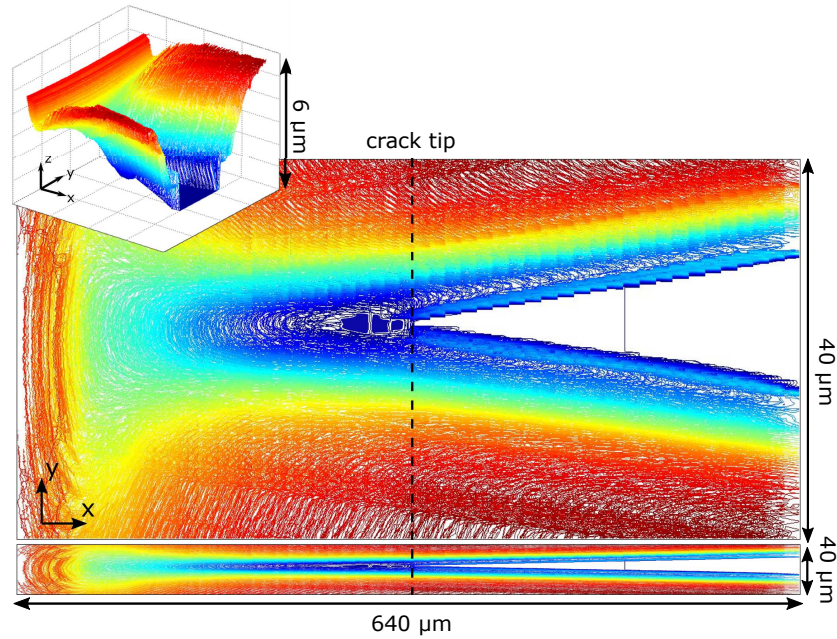


Figure 10: AFM reconstruction of the out-of-plane displacement field of the free surface around the crack tip, top view (the color bar spans $6 \mu\text{m}$). The left insert represents a 3D view to appreciate the vertical scaling. Bottom insert represents the top view with the real aspect ratio. It should be noticed that the blue saturated region ahead of the crack tip in the central figure corresponds to the maximum measurable depth allowed by the vertical scan size of the AFM during a uniform image series.

386 from what was previously observed on DCDC samples made of silicate glasses
 387 (Pallares *et al.*, 2015), where the surface depression region has a more rounded
 388 shape centered at the crack tip on a millimetric scale. In the case of silicate glasses,
 389 comparison with numerical simulations and AFM measurements showed that the
 390 surface depression can be fully described by linear elastic crack tip fields down
 391 to 10 nm from the crack tip (Han *et al.*, 2010). The change of shape as revealed
 392 by the out-of-plane surface displacement field observed in PMMA involves large
 393 strains at a much larger scale ($\sim 100 \mu\text{m}$). The “permanence” of this surface shape
 394 change at the crack lips can be seen through the fact that the height depression
 395 remains constant after the crack tip has passed through and the associated stresses
 396 are released along the crack lips. In other words, the topography on the right of the
 397 crack tip in Fig. 10 is a single function of the distance to the crack lips (invariance
 398 along the direction that corresponds to the crack opening). This demonstrates
 399 clearly the dominantly plastic nature of this necking region in PMMA. Although

400 the length of this necking region is much larger than the 30-40 μm extension
 401 of the crazing region reported in the literature, the surface depression presents
 402 a maximum depth at a comparable distance from the crack tip, which frequently
 403 induces a local saturation of the AFM topographic signal (cf. blue saturated region
 404 in Fig. 10). Moreover, the surface depression presents a slight broadening in the
 405 terminal part of the main necking region, located between 200 and 300 μm ahead
 406 of the crack tip, more akin to the expected behavior from linear elasticity.

407 4.1.3. 2D analysis of the in-plane displacement field

408 Since the free surface of the sample is initially flat, the *in situ* topographic
 409 AFM images (the traditional height images) directly provide with the vertical
 410 component u_z of the crack tip displacement field. In order to obtain the in-plane
 411 components (u_x, u_y) of the crack tip displacement field it is convenient to get rid
 412 of the large out-of-plane dynamics u_z of the images. This can be done by using
 413 the deflection error signal of the feedback loop that is used for AFM imaging in
 414 contact mode (cf. the footnote 2 and Binnig and Quate, 1986). The obtained im-
 415 ages are much flattened and allow for a good visualization of the surface defects
 416 (cf. Fig. 11 and the full movie in the SI), which mainly consist of a dense array
 417 of crossed polishing lines. These lines are initially straight (Fig. 11 left), and they
 418 constitute a very convenient surface marking to track the in-plane surface defor-
 419 mations along the whole series of AFM images (cf. Fig. 11 right).

