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Physical mechanisms of fatigue in neat polyamide 6,6

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Abstract

The fatigue durability of polyamide 6,6 has been studied for various maximal stresses. We focus on the identification of the microscopic mechanisms responsible for damaging in fatigue regime. We show that the apparent stiffness, or dynamic modulus, decreases linearly as a function of the logarithm of the number of cycles during fatigue tests, except at the very end of the lifetime, prior to failure. This suggests a progressive, accumulative and generalized damage in the material. This damage mechanism has been characterized at various scales with electron microscopy and X-ray scattering. These analyses show that low density domains are formed at nanometric scale at the early stages of fatigue. The number and size of these domains increase as a function of the number of cycles, explaining the logarithmic decrease of dynamic modulus. These low density domains become anisotropic and evolve into crazes at the ultimate stages of fatigue. The size distribution, density and form factor of the defects have been characterized during fatigue. The damaging mechanisms and the different steps of damage are discussed in the context of a recent theoretical model.

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I. INTRODUCTION

Semi-crystalline polymers show high mechanical performances and find numerous industrial applications, more specifically in the automotive field where they compete with metals. For example, polyamides are now used for applications requiring strength in demanding environments (high temperature, resistance to various type of fuel, glycol, etc.). Semi-crystalline polymers are now well characterized. Their crystalline morphology is complex and multi-scale [1–3], composed by a lamellar crystalline phase and by an amorphous phase between the lamellae. The typical thickness of a polymer lamella is about 10nm. The lamellae grow radially from a nucleus in the molten polymer [4]. At a microscopic scale, the crystalline phase is formed by spherulites of a diameter about tens of microns. The mechanical behaviour of semi-crystalline polymers has been widely studied [5–10]. Bowden and Young have studied the relationship between the mechanical behaviour and the mechanisms of deformation of the polymer [5]. According to them, at small stresses, the elastic and viscoelastic behaviour of semi-crystalline polymers involves the interlamellar amorphous phase, and at higher stresses the plastic behaviour involves the crystalline phase. Semi-crystalline polymers show two main localized plastic deformation mechanisms: crazes and shear bands. Crazes are cracks that remain bridged by fibrils of polymer and are perpendicular to the stress [11–13]. Shear bands do not imply volume deformation and in semi-crystalline polymers are found at an angle of about 52° to the stress direction [14]. Friedrich has shown that crazes and shear bands coexist in semi-crystalline polymers [11].

However, the mechanical behaviour in the case of repeated small stresses is still hard to explain. The understanding of the mechanisms of damage in polymers is of great importance, because the stress at break in fatigue is much lower than the stress at break for tensile loading. The mechanical properties of the polymers submitted to fatigue drop as a function of the duration of test, even if the maximum stress belongs to the elastic or viscoelastic domain. A part of irreversible damage occurs at small stresses and the origin of this damage is not completely understood. Since the 1980's, fatigue of polymers has been widely studied [15–27]. Nevertheless, the characterization and understanding of the mechanisms of damage in semi-crystalline polymers during fatigue is not clear. Some works focus on the study of the mechanical properties at a macroscopic scale [28], others on observations at the microscopic scale [29, 30], and some others on both scales [31–33]. As far as we know, there are very little studies dealing with the characterization of damage during fatigue at a nanometric scale.

Kuksenko and Tamusz and other authors have shown the formation of microvoids during tensile

experiments on polymers characterized in situ by SAXS [34, 35]. The size of the microvoids remains constant and the breaking occurs when a critical density of microvoids is reached. In oriented polymers the size of the cavities is of a few tens of nanometers, whereas in non oriented polymers the size of the cavities is about some thousands of nanometers. Recently, Castagnet *et al* characterized PVDF by volumetric measurements during tensile test and by SAXS [36]. They have shown that cavities occur in the interlamellar amorphous phase just before yielding. Pawlak and Galeski [37] studied the competition between cavitation and crystal shearing. In polyamides, because of the high resistance of the crystals, the main damage mechanism is cavitation [37]. The observed cavity size is about 4 to 5 nm. Smaller cavities are assumed to close back because of the high surface tension of polyamide. It was observed that cavities grow first perpendicular to the applied stress, then elongate in the direction of the stress [38].

Cracks in semi-crystalline materials have been studied by Narisawa [13], Kausch et al. [12]. The crack initiation step has been studied in details by Friedrich [11]. This first step involves shear in the crystalline phase and appearance of voids of sub-micron size. When the concentration of local stress becomes larger than a critical value corresponding to plastic flow, crystalline lamellae are fragmented in crystalline blocks which have a typical size of about 10 to 30 nm and orient in the direction of the applied stress. Simultaneously, voids are created with typical sizes 10 to 50 nm in the direction parallel to the applied stress and 2 to 6 nm in the direction normal to the stress. These voids are probably nucleated in the regions where the stress is the most concentrated. These nucleation zones are located within the amorphous phase, between crystalline lamellae at an angle of 45° with respect to the applied stress [11], which corresponds to regions where the shear is maximum, or between lamellae oriented perpendicularly to the applied stress, because there the local variation of volume is maximum, which favors cavitation.

Cracks in polystyrene, in styrene-acrylonitrile copolymers, in various poly(methyl)methacrylates and in toughened poly(styrene) blended with elastomers have been studied by Sauer et al [39]. The damaging mechanism observed in fatigue for these materials is the development of cracks. Lifetime in fatigue increases when increasing the molecular weight and entanglement density.

Materials, and in particular polymer materials, can be brittle or ductile. When submitted to an increasing stress, they can either break suddenly above a critical value, or undergo progressive damage as stress increases up to a stress level where final rupture of the sample occurs. An important parameter in the appearance of progressive damage is the disordered nature of materials [40–42]. When submitted to a constant load, materials break due to thermally activated processes which produce a slow rupture dynamics (see [43] and references therein). Depending on the nature

of the material and the constant load level, the amount of damage accumulated at the time of catastrophic rupture can be almost negligible or instead very large. Polymer materials can display an important range of stress levels over which slow and significant progressive damage will be observed, contributing to creep until the final rupture. As regard to the experiments reported here, we had to determine the stress range of interest for fatigue experiments, *i.e.* the stress range for which progressive damaging could be observed over a long but experimentally accessible time scale.

It has been argued in [44] that some generic features should be present in a very wide class of materials for which time plays an essential role in the damage mechanisms. In such circumstances, it was assumed that damage is related to nucleation of cavities, which grow in number, and which may grow in size. The dominant damage mechanism results from the competition between the two following mechanisms: either 1) the increase of the number of cavities thanks to independent nucleation processes throughout the sample, until the number of cavities reaches a critical value above which the material crumbles, or 2) the growth of a single cavity which results in the apparition of a fracture in the material.

This paper deals with fatigue of neat polyamide and aims at characterizing the fatigue damage at the different scales of the microstructure of the material, from nanoscale to mesoscale. The aim is identifying the microscopic mechanisms responsible for damaging during fatigue experiments. We do it through a complete study of the material, by combining mechanical results, multi-scale X-ray characterizations and electron microscopy observations of fatigued samples, at different steps of their life-time. We consider only a single value for the R parameter ($R = 0.1$) and a single frequency. It is known that the kinetics of fatigue depend on both R and frequency. However, our point of view is that the microscopic mechanisms are generic, provided one remains in the fatigue regime, corresponding to slow damaging processes at low stress level. The results are discussed in the context of the theoretical model proposed by Fusco et al [44].

II. EXPERIMENTAL

A. Materials

The neat polyamide (PA) used in this study is a polyamide 6,6 (PA 6,6) which has been processed in standard conditions to obtain plate specimen (Fig. 1).