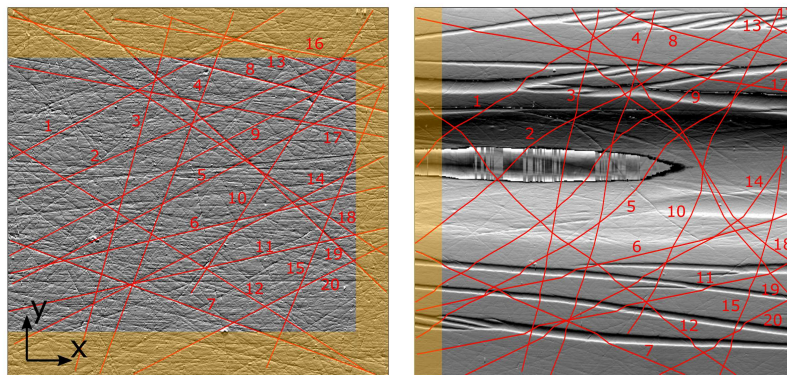


Figure 11: Measurement of the strain field by tracking the shape of the polishing lines network. A limited series of remarkable lines has been highlighted in red and numbered in order to allow for an easier interpretation of the complex deformation field. Note that, once again, the AFM saturation region is visible in the middle of the right image, but this does not limit the tracking of individual lines, which vehiculates the kinematic information.

420 In order to provide a straightforward measurement of the 2D projected strain
 421 tensor averaged over a gage length of about $2\ \mu\text{m}$, it is convenient to select a series
 422 of triplets of remarkable points, each one constituting an initially orthogonal basis
 423 in the undeformed reference frame. In practice, we check all intersections between
 424 polishing lines in the first (undeformed) image of the series until we identify some
 425 suitable triplets that correspond to a couple of segments aligned on the x and y
 426 directions and with a length close to the chosen gage length, as represented in
 427 black and red in the inset of Fig. 12. The change of length and orientation of the
 428 base vectors of a triplet are then monitored through the whole image series as a
 429 function of the distance X of the center of the gage region from the crack tip and
 430 of the distance Y_0 of the center of the gage region from the symmetry axis of the
 431 crack. When the gage region is not intersected by the secondary grooves, these
 432 data can be expressed in terms of the in-plane (x - y) nominal strain field (averaged
 433 over the micrometric gage length of the triplet). Fig. 12 presents the evolution
 434 of the normal strain component $\varepsilon_{yy}(X)$ (extension in the direction normal to the
 435 crack axis) for two such triplets centered at different distances from the crack axis
 436 ($Y_0 = 0.2$ and $2\ \mu\text{m}$). At large distances from the crack tip ($X < -150\ \mu\text{m}$) the
 437 strain is well below the detection limit (about 5%). For both curves, the nominal
 438 strain presents a significant rise starting at about the same distance of $150\ \mu\text{m}$ and
 439 then follows an approximately linear trend with distance. For the triplet that is the
 440 closest to the crack axis ($0.2\ \mu\text{m}$ offset was chosen in order for the whole triplet
 441 to belong to the same side of the crack opening) the nominal strain keeps raising
 442 linearly up to the crack tip. At this position a large extension of about $\varepsilon_{yy} = 70\%$
 443 (corresponding to a Hencky logarithmic strain $\varepsilon_H = \log(1 + \varepsilon_{yy}) = 0.5$) is reached,
 444 which remains frozen in the region behind the crack tip. Since the scatter in the
 445 data corresponds to 5% strain, which is comparable to the elastic strain limit of
 446 PMMA (Monnerie *et al.*, 2005), the measured strain field can be safely attributed
 447 to irreversible plastic deformations arising in a process zone region extending 150
 448 μm ahead of the crack tip. The longitudinal strain component ε_{xx} (extension along
 449 the direction of the crack axis) did not present any significant trend out of the 5%
 450 scatter that constitutes the detection limit. It was thus not plotted in the figure
 451 for better clarity (data can be found in Nziakou, 2015). The second triplet —
 452 centered at a larger $2\ \mu\text{m}$ offset from the crack axis — displays a similar trend
 453 for the nominal strain $\varepsilon_{yy}(X)$. But the saturation takes place at a larger distance
 454 from the crack tip ($\sim 80\ \mu\text{m}$) and thus for a lower nominal strain value ($\sim 20\%$,
 455 $\varepsilon_H = 0.18$). This manual image correlation technique is thus very efficient for
 456 identifying the plastic process zone and to evaluate the plastic strain field inside
 457 it. It should be emphasized that the $150\ \mu\text{m}$ length of the plastic process zone is

458 only half of the wide $300\ \mu\text{m}$ valley seen in the topography surrounding the crack tip
 459 tip (Fig. 10). In the remaining part of the necking region, the material strain is
 460 very small and elastic, except in the thin secondary grooves that will be described
 461 further down, in section 4.3.