After moulding, the samples were stored in sealed bags to maintain them dry. This geometry

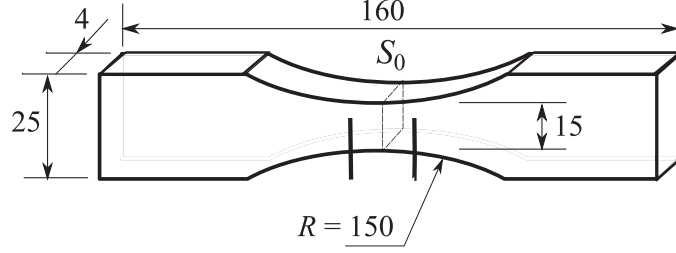


FIG. 1: Specimen geometry used for fatigue tests. The stress is computed at section S_0 . **The extensometer used to measure the strain at the centre of the test sample is indicated by two broad line segments.**

corresponds to the standard NF A03-401 for fatigue tests on metals. The large radius of curvature of the sides creates an increase in stress concentration factor of about 3% in the central part of the specimen where most of the damage will nevertheless occur.

B. Fatigue testing

Fatigue tests were carried out on a servohydraulic machine (INSTRON 8872). Unless otherwise specified, we worked with a fatigue frequency of 5Hz which is high enough to get reasonable test durations while limiting the temperature rise due to the self-heating of the material. Buckling of the specimen was avoided by using stress-controlled as opposed to displacement-controlled tests. A sinusoidal stress with a ratio $R = \sigma_{min}/\sigma_{max} = 0.1$ was applied to the materials. All tests were carried out in a temperature chamber with air atmosphere regulated at 50% humidity.

We have checked that the effect of water sorption in the material is negligible during the time scale of the fatigue experiments. Equilibrium water sorption in a 50% humidity atmosphere is about 30 mol% (number of water molecules referred to the number of amide groups in the amorphous phase content in the material, assuming a crystallinity of about 36%). The kinetic of sorption is extremely slow. For a test sample of 4 mm thickness, it would take about 300 days to reach full sorption equilibrium, while the maximum duration of fatigue experiments shown here (typically 10^6 cycles at 5 Hz) is 2×10^5 s, that is less than 3 days. Within this duration, global water uptake does not exceed 3 mol% typically [45]. Water is a plasticizer for PA6,6, i.e. it drops the T_g of the amorphous phase, while it has negligible short term effects on the crystallinity. The T_g drop resulting from this small water intake would be of the order 5°C at most typically [2], resulting in a T_g of order 55°C , still well above the studied temperature 25°C . The corresponding effect on the modulus at 25°C , which would result from a combined drop due to the decrease of the quantity

$T - T_g$ and a slight increase in the presence of water at a given $T - T_g$ value, would be negligible compared to the observed variations during fatigue experiments (which are shown in Figure 4).

The temperature at the surface of the specimen was measured with a thermocouple at the location of the damage, i.e. in the smallest section area, with an accuracy of 1°C . Mechanical data (force, displacements) were acquired at 1kHz for fatigue tests at 5Hz, which corresponds to 200 points per cycle. The fatigue tests were repeated 3 to 5 times for each condition. We studied the macroscopic properties of the material as a function of the number of cycles during the fatigue test by following the shape of the fatigue cycles. **The stress is computed at the level of the smallest section S_0 of the test samples and the strain is measured by an extensometer of initial length 12.5 mm located in the center of the test samples (see Figure 1).** Fatigue cycles were fitted by a model ellipsoid curve by means of a homemade algorithm. We have studied the evolution of the following macroscopic properties: minimum and maximum stress ($\sigma_{min}, \sigma_{max}$); minimum and maximum strain ($\epsilon_{min}, \epsilon_{max}$); dynamic modulus E_d , calculated with the equation:

$$E_d = \frac{\sigma_{max} - \sigma_{min}}{\epsilon_{max} - \epsilon_{min}} \quad (1)$$

Damage accumulation in the material is usually monitored by the evolution of the elastic modulus which is different from the dynamic modulus E_d . However, the phase angle between stress and strain in our material is always smaller than 10° , so that the contribution of dissipation in E_d is always very small. For fatigue tests, we will thus simply use the dynamic modulus E_d to evaluate damage.

C. Density measurements

Density measurements were performed on reference and fatigued samples in density gradient columns prepared with the partially miscible solvent pair tetrachloromethane/toluene. Cube specimen of $(2\text{mm})^3$ were cut in the center region of the samples (± 2 mm from the center section S_0 as indicated in Figure 1) and immersed for 2 hours before measuring the density. The density is measured within 2×10^{-4} relative uncertainty.

D. Scanning electron microscopy

The fracture surfaces of broken samples were observed using Scanning Electron Microscopy (SEM) after metallizing with a 2nm Pt layer. In order to observe the morphologies of non broken

specimens (either fatigued samples or the reference, unfatigued sample), cryo-fractured surfaces were obtained on samples dipped in liquid nitrogen for one hour.

E. X-ray Scattering

Small Angle X-ray Scattering (SAXS) was used to characterize the polymer matrix organization at a scale from 5 nm to about 150 nm. The experiments have been carried out in the BM2 line (wavelength $\lambda = 0.111$ nm) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The scattered intensity is analyzed as a function of the scattering vector $q = \frac{4\pi}{\lambda} \sin(\theta/2)$, where θ is the angle between the incident ray and the scattered rays. The accessible q range goes from $q_{min} = 6 \times 10^{-2} \text{ nm}^{-1}$ to $q_{max} = 1.05 \text{ nm}^{-1}$. The acquisition time of 2D scattering patterns was typically 2 s. Primary data corrections, i.e. dark current, flat field response and taper distortion were performed. In-situ tensile stress could be applied during SAXS experiments with a home-made tensile device in which a static, controlled stress may be applied to the sample and the temperature may be controlled. Ultra Small Angle X-ray Scattering (USAXS) characterizations have been carried out in the ID2 line ($\lambda = 0.099506$ nm) at ESRF using a Bonse-Hardt setup [46], which gives access to a range of scattering vectors from $q_{min} = 10^{-3} \text{ nm}^{-1}$ to $q_{max} = 5 \times 10^{-2} \text{ nm}^{-1}$ with a total acquisition time 5 min. In this experiment, the scattering is detected along one direction. To analyze the scattering in various orientations with respect to the stress direction, the experiment has to be repeated after rotating the specimen in the appropriate orientation. For SAXS and USAXS characterizations, test samples were cut with a diamond saw in the central section of the fatigued specimen. Unbroken fatigued specimen were analysed in the middle of the sample. Specimens broken in fatigue were characterized in the close vicinity of the fracture surface, about 1mm underneath the surface.

III. RESULTS

A. Fatigue lifetime

Figure 2 shows the relation between the maximum stress σ_{max} applied at each cycle of the fatigue test and the number of cycles up to failure N for neat PA samples, for experiments performed in an environment at 25°C, that is, below T_g . Values of N range between 100 and $3 \cdot 10^6$ cycles. The stress value for $N = 1$ corresponds to the strength of the material measured in a uniaxial tensile test. The data approximately follow a Wöhler curve of the form $\sigma_{max} = -A(T) \log N + B(T)$

usually observed for fiber glass reinforced PA [16, 24, 28, 33], only for large values of the number of cycles N . For lower values of N , there is a strong variation in the number of cycles to failure at a nearly constant stress around 67 MPa (as indicated by the grey line), as already observed [47].

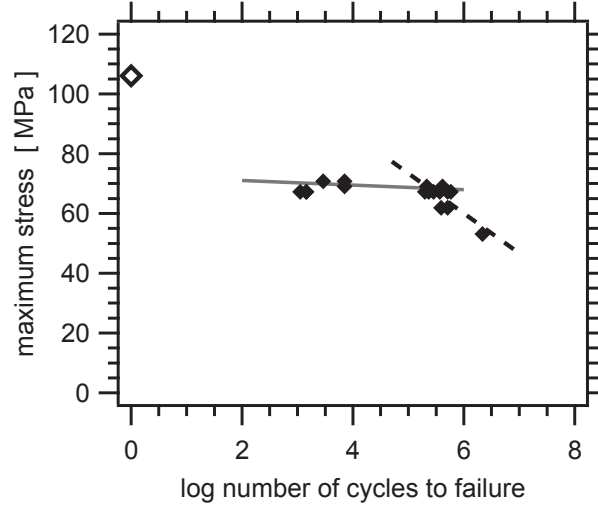


FIG. 2: Wöhler curve for neat PA6,6 in an environment at 25°C. The dashed line is a linear fit of the late regime of fatigue (for $\log N$ between 5.5 and 6.5). The full grey line is a guide for the eyes. Empty symbol corresponds to failure obtained in one cycle.