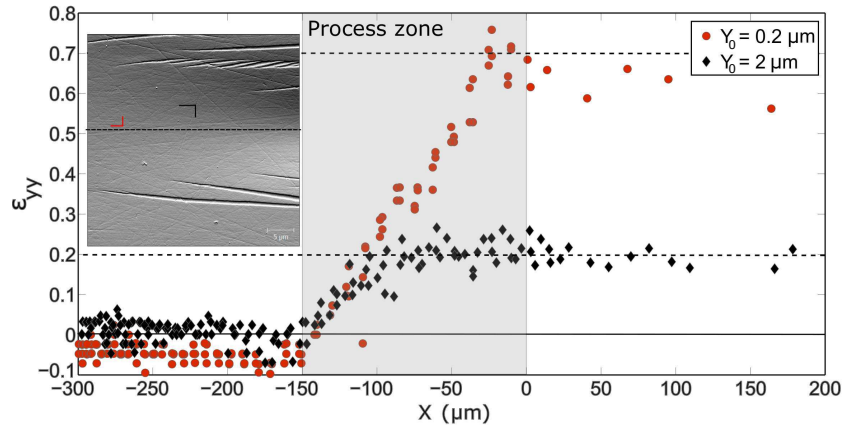


Figure 12: In plane nominal strain field in the direction normal to the crack as a function of the distance X from the crack tip and for two values of the initial offset Y_0 from the central axis of the main necking region.

462 4.2. Interpretation of the main necking region

463 The main necking region that has been observed by both optical microscopy
 464 and AFM to extend over $300\ \mu\text{m}$ length and $20\ \mu\text{m}$ width is now discussed. We
 465 combine here the information on the surface strain field obtained by the tracking
 466 of the polishing lines (Fig. 11) and the surface plastic strain profiles in the process
 467 zone ahead of the crack tip (Fig. 12). The main necking region presents essentially
 468 along its surface a uniaxial extension field normal to the crack axis with a slow and
 469 smooth evolution from the small strain elastic values ($< 5\%$) out of the process
 470 zone size of $150\ \mu\text{m}$ length up to the maximum measured values of 70% ($\epsilon_H = 0.5$)
 471 in the close neighborhood of the crack tip. The curved nature of the strained
 472 polishing lines (cf. Fig. 11) shows that the strain field in the main necking region
 473 is also smooth in the direction y transverse to the crack propagation direction.

474 Not only this plastic region is 5 times larger than what expected for a craze
 475 propagating in PMMA, but the features of the strain field itself are essentially
 476 different from the typical craze field. The strain field in a craze should abruptly
 477 change when crossing the craze boundaries from a weak elastic value to a large
 478 strain of $100\text{-}400\%$ ($\epsilon_H = 0.7 - 1.6$) with a quite uniform distribution inside

479 the process zone (Doll, 1983; Kramer and Berger, 1990). If this information is
480 combined with the extended surface depression observed in Fig. 10, the nature of
481 this plastic region at the free surface of the sample should rather be attributed to a
482 bulk shear yielding of the surface region.

483 The transition in plastic deformation mechanisms from crazing in the inner
484 parts of the sample to shear yielding in the free surface layer can be explained as
485 an effect of the progressive change in triaxiality of the stress field. The inner part
486 of the sample is governed by plane-strain conditions, where the crack front region
487 presents a very high hydrostatic traction. This favors the nucleation of nanometric
488 cavities, which are the precursor for the formation of the fibrillar regions of crazes.
489 The normal stress component z vanishes when approaching the external surface
490 of the sample. The hydrostatic part of the stress field and thus the stress triaxiality
491 are significantly reduced, so that shear yielding at constant volume is favored with
492 respect to cavitation and crazing (Kramer, 1983; Si *et al.*, 2005). The plane-strain
493 extension ε_{yy} of the craze region in the bulk of the sample is accompanied by
494 a local volume expansion of the material in the same proportion as the nominal
495 strain (factor 2 to 5 after Doll, 1983 and Kramer, 1983). On the other hand, the
496 occurrence of constant volume shear yielding in the surface region implies that the
497 extension $\varepsilon_{yy} = 70\%$ ($\varepsilon_H = 0.5$) in the normal direction to the crack axis, without
498 any measurable ε_{xx} deformation, is compensated by an equivalent contraction ε_{zz}
499 in the out-of-plane direction normal to the free surface. This is at the origin of the
500 observed large surface necking region.