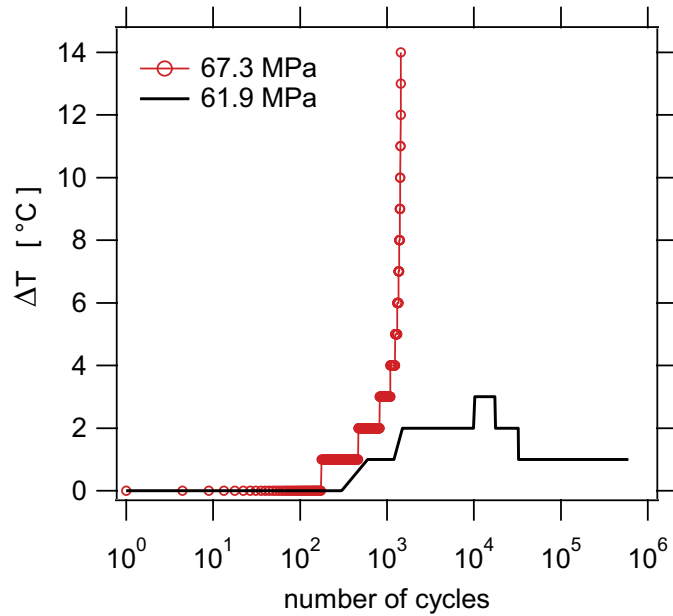


FIG. 3: Temperature evolution at the neat PA6,6 surface during a fatigue test for two different values of σ_{max} . The difference ΔT with respect to the environment temperature (25°C) is plotted.

Figure 3 shows the difference ΔT between the sample temperature (measured at the surface

of the sample) and the environment temperature (25°C) during fatigue tests. Two different cases can be distinguished. On the one hand, if the applied stress is high (67 MPa in the example shown in Figure 3), breaking occurs in so-called thermal fatigue conditions, with a temperature of the material significantly increasing during the test [32]. For thermal fatigue, Lesser et al have shown that the temperature inside the material can reach the melting temperature of the polymer matrix, and Differential Scanning Calorimetry (DSC) measurements also revealed a decrease of the crystallinity ratio of the thermoplastic matrix [47]. On the other hand, for lower applied stresses (62 MPa), standard mechanical fatigue conditions are observed with a small temperature rise during the first 1000 cycles and then a temperature plateau. For both thermal and mechanical fatigue, our DSC measurements proved that the crystallinity ratio was not affected. Moreover, Wide Angle X-ray Scattering characterizations revealed no change in the crystalline structure during fatigue. For stresses between 65MPa and 70MPa, some specimens have broken in thermal fatigue conditions and others in mechanical fatigue. This could explain the scatter of data points in Figure 2. In Figure 2, lifetimes shorter than typically 10^4 cycles correspond to thermal failure.

B. Macroscopic characterization of damage

We studied the dynamic modulus E_d as a function of the number of cycles for different stresses for neat polyamide at $T < T_g$ (Figure 4). Except for cases of thermal fatigue (71 MPa in the example shown in Figure 4), the decrease of E_d is mostly logarithmic with the number of cycles. At some point during this logarithmic decrease, and after a 5 to 10% drop of the modulus E_d , the sample breaks apart suddenly. This very fast rupture dynamics corresponds to an instability threshold that is not preceded by any sign of an accelerated damage dynamics. The evolution of the density of samples in the vicinity of the rupture region has been characterized. As compared to non-fatigued samples, a decrease in density smaller than 0.1% was measured in the zone of minimal section. This decrease is quite small in comparison with that of the modulus. Even if, as expected, cavities were formed during damage, they may close up at least partially when the applied stress is removed and the decrease of the density may then underestimate the appearance of voids in the samples, as already suggested in [37].

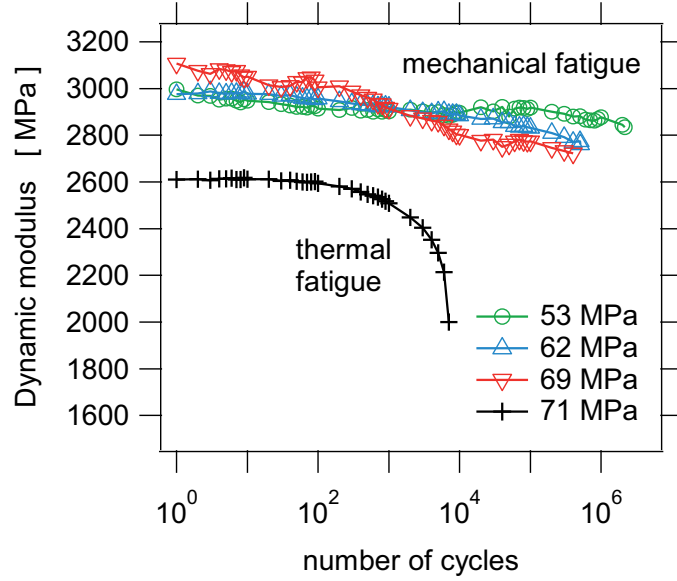


FIG. 4: Evolution of the dynamic modulus E_d as a function of the number of cycles at $T < T_g$ for neat PA6,6.

C. Microscopic observations of damage

Cryo-fracture of broken samples show a variety of damage features in the material (Figure 5). Just underneath the final fracture surface, and up to $50 \mu\text{m}$ from the surface, cracks are observed. Note that such large cracks may be partly generated by cryo-fracture, even though the cracks we observe are always located in the vicinity of the fracture surface. Up to $60 \mu\text{m}$ from the surface, crazes (or cracks bridged by polymer fibrils), are observed. Beyond $60 \mu\text{m}$, only cavities, mostly spherical, are observed. Crazes can be better observed in TEM images of thin polyamide slices ($\sim 100\text{nm}$ thick) normal to the applied stress (Figure 6). Large numbers of crazes can be observed at distances up to $150 \mu\text{m}$ from the rupture surface. Crazes often initiate from a large cavity (diameter larger than 500nm) and propagate in the direction normal to the applied stress. They are expected to localize in the equator of the spherulites [11–13, 48–50]. On the other hand, one cannot be sure that all crazes and damage defects can be identified and located in TEM observations. This study will be made quantitative with USAXS experiments in what follows.

Similarly, TEM images can be used to visualize the cavities (Figure 7). Interestingly, the reference samples, i.e. before fatigue, exhibit a small number of spherical cavities of diameter typically 500 nm . These cavities are probably produced during the injection process due to thermal stresses during rapid cooling of the samples. We have analyzed the distribution $n(R)$ of sizes of these spherical cavities and their evolution during fatigue, in the zone of maximal stress (minimal

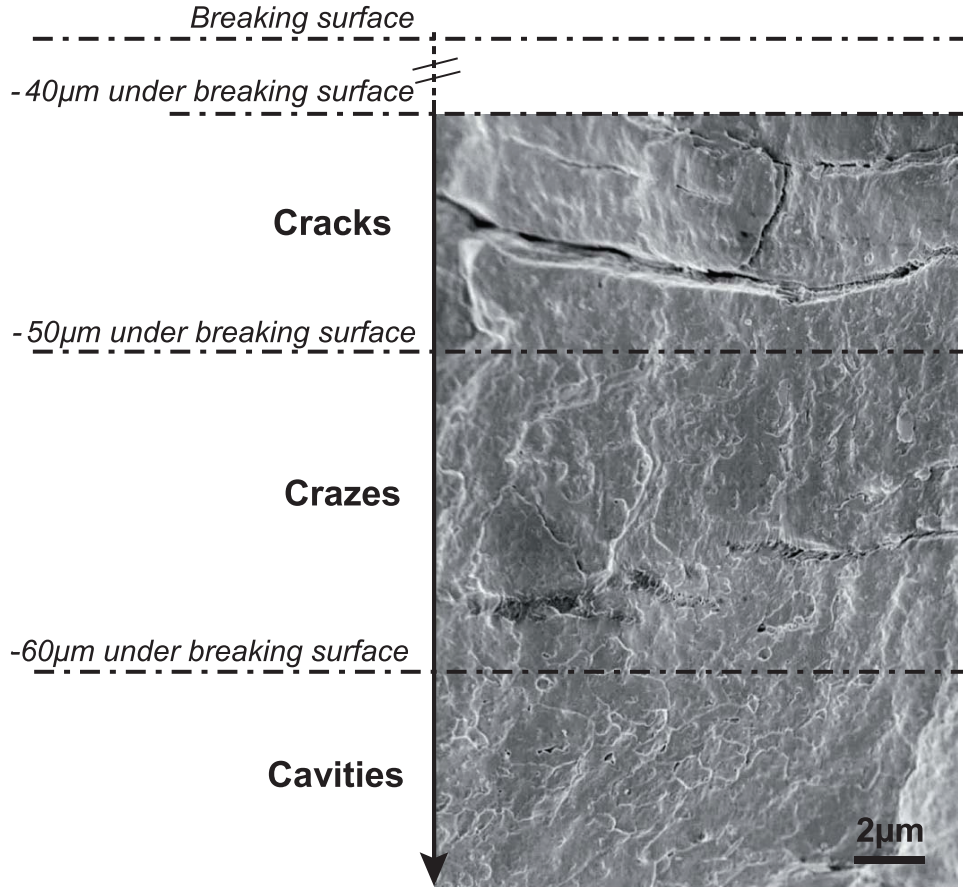


FIG. 5: Cryo-fracture in the direction parallel to the stress in neat PA after breaking in fatigue (412 000 cycles) at $\sigma_{max} = 69$ MPa and at 25°C. The rupture surface is localized about 50 μm above cracks visible in this picture. The stress direction is vertical.

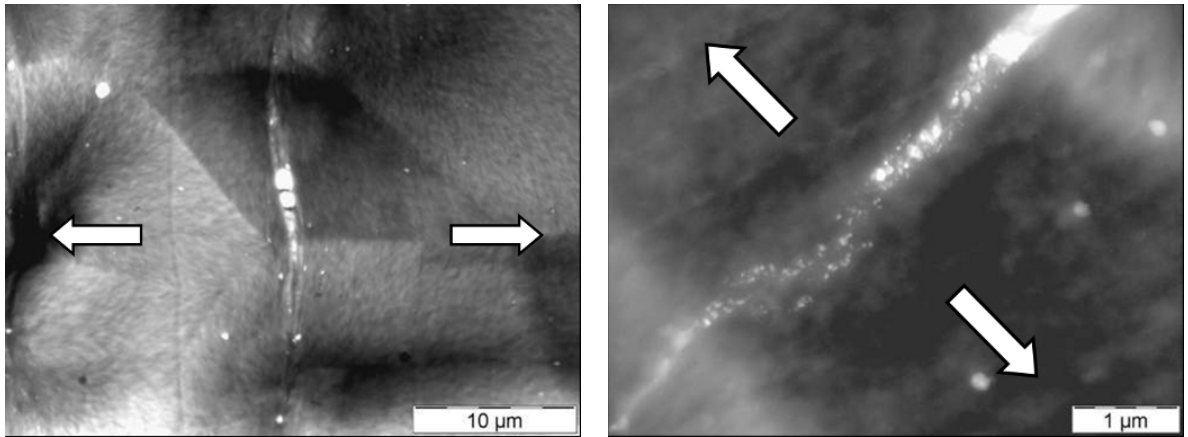


FIG. 6: TEM observation of thin slices of fatigued polyamide just below rupture zone in the plane normal to the applied stress. Arrows indicate the direction of the stress. Left: growth of a crack in the direction normal to the applied stress, at the equator of a spherulite, is observed. Right: Fibrils can be observed.

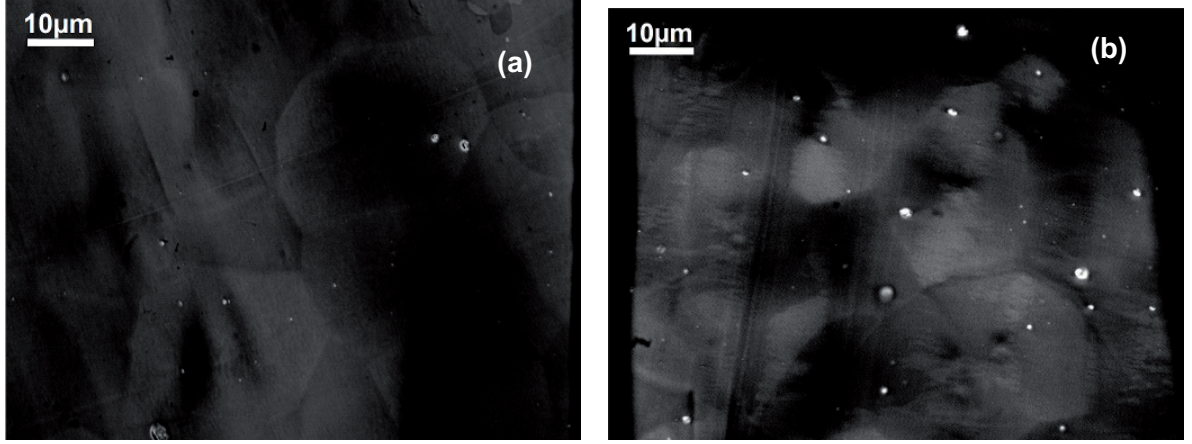


FIG. 7: TEM observations of slices of polyamide in the plane parallel to the stress (a) non fatigued sample; (b) fatigued sample after 300000 cycles with $\sigma_{max} = 61.9$ MPa and at an environment at 25°C.

section). The crazes could not be studied using this method (except at the very late stage of final rupture), because the contrast between crazes and the matrix was too small, whereas that of the spherical cavities is large. The distributions of sizes before and after fatigue are shown in Figure 8. The resolution of the method allows for determining their diameter within an uncertainty of $+70$ nm/ -30 nm for the x5000 magnified images and $+300$ nm/ -100 nm for the x1300 magnified images. The number of cavities down to about 100 nm can be determined. The diameter of the largest cavities is about $3\mu\text{m}$. The distribution of cavity sizes per unit volume can be approximated by a power law $n(R) \propto R^{-\alpha}$ where $\alpha \simeq 3.5$. The number of cavities with diameters larger than 500 nm is slightly larger after fatigue than before. The cavities may grow somewhat, but this effect is quite limited. The total void fraction corresponding to these spherical cavities is 0.1% for the reference specimen and 0.15% for the fatigued ones. We do not consider that this evolution is significant and sufficient to explain the decrease of mechanical properties and final failure of the materials. We shall thus investigate the presence of other types of damage defects in a complementary, more quantitative way, using scattering experiments.