501 A first rough estimation of the depth of the surface layer affected by shear
502 yielding can be obtained by imposing the conservation of volume. In the crack tip
503 region the main necking has a width of about 20 microns and a depth of 4 microns.
504 Since the measured stretches in the $x - y$ plane are $\lambda_y = 1 + \varepsilon_{yy} = 1.7$ and $\lambda_x = 1$,
505 the stretch in the vertical direction should be $\lambda_z = 1/\lambda_y \simeq 0.6$. The depth of the
506 region affected by the shear yielding can thus be estimated to about $b = 10 \mu\text{m}$, as
507 sketched in the left part of Fig. 13.⁴ We remark that the for a 4 mm thick sample,
508 the inner part of the sample affected by classic crazing mechanism (denoted as c
509 in the figure) constitutes the large majority of the thickness.

510 In order to test this scenario, a post-mortem investigation on the edge regions
511 of the crack surfaces was performed by Scanning Electron Microscopy (SEM)
512 (right part of Fig. 13). For the four investigated PMMA samples, this systemati-

⁴In this rough estimation we neglected the effect of elastic deformation. In light of the large plastic stretch, this can induce a bias of about 10%, i.e. $1 \mu\text{m}$.

513 cally reveals a marked change in the appearance of the fracture surfaces at a depth
 514 of $9\ \mu\text{m}$, that confirms a change in the fracture mechanism. A sound interpretation
 515 of the lighter hue of the surface layer is the increased roughness of the fracture sur-
 516 faces produced by tearing under shear yielding. This can induce a stronger electric
 517 charge concentration on the asperities, which results in a stronger SEM signal.

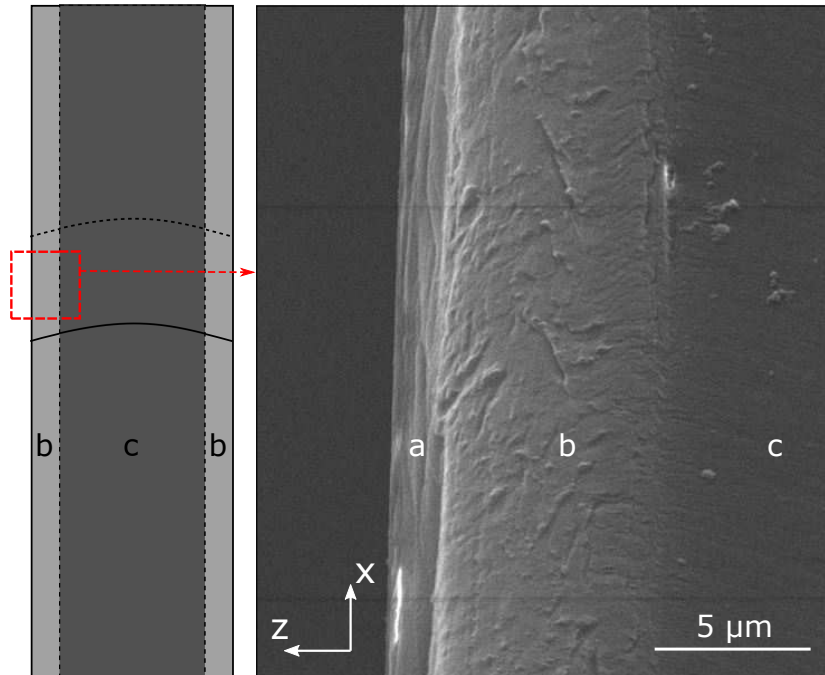


Figure 13: The sketch on the left represents the change of fracture mechanism at a depth b on the fracture surface ($x - z$ plane, the parabolic crack front propagated in the upward direction). The SEM image on the right corresponds to the region highlighted in red, close to the external sample surface. In the first $9\ \mu\text{m}$ region (denoted as b) the fracture surface properties are remarkably different from the rest of the fracture surface (denoted as c) indicating a change in the fracture process. The small region a on the extreme edge of the sample represents a side vision of the surface necking region observed by AFM in Fig. 8.