D. Effect of fatigue on the crystalline morphology

The evolution of the crystalline structure during fatigue has been characterized by small angle X-ray scattering (SAXS) either in the relaxed state, or under tensile stress, using an in-situ stretching device, on test samples which have been fatigued prior to SAXS observation. The direction of the in-situ applied stress is the same as during fatigue cycles. 2D SAXS patterns are shown after 0,

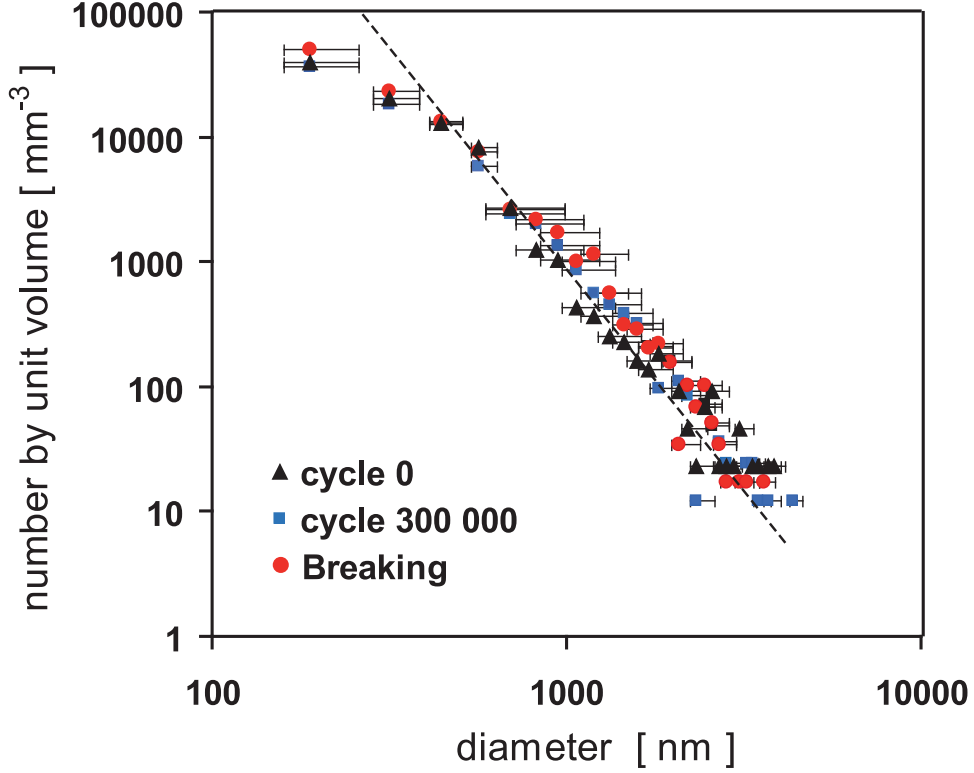


FIG. 8: Evolution of the size distribution of spherical cavities during fatigue as observed by TEM on thin polyamide slices. The dashed line indicates a $R^{-3.6}$ power law, in quantitative agreement with distributions determined by USAXS (see section III E). The distribution does not change significantly during fatigue tests.

2000 and 300 000 fatigue cycles at 25°C in Figure 9, in the relaxed state (patterns (a),(b),(c)) and under constant in-situ applied stress (patterns (e),(f),(g)). Pattern (d) in Figure 9 corresponds to a broken sample. These patterns exhibit two characteristic features. The small angle (central) scattering intensity corresponds to large scale heterogeneities in the sample. The central scattering evolves during fatigue, as a result of the damage mechanism creating heterogeneities, such as cavities, in the material. It will be analyzed in section III. E. The ring at intermediate q values is due to the periodic stacking of crystalline lamellae, which has a typical long period of about 8 to 9 nm. Thus, the evolution of the lamellar stacking under applied deformation and during fatigue may be analyzed in the range of scattering vector q used here. Details on the analysis are given in Supplementary Information. Fatigue has little impact on the position of the ring, whatever the scattering direction. Under zero applied stress, the scattering ring is isotropic, because the crystalline lamellae are oriented isotropically in all directions. The scattering pattern is reversibly modified under applied stress, with more scattered intensity in the ring in the tensile direction.

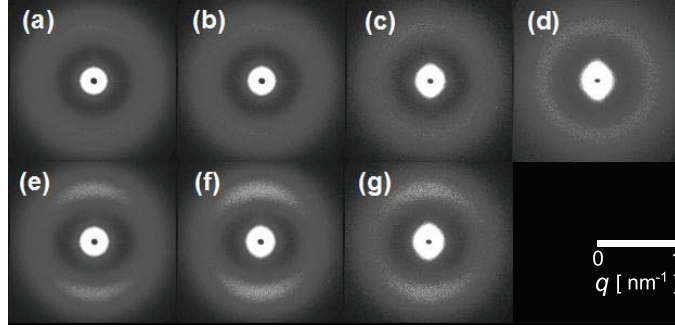


FIG. 9: 2D SAXS patterns for PA6,6 samples fatigued at different number of cycles under an applied stress of 69 MPa at 25°C (a) before fatigue (reference) ; (b) after 2 000 cycles; (c) after 300 000 cycles; (d) at break; the same samples under in situ applied stress (e) reference under applied stress of 50 MPa; (f) fatigued sample (2 000 cycles) under an in situ applied stress of 51MPa; (g) fatigued sample (300 000 cycles) under in situ applied stress of 42 MPa. Stress direction is vertical. The range of scattering vector q is indicated.

The angular dependence of the scattering intensity with respect to the direction of the applied stress provides information on the distribution of lamellae orientations, while the q position of the ring gives the lamellar spacing.

The variation of the lamellar period has been analyzed as a function of the orientation Ψ of the lamellae (see inset in Figure 10). The in-situ applied strain has almost no effect on the lamellae oriented parallel to the applied stress ($\Psi = \pm 90^\circ$). Conversely, the signal of the lamellae normal to the stress ($\Psi = 0^\circ$) increases, which indicates that their relative number increases. In addition, the peak is shifted towards smaller q -values, which means that the lamellae spacing increases. Spherulites are spherically symmetrical structures, with lamellae oriented radially. Thus, in the spherulite morphology, the lamellae which are oriented perpendicularly to the strain are located in an equatorial plane, where most of the strain takes place.

The local strain can then be estimated from the measured increase in the lamellar period under the effect of the in-situ applied stress, for the lamellae oriented in the direction normal to the applied stress ($\Psi = 0^\circ$). For a macroscopic strain of about 1.5%, the relative variation of lamellar period is about 3% for perpendicular lamellae, taking the non-fatigued sample under zero stress as a reference (see Supplementary Information). Since lamellae cannot contract in the lateral direction [17], a local volume change of the amorphous layer in the lamellar stacking of about 4% may be deduced (assuming that the crystalline-to-amorphous ratio within the lamellar stacking is equal to the overall crystallinity, of the order 35%). This is essentially reversible, since it is observed that the lamellae recover their initial spacing even after a large number of fatigue cycles (see Figure 2 in Supplementary Informations).

The variation of the strain in the amorphous phase between lamellae is shown in Figure 10 as a function of the angle Ψ , between -90° and 90° . The average interlamellae strain is 2.3%. The volume variation is maximum in a range of angle $\pm 30^\circ$. We assume that the damage, e.g. the nucleation of cavities, will be mostly localized in this region where the lamellae separation, thus the local strain, is the largest. Therefore, damage should be essentially localized within an angle of $\pm 30^\circ$ around the equatorial plane, corresponding to a volume of about 33% of a spherulite.

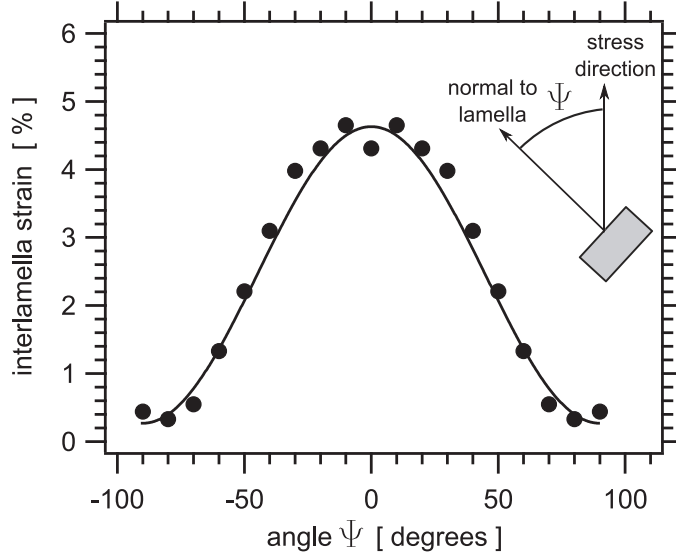


FIG. 10: Relative shift of the lamellar period as a function of the angle Ψ between the normal to the lamellae and the direction of the applied stress, for the fatigued sample submitted to an in-situ stress 40 MPa. The value for the non-fatigued sample under zero stress is taken as a reference.

E. Characterization of damage by Ultra Small Angle Scattering (USAXS)

At the center of the 2D SAXS patterns, i.e. at small scattering angles, the intensity increases with the number of cycles and becomes anisotropic (see Figure 9), which can be interpreted as a result of a damage mechanism creating heterogeneities in the material, such as cavities. From the q range involved in this central scattering, these cavities would have typical sizes larger than about 20 nm.

At scales large with respect to the lamellar period L_p , the PA material can be considered homogeneous. It contains a distribution of non-correlated cavities with different sizes, represented by a density $n(R)$ (in m^{-4}), such that the number of cavities per unit volume with radius R (within dR) is $dn = n(R)dR$. For a sample of thickness h containing a density $n(R)$ of spherical cavities, the total scattered intensity $I(q, R)$ (in W) is given quantitatively by [52]:

$$\frac{I(q)}{I_0} = T_r \beta^2 (\rho - \rho_0)^2 h \int_{R_{min}}^{R_{max}} V(R)^2 \left(3 \frac{(\sin(qR) - qR \cos(qR))}{(qR)^3} \right)^2 n(R) dR \quad (2)$$

where I_0 is the intensity of the incident beam (in W), T_r is the (dimensionless) transmission coefficient of the sample, β^2 is the electronic scattering cross section ($\beta^2 = 7.8 \times 10^{-30} \text{ m}^2$), ρ_0 (resp. ρ) is the electron density of the material (resp. inside cavities), in m^{-3} , $V(R) = \frac{4}{3}\pi R^3$ the volume of a cavity of radius R and h the sample thickness (in m). The function between brackets is the form factor of a homogeneous sphere. The differential scattering cross-section per unit volume (in m^{-1}) is then obtained by normalizing $I(q)/I_0$ by the sample thickness h and sample transmission T_r (in the following, cross-sections will be expressed in cm^{-1} and densities $n(R)$ in cm^{-4} , in agreement with usual convention). The electron density in PA is $\rho_0 = n_e d N_A / M$, where $n_e = 113$ is the number of electrons per repeat unit, d is the density ($d \approx 1.14 \times 10^3 \text{ kg.m}^{-3}$), N_A is Avogadro's number and $M = 226 \text{ g.mol}^{-1}$ is the molar mass of the repeat unit, which gives $\rho_0 = 3.43 \times 10^{29} \text{ m}^{-3}$ for PA6,6.

In practice, in order to determine quantitatively the size of the scattering objects, it is necessary to observe the cross-over between the so-called Guinier's regime $q < R^{-1}$, in which $I(q)$ shows a plateau, and the so-called Porod's regime $q > R^{-1}$, in which $I(q)$ decreases as a q^{-4} power law. In SAXS experiments (Figure 9), the central scattering signal corresponds to the Porod's regime (because cavities are too large), and it is necessary to access to much smaller values of the scattering vector q . Thus, we performed Ultra Small Angle X-ray Scattering (USAXS) experiments, which allow for studying objects up to one micrometer in a given direction. As noted already, in Figure 9, the central scattering at a given level of fatigue is not significantly affected by an in-situ stress, which indicates that these cavities do not increase in volume (or open) under the applied stress. Thus, in-situ stress was not applied here.

The normalized USAXS intensities $I(q)/(I_0 T_r h)$ (expressed in cm^{-1}) for the reference (not fatigued) sample (a) and the samples after different numbers of fatigue cycles ((b), (c), (d)) at 25°C are shown in Figure 11, in directions parallel and perpendicular to the direction of the fatigue loading.

The level of scattering observed in Figure 11(a) (as well as from Figures 7(a) and 8) shows that the samples before fatigue already contain cavities with an initial distribution of sizes. As discussed in Section IIIC, these preexisting, relatively large spherical cavities have been likely created during the injection process. Their evolution under fatigue cycles cannot explain the decrease of mechanical properties and final failure of the materials.

During the first 10 000 cycles, the scattering does not increase significantly and remains isotropic (Figure 11(a) and (b)). At larger number of cycles, it becomes anisotropic and increases considerably in the direction parallel to the fatigue stress (Figure 11(c) and (d)). Note that the studied polymer is formulated with a small amount of de-moulding wax and does not contain additives which could contribute to the scattering intensity. Also, differential scanning calorimetry (DSC) measurements have shown that the crystallinity is not modified during fatigue experiments. Thus, the increase of the scattered intensity cannot be related to a change in the crystallinity of the material, but it is rather due to the appearance of density inhomogeneities in the material.

In order to analyze the scattered intensity, we have assumed that two distinct populations of cavities coexist in the fatigued samples, both described by power law densities of the form

$$n_0(R) = P_0 R^{-\alpha_0} \quad (3)$$

corresponding to initial cavities, and

$$n_F(R) = P_F R^{-\alpha_F} \quad (4)$$

for fatigue-induced damage. The overall signal is then obtained by adding both contributions. The adjustable parameters are the cut-off sizes R_{min} and R_{max} , exponents α_0 and α_f and pre-factors P_0 and P_F of the power law distributions.

Cavities observed in all non-fatigued samples (resulting from the injection process) are assumed to be spherical, since USAXS spectra are similar in the two orthogonal directions at small number of fatigue cycles (see Figure 11(a)). The electron density inside cavities (voids) is supposed to be zero. This population of cavities is modeled by equation 3, with an exponent $\alpha_0 = 3.6$ and radii ranging from $R_{min} \approx 10$ nm to $R_{max} \approx 1300$ nm. The scattered intensity increases only slightly with the number of cycles and remains isotropic. A small increase of the number of spherical cavities is observed in samples fatigued up to breaking point. The corresponding volume fraction increases from 0.05% up to about 0.15% at break. These results are fully consistent with TEM observations (see Figure 8). Note again that this population of defects does not contribute significantly to the evolution of the material properties (decay of the elastic modulus), because these cavities are isotropic and remain at very small volume fraction.

On the other hand, since the scattered intensity at large number of fatigue cycles becomes anisotropic, cavities induced by fatigue are assumed to be anisotropic (ellipsoidal), with an aspect ratio $\psi = R_x/R_y$, where R_y (resp. R_x) is the dimension of the ellipsoidal cavities in the direction parallel (resp. normal) to the applied stress. Intensities in both parallel and normal directions must of course be fitted with a single distribution $n_F(R)$.