518 ζ From the point of view of mechanics the characteristic $10\ \mu\text{m}$ depth where the
 519 change of mechanism is observed can be interpreted by the following arguments.
 520 It is well known that in materials dominated by shear yielding all over the crack
 521 front, like polycarbonate, the progressive loss of triaxiality when approaching the
 522 free surfaces has the effect of modifying the shape and size of the shear yielding
 523 process zone over a depth equivalent to the size of the process zone itself (as mea-

524 sured in the inner plane-strain region, cf. Williams (1984), sec. 5.3)⁵. For those
525 materials, the effect of the loss of stress triaxiality at the surface is simply that
526 of increasing the extension of the process zone and enhancing the local material
527 toughness towards the higher value that is measured on thin samples, where the
528 plane-stress condition is dominant. The effective toughness of a thick sample can
529 thus be estimated with a good approximation by a weighted average between the
530 plane-strain and plane-stress values of the toughness. The weight factor is given
531 by the ratio between the thickness of the altered surface layer (comparable to the
532 Dugdale length) and the total thickness of the sample (Williams, 1984).

533 In the case of PMMA, the reduction of stress triaxiality involves both a change
534 of mechanism from crazing to shear yielding and a change of the process zone
535 size. The shear necking region presents an approximately five fold increase of
536 the crack opening displacement h_{COD} and a five fold reduction of the maximum
537 extension ε_{max} . Since for both mechanisms the fracture energy is approximately
538 given by the plastic work $\Gamma \sim h_{COD}\sigma_y\varepsilon_{max}$, and the shear yielding stress is quite
539 close to the crazing stress (Halary, 2011), the resulting estimation for the fracture
540 energy does not change significantly. This is also supported by the substantial
541 continuity of the shape of the crack front (measured by characteristic crack arrest
542 markings on the fracture surfaces) when crossing the transition region between
543 the two fracture mechanisms. According to the arguments given above for the
544 transition in the shear yielding process zone size, the depth of the transition from
545 crazing to plastic yield in PMMA should be driven by the 30 μm extension of
546 the crazing region in the bulk of the sample. This is quite close to the 10 μm
547 order of magnitude observed here, and constitutes a sound mechanical argument
548 for a change of mechanism at a similar scale. To go beyond this rough predictions
549 would require a full 3D finite element modeling of the elasto-plastic deformation
550 of the DCDC sample including large yielding strains and crazing, which is out the
551 scope of the present work.

552 It should be noted that for our millimeter thick samples the presence of these
553 micrometric surface layers does not affect significantly the effective toughness.
554 On the other hand, a stronger perturbation should be expected when the thickness
555 of the sample is reduced close to the transition range.

⁵This can be explained by the fact that the depth of transition of triaxiality is governed by the lateral scales where the stress field is changing, so that for a crack tip singular field the transition depth is progressively shifted towards the free surface when considering smaller and smaller lateral regions close to the crack tip, down to the size of the process zone where the yield onsets.

556 *4.3. Interpretation of the secondary grooves*

557 Once the nature of the main necking region has been clearly identified, the
558 network of secondary grooves can be more easily interpreted. They develop sym-
559 metrically on both sides of the main necking region and their propagating tips are
560 $270\ \mu\text{m}$ ahead of the crack tip, i.e. in the region where the main necking starts to
561 develop. They thus appear to be a secondary surface crazing phenomenon driven
562 by the local stretching normal to the propagation axis induced by the elastic neck-
563 ing at the surface of the sample. This hypothesis is also supported by a finer
564 description of their associated plastic strain field.

565 Considering the snapshots of AFM error signal images presented in Fig. 14 for
566 two different times of the secondary grooves formation (separated by 3 hours), the
567 initially straight polishing lines are abruptly tilted when they enter the secondary
568 grooves and recover the same direction on the opposite side. This feature reveals
569 the homogeneity of the strain field inside these grooves and the change in angle,
570 which remains constant once the groove is formed, can be used -knowing that
571 the longitudinal displacement in x direction is null⁶- to estimate the strain level to
572 very large values between 400 and 500% ($\varepsilon_H = 1.6 - 1.8$), while the surrounding
573 regions remains essentially unstrained. When accounting for all the features of
574 our images, the lateral resolution for the angle estimation can be estimated to 5
575 pixels, i.e. 400nm.

576 Thanks to this information on the homogeneity of the strain field inside the
577 secondary grooves, we can extract some important complementary information
578 from the manual digital image correlation applied to a triplet that is progressively
579 crossed by one of these grooves that propagates parallel to the direction x of the
580 main crack axis, as shown in Fig. 15.

581 In order to obtain a better estimate for the average nominal strain ε_{yy} inside
582 these localization bands, the measured displacement difference Δu_y of the two
583 ends of the vertical segment crossing a secondary groove was divided by an es-
584 timation h_{SG} of the unstrained width of the secondary groove, which constitutes
585 a better gage length. As observed in Fig. 15, the average plastic strain field in-
586 side the secondary grooves builds up at their propagating tip (about $270\ \mu\text{m}$ ahead
587 of the crack tip) and keeps rising over a $50\ \mu\text{m}$ region before saturating to large
588 values of about 450% ($\varepsilon_H = 1.7$) with no further evolution during the approach
589 of the propagating crack tip. The unstrained width h_{SG} of the secondary groove

⁶Displacement Δu_x between points A and B in Fig. 14 was measured to be $45 \pm 90\ \text{nm}$ during the whole crack propagation and formation of the groove

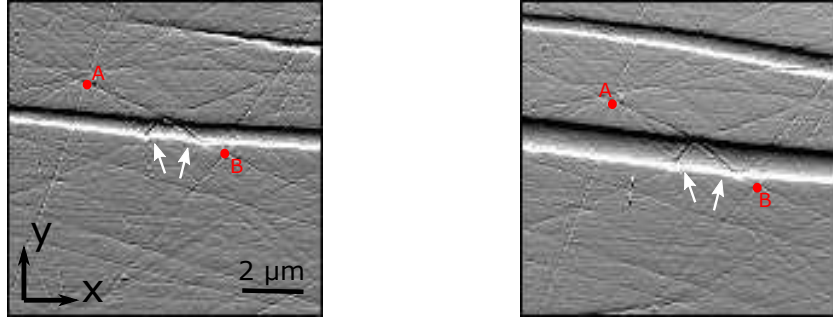


Figure 14: AFM observation in error signal mode of the abrupt tilt of initially straight polishing lines when they come across a secondary groove (as indicated by white arrows). Left and right images present the same area at two different times (separated by 3 hours) of the formation of the secondary groove. Points A and B are visual indicators located at polishing lines intersections on opposite sides of the groove to help visualisation of the polishing lines tilt. It can be noticed that during crack propagation and development of the groove, $x_B - x_A$ remains nearly constant.

590 can be estimated by subtracting to the initial unstrained length L_0 of the vertical
 591 segment, the length L_{out} of the unstrained portions of the segment that are out of
 592 the secondary groove. The unstrained width h_{SG} progressively increases during the
 593 development of the secondary groove in its first $50 \mu\text{m}$ portion. However, due to
 594 the limited resolution of the images, an accurate estimate of the length L_{out} and
 595 thus of the unstrained width could only be performed for the final value corre-
 596 sponding to the fully developed secondary groove: $L_{out} = 1.8 \mu\text{m}$, $h_{SG} = 0.3 \mu\text{m}$.
 597 The stretched length of the groove is $1.35 \mu\text{m}$. Since the values reported in Fig. 15
 598 are obtained by simply dividing the measured displacement difference Δu_y by this
 599 constant estimation h_{SG} , the transient increase in the first $50 \mu\text{m}$ should only be
 600 interpreted in terms of displacement difference $\Delta u_y(X)$, while the average strain
 601 is expected to be spatially constant according to the previous observations on the
 602 tilt of the polishing lines. The displacement difference Δu_x on the same vertical
 603 segment crossing the secondary groove was negligible within experimental incer-
 604 titudes, which reveals the absence of shear on the secondary grooves. Once again
 605 the 2D projection of the average strain field is essentially a uniaxial extension
 606 perpendicular to the propagation axis.

607 We remark that the features of the strain field inside the secondary grooves are
 608 quite different from the main necking region. Both the spatial homogeneity and
 609 the large values of the plastic strain field in the secondary bands are consistent
 610 with what is expected for crazes.

611 However, these secondary crazes are not directly associated with the main

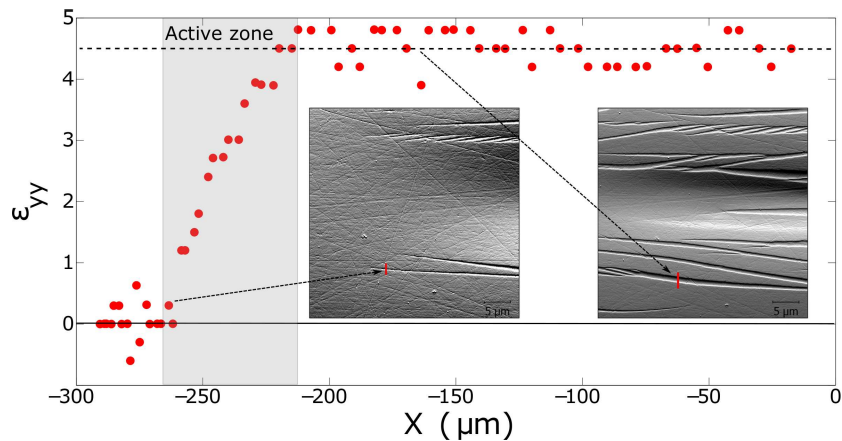


Figure 15: In plane nominal strain field in the direction normal to the crack as a function of the distance X from the crack tip, calculated along a secondary groove as indicated in the inserts.