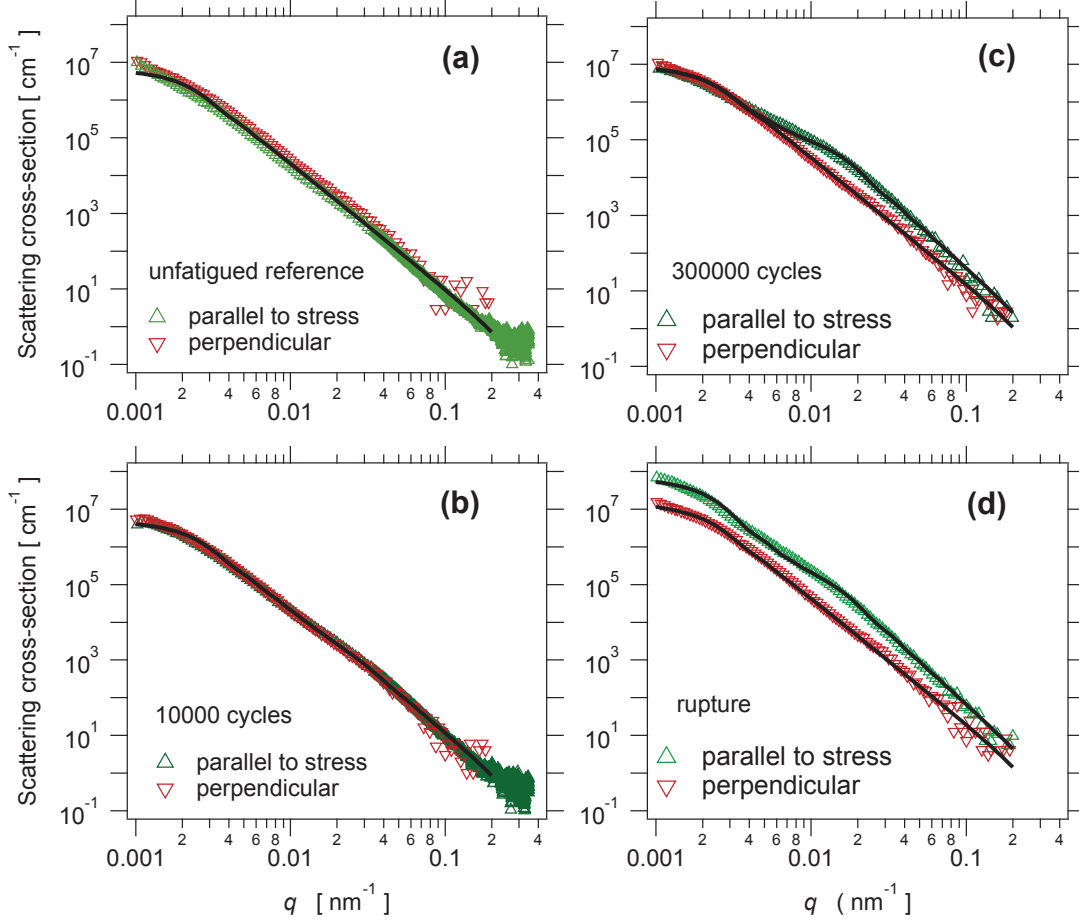


FIG. 11: Modeling of the scattered intensity in the directions y (parallel to the stress) and x (perpendicular to the stress) for the sample fatigued at 3×10^5 cycles with two power law distributions of cavity sizes.

We consider that anisotropic cavities nucleated during fatigue are probably related to an early stage of craze development (see Figure 6) and may still contain some polymer, though no longer able to transmit stress. Thus, an adjustable electron density $\rho = \varphi \rho_0$, where φ is the volume fraction of polymer inside the anisotropic cavities, is attributed to this population. All fitting parameters (parameters of the distributions in equations 3 and 4, form factor ψ and volume fraction φ of polymer within the anisotropic cavities nucleated during fatigue) have been adjusted in order to be consistent with both the drop of modulus of order 10 %, the variation of density and the scattering in directions parallel and normal to the applied stress. Examples of modeled spectra are given in Figure 11. Modeling parameters for both pre-existing cavities formed during injection and for cavities nucleated during fatigue are summarized in Table I.

The samples fatigued at 2000 and 10 0000 cycles show a population of isotropic nucleated cavities, with radii between 10 nm and 110 nm. At 300 0000 cycles, these domains evolve towards

Number of cycles	initial cavities			cavities nucleated in fatigue			
	$R_{min}^{(0)}$ (nm)	$R_{max}^{(0)}$ (nm)	P_0	$R_{min}^{(F)}$ (nm)	$R_{max}^{(F)}$ (nm)	P_F	ψ
0	10	1350	2×10^{-10}	-	-	-	-
2×10^3	10	1230	2×10^{-10}	10	110	5×10^{-3}	1
1×10^4	10	1230	2×10^{-10}	10	110	6×10^{-3}	1
3×10^5	10	1250	3×10^{-10}	10	190	6×10^{-4}	3
at break	10	1350	4×10^{-10}	10	200	1.2×10^{-4}	5
				10	1310	7×10^{-6}	5

TABLE I: Modelling parameters for pre-existing spherical cavities formed during injection (see equation 3). Modelling parameters for anisotropic cavities formed during fatigue (see equation 4). φ is the volume fraction of polymer inside cavities, ψ the aspect ratio R_x/R_y , with R_x (resp. R_y) the radius in the direction perpendicular (resp. parallel) to the fatigue stress. R_{min} and R_{max} are the radii in direction y (parallel to the fatigue stress). At break, the modeled distribution is binodal, with a fraction of cavities having radii up to $1.3 \mu\text{m}$ in y direction.

anisotropic cavities with a dimension R_y between 10 nm and 190 nm in the y direction (parallel to the applied stress) and R_x between 50 nm and 950 nm in the x direction (normal to the applied stress), corresponding to a form factor of about 5. At failure, the spectra can be best fitted in both directions by a bimodal distribution of anisotropic nucleated cavities, suggesting that a fraction of the cavities nucleated during fatigue (which have radii between 10 and ~ 200 nm in y direction and between 50 nm and $\sim 1 \mu\text{m}$ in x direction) have coalesced into larger damage zones with radii up to $1.3 \mu\text{m}$ in y direction and $6.5 \mu\text{m}$ in x direction. The parameters of this bimodal distribution are reported in Table I (bottom line).

For a density $n(R)$, the total number of cavities per unit volume is:

$$N = \int_{R_{min}}^{R_{max}} n(R) dR \quad (5)$$

while the total void fraction in the material is estimated by:

$$V = \int_{R_{min}}^{R_{max}} V(R) n(R) dR \quad (6)$$

The total numbers of cavities and void fractions corresponding to fitting parameters summarized in Table I are given in Table II. This total void fraction is an average value and does not account for local variations at small scale. Note that it strongly depends on the maximum cavity diameter R_{max} .

Thus, in our calculation, the volume fraction of the anisotropic cavities does not grow linearly with the number of cycles. It is about 1.4% at break. The polymer fraction within the cavities is

Number of cycles	N_0 (cm ⁻³)	V_0 (%)	N_F (cm ⁻³)	V_F (%)
0	3.1×10^{12}	0.05	-	-
2×10^3	3.1×10^{12}	0.05	3.54×10^{13}	0.54
1×10^4	3.1×10^{12}	0.05	4.25×10^{13}	0.64
3×10^5	4.7×10^{12}	0.075	4.16×10^{12}	1.29
at break	6.2×10^{12}	0.1	8.8×10^{11}	1.51

TABLE II: Total numbers of cavities N_0 (in cm⁻³) and volume fractions V_0 of initial spherical cavities due to the injection process, and N_F and V_F for cavities nucleated during fatigue.

quite high, about 90%. This result is consistent with the hypothesis that these cavities are the onset of cracks. This high value allows also for explaining that the overall drop of density is relatively small, of the order 0.1%. On the other hand, these cavities have a pronounced anisotropy, with a form factor of about 5 and their larger dimension perpendicular to the stress direction. Assuming that the damage is located within a solid angle of 30 degrees around the equator (the plane perpendicular to the stress direction), it may explain a drop of modulus of order 10%, consistent with the results of mechanical measurements.

IV. DISCUSSION

We have studied the evolution of mechanical properties of PA6,6 samples in the fatigue regime. One of the main features we have observed is the slow decrease of the modulus with the number of cycles. This decrease is logarithmic in the number of cycles. As such, this is the signature of a decreasing rate of damage within the samples. At the end of the logarithmic regime, the system enters a more catastrophic process before final breaking of the material. TEM observations show that cracks grow preferentially in the direction parallel to the crystalline lamellae, and normal to the applied stress. This corresponds to the equator of spherulites. During a first stage of fatigue tests, USAXS observations show that essentially spherical damage domains with diameters comprised between 10 and 100 nm nucleate (see Table I). Up to 10^4 cycles, the number of these cavities increases while their average size remains essentially constant. These cavities involve several crystalline lamellae (the lamellar period is roughly 10 nm). This is compatible with the mechanism proposed by Friedrich [11]. At a later stage, some of these domains grow in the direction normal to the applied stress. At break, anisotropic damaged domains have sizes between 10 nm and 1.3 μm in the direction parallel to the stress and between 50 nm and 6.5 μm in the direction normal to the stress. The initial spherical cavities, generated in the injection process, do not explain the