612 crack propagation through the whole thickness of the sample. They rather propa-
 613 gate from the free surface of the sample towards the interior, driven by the local
 614 stretching field originating from the main necking as argued above. Their lateral
 615 propagation along the crack direction x is thus simply caused by the propaga-
 616 tion of the necking field ahead of the main crack. The depth of penetration of
 617 these secondary crazes in the sample in direction z can be inferred to amount to
 618 a few microns by considering both the average distance between them and their
 619 mutual interaction during propagation when they approach to smaller distances.
 620 This order of magnitude is also consistent with the $10\ \mu\text{m}$ depth of the surface
 621 layer affected by the main necking region, which is the cause for these secondary
 622 grooves.

623 The few micron propagation distance of these secondary surface crazes to-
 624 wards the interior of the sample (direction z) is less than the typical $30\ \mu\text{m}$ craze
 625 length observed by Doll (1983) during bulk crack propagation (direction x). This
 626 provides a sound explanation for the absence of fractures inside these secondary
 627 grooves. In other words, these secondary crazes propagate towards the inner part
 628 of the sample over too short a distance to nucleate a fracture. They thus remain ar-
 629 rested by the stress gradient within the depth as “unaccomplished” surface crazes
 630 that decorate the neighborhood of the main necking region at the free surface of
 631 the sample, without major consequences on the propagation of the main crack in
 632 the bulk.

633 In the main crack the craze propagation close to the free surface is hampered

634 by the reduction of stress triaxiality, leading to the formation of the main sur-
635 face necking as discussed in section 4.2. On the contrary, the presence of these
636 secondary crazes at the free surface can be justified since their direction of propa-
637 gation is different. On the one hand, the craze associated to the main crack propa-
638 gates in the direction x parallel to the free surface and the associated 2D crack tip
639 field (in the $x - y$ plane) undergoes a change in triaxiality while approaching the
640 free surface. On the other hand, the secondary surface crazes propagate in the di-
641 rection z that is perpendicular to the free surface and the 2D strain field associated
642 to their propagating front (in the $y - z$ plane) is essentially in plane-strain since it
643 does not approach to any free surface when moving along a direction orthogonal
644 to its plane. Moreover, the stress triaxiality at their propagation region is locally
645 enhanced by the stretch induced by the formation of the main valley.

646 5. Perspective for future work

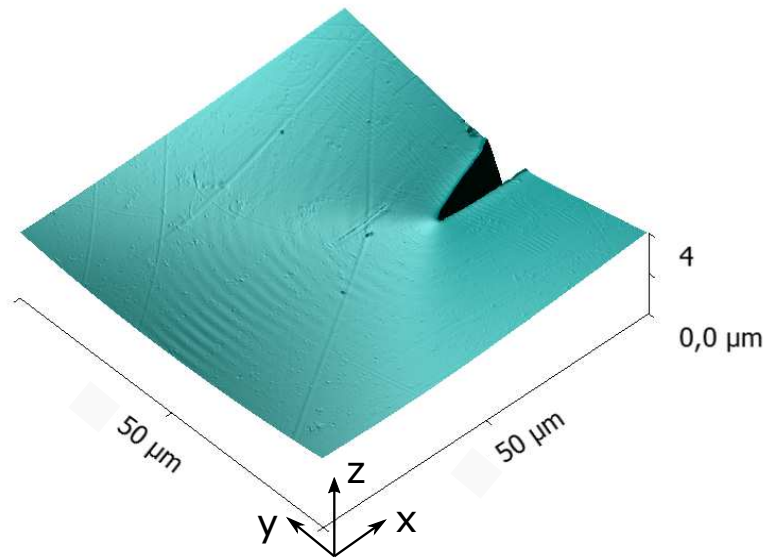


Figure 16: 3D representation of the topography of the crack tip region ($50 \times 50 \mu\text{m}^2$) measured by AFM at the free surface of an epoxy resin sample.

647 In order to appreciate the high potential of this novel technique in discriminat-
648 ing the deformation mechanisms in the process zone for different glassy polymers,
649 Fig. 16 shows a preliminary result on the *in situ* AFM imaging of fracture propa-
650 gation in a model epoxy resin. When compared to Fig. 8, the surface displacement

651 field in the process zone region of the epoxy resin appears to be very different. The
652 absence of both the very extended surface necking region and of the secondary
653 grooves are to be noticed. The surface displacement field rather appears as a very
654 smooth shear yielding field with a clear strain concentration towards the crack tip.
655 This process zone mechanism is essentially the same as the one expected for the
656 crack propagation in the bulk, even if probably enhanced in size due to the surface
657 loss of triaxiality (Williams, 1984). The absence of crazing in epoxies is generally
658 attributed to the high crosslinking density (Halary *et al.*, 2011). In the presence of
659 such a smooth strain field, the present technique can be enriched by the possibility
660 of computing the full strain field by digital image correlation.

661 **6. Conclusion**

662 A very promising novel technique is presented for investigating the mecha-
663 nisms of crack propagation in glassy polymers and measuring the strain fields
664 at the scale of their micrometric process zone during steady-state propagation by
665 atomic force microscopy. The first important required achievement is the ability to
666 properly initiate and propagate a very well conditioned mode I fracture in a glassy
667 polymer (PMMA) and to ensure a stable steady-state condition over several days
668 in order to allow for an extensive campaign of AFM observations. The second
669 achieved step is to obtain a valuable estimation of the crack driving conditions (in
670 terms of a stress intensity factor K_I) even when the DCDC sample undergoes some
671 bulk plastic yielding in the central hole region due to its low strength/toughness ra-
672 tio. This is assessed by the agreement of the measured $K_{Ic}(v)$ crack propagation
673 curves with the ones reported in the literature. These two achievements are a
674 necessary condition to link the microscopic scale observations of the crack tip
675 mechanisms with the macroscopic scale of the sample loading.

676 The acquisition of long AFM image series during several days of slow steady-
677 state crack propagation allows for a rich and quantitative real-time evaluation of
678 the damage mechanisms and the related strain fields at the free surface of the sam-
679 ple in a region that is progressively crossed by the crack tip process zone. While
680 the out-of-plane displacement field is directly provided by the AFM topographic
681 images, the in-plane displacement field can be obtained by tracking the relative
682 motion of remarkable surface points.

683 The AFM observations presented for PMMA reveal a very rich and unex-
684 pected surface fracture pattern, which is quite different from the well known cra-
685 zing behavior that occurs at the crack front in the bulk of the PMMA samples where
686 plane-strain conditions are prevailing (Doll, 1983; Kramer, 1983). The analysis

687 of the surface displacement field associated with crack propagation, together with
688 post-mortem investigation by SEM, leads to the interpretation of these observa-
689 tions as a change of fracture mechanism from crazing in the bulk to shear yielding
690 in a surface layer, where the prevailing plane-stress conditions involve a local re-
691 duction of stress triaxiality. The thickness of the layer affected by this change of
692 mechanism is about $10\ \mu\text{m}$, which is the same order of magnitude as the Dugdale
693 length in plane-strain as argued by Williams (1984). While changes in the process
694 zone size are well known to occur in plane-stress surface layers (Williams, 1984),
695 it is the first time to our knowledge that a clear observation of a global change of
696 mechanisms is reported at the surface of a thick sample.

697 The surface shear necking region presents a ten fold increased length with
698 respect to the craze in the bulk of the sample. The plastic strain field is shown
699 to affect only half of this length and it presents a very smooth evolution up to
700 70% plastic extension close to the crack tip. This is comparable to the maximum
701 plastic extension obtainable in uniaxial tensile tests on PMMA close to its glass
702 transition temperature (G'Sell and Jonas, 1979). This observation is a nice proof
703 that although PMMA is macroscopically brittle in tension at ambient temperature,
704 it can be plastically cold drawn at scales smaller or comparable with the Dugdale
705 length. The limiting extension is provided by the entanglement network, which
706 still resists plastic flow before the material is broken.

707 The complex pattern of secondary grooves that develops along the main neck-
708 ing region can be attributed to secondary surface crazing by carefully analyzing
709 the real-time development of the surface strain fields. These secondary surface
710 crazes are shown to be formed in the first half of the main necking region, where
711 only elastic tensile deformations are prevailing with a principal direction orthog-
712 onal to the fracture plane. The secondary crazes are shown to be nucleated on
713 these polishing lines (cf. movie in the SI) that are more closely orthogonal to the
714 surface tensile stress and which act as surface defects for nucleation. These sec-
715 ondary crazes are soundly propagating towards the bulk of the sample on a limited
716 depth of about 10 microns, which corresponds to the region affected by the tensile
717 stresses associated to the surface necking layer. This depth is consistent with the
718 relative distance where these surface crazes are observed to mutually interact.

719 The preliminary images reported for an epoxy resin confirm the general ap-
720 plicability of the technique to different glassy polymers and allow to appreciate
721 a very different organization of the plastic strain fields in the process zone. This
722 novel technique is thus very promising to achieve important insights on the effect
723 of the different macromolecular structures of glassy polymers on their fracture
724 toughness.

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