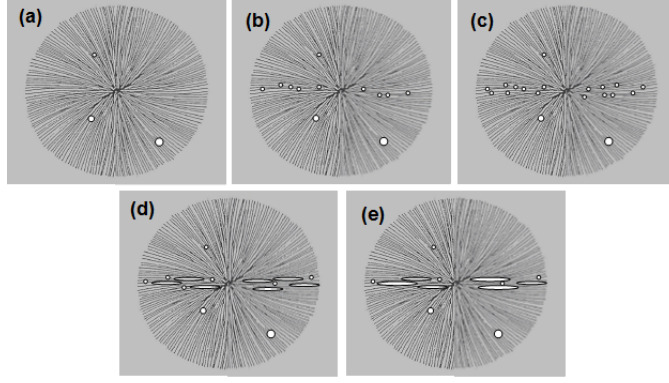


FIG. 12: Growth of sub-micron cavities in the amorphous phase between lamellae oriented in the direction normal to the applied stress (a) micron sized cavities with broad distribution of size in the non fatigued sample. (b) nucleation of cavities in the amorphous phase with diameters comprised between 20 and 180 nm; (c) increase of the number of the spherical cavities in the course of fatigue testing; (d) and (e) growth of the cavities in the direction normal to the applied stress.

evolution of the mechanical properties. They may contribute to the nucleation of cavities because the stress in their very close vicinity is larger than the average stress [11, 53], up to a factor of 3 at the equator of a spherical cavity [54]. On the other hand, the distribution of stress amplification in a disordered material like semi-crystalline PA may extend to much larger values. We estimate the latter to be as large as 10 as we shall see below. As a consequence, we do not expect the effect of stress amplification in the vicinity of initial cavities to be significant. Indeed, we do not observe that cracks or damage is initiated preferentially in the vicinity of the pre-existing cavities. Final rupture takes place when the volume fraction of damaged material is of order 1%, whereas the density reduction of the sample is less than 10^{-3} in relative amplitude. This feature could be explained by the fact that the cavities contain about 90% of polymer, though the latter is unable to transmit stress. We have seen that mechanical and scattering data could be made quantitatively consistent with this assumption.

Damaging in PA6 submitted to plastic deformation, i.e. strained beyond the yield stress, has been described in [51]. The situation described here is quite different. Strain amplitude remains small (typically 2%), still in the elastic regime and in any case well below the yield stress. Damage occurs progressively over the long time scale of the experiments. Nevertheless, initial cavities observed here, generated during processing, may correspond to 'weak spots' mentioned in [51]. Anisotropic cavities (as described in [51]) are observed here only in the later stage of fatigue, in which damaging of the material becomes comparable to that observed under directly straining the material at large amplitude. Moreover, as mentioned in Section IIID, damage is most likely

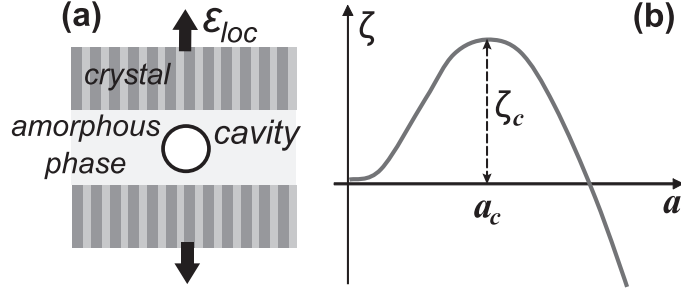


FIG. 13: Nucleation of a cavity: (a) cavities are nucleated in the amorphous phase, due to 3D dilatational stress (see text); (b): variation of the excess of free energy as a function of the cavity diameter a .

located in the equator of spherulites, as also observed in [51]. Note also that USAXS experiments performed here do not give access to cavity locations.

In the following, we discuss the different steps of damage mechanisms, based on our experiments and on a theoretical model proposed in reference [44]. The elementary nucleation process is discussed in subsection **A**. The ensuing different regimes, which correspond to accumulation of cavities or to cracks propagation, are discussed in subsection **B**, based on the model developed in [44]. Note that the slow logarithmic decay of the elastic modulus can be explained by a broad distribution of strain amplification factors on a microscopic scale within a simple mean field model. We refer to Appendix for further details. The cross-over between the initial logarithmic regime and final breaking of the material is discussed in subsection **C**. The proposed scenario for rupture in fatigue is summarized in subsection **D**.

A. Nucleation of a cavity

The elementary damage mechanism is cavity nucleation. According to traditional criterions, cavitation occurs when the isotropic component of the stress, i.e. the negative pressure, exceeds a given value [55]. Based on our experiments, we propose that the nucleation of cavities is initiated within the amorphous phase between lamellae oriented in the direction normal to the applied stress, as it has been proposed for poly(fluor vinylidene) [36] (Figure 12). In the case of non oriented semi-crystalline polymers, Kuksenko and Tamusz have observed cavities with diameters of a few hundreds of nanometers [34]. It is generally considered that nucleation is thermally activated [43, 56]. The nucleation time of a cavity with energy barrier ζ is given by

$$\tau = \tau_0 \exp\left(\frac{\zeta}{k_B T}\right) \quad (7)$$

where τ_0 is a microscopic time of order 10^{-12} s [57]. The free energy ζ of a cavity contains two terms. One, corresponding to the release of elastic energy, favors cavitation. The second one is the surface energy excess, which tends to prevent cavitation.

The macroscopic deformation of the sample under an applied stress σ is given by

$$\epsilon_{macro} = \frac{\sigma}{E} \quad (8)$$

where E is the Young's modulus of the material. The local deformation may be amplified by a factor μ . In addition, due to the presence of crystallites, the macroscopic deformation results at the microscopic level into a volumetric strain, which we denote $\epsilon_{v,loc}$, given by

$$\epsilon_{v,loc} = \frac{\mu\sigma}{E} \quad (9)$$

The factor μ is a strain amplification factor, which is due to the heterogeneous and disordered nature of the material. At a microscopic level, a crystallite is submitted to an applied deformation $\epsilon_{v,loc}$ (see Figure 13(a)). Because crystallites are rigid, even though the macroscopic deformation is uniaxial, the local deformation within the amorphous phase may be triaxial, which favors nucleation of cavities in the amorphous phase. The elastic energy contained in a sphere of diameter a in the amorphous phase is given by

$$E_{el} = \frac{1}{2} \frac{\pi}{6} K \left(\frac{\mu\sigma}{E} \right)^2 a^3 \quad (10)$$

where K is the bulk modulus of the amorphous phase. The free energy barrier for cavity nucleation is thus given by

$$\zeta = -\frac{1}{2} \frac{\pi}{6} K \left(\frac{\mu\sigma}{E} \right)^2 a^3 + \pi\gamma a^2 \quad (11)$$

where γ is the surface tension of the amorphous phase of polyamide. The variation of the free energy barrier as a function of the cavity radius is plotted in Figure 13(b). The critical diameter a_c , given by $d\zeta/da = 0$, is thus

$$a_c = 2\pi\gamma \left(\frac{\pi}{4} K \left(\frac{\mu\sigma}{E} \right)^2 \right)^{-1} \quad (12)$$

The corresponding activation energy is

$$\zeta(\sigma) = \frac{64\pi}{3} \frac{\gamma^3}{K^2 \left(\frac{\mu\sigma}{E} \right)^4} \approx 60 \frac{\gamma^3}{K^2 \left(\frac{\mu\sigma}{E} \right)^4} \quad (13)$$

Cavities with diameter smaller than a_c are unstable, whereas cavities with diameter larger than a_c grow.

Cavities can nucleate everywhere in the sample. The nucleation process involves fluctuations which take place on the scale of the critical nucleation radius a_c . A sample of volume V can thus be seen as an ensemble of $N = V/a_c^3$ independent cells of volume a_c^3 . Each cell has a probability of nucleation per unit time $1/\tau$. The number of nucleation per unit time is thus N/τ , which corresponds to a nucleation rate R (number of nucleation events per unit volume and per unit time):

$$R \sim \frac{1}{a_c^3 \tau} \quad (14)$$

For more details regarding nucleation processes, see *e.g.* [58]. The typical time scale of fatigue experiments is $t_{break} \sim 10^5 - 10^6$ s. Let us assume that, after cavitation has taken place, the cavity diameter grows up to $d \sim 10$ nm in a short time scale (we do not observe smaller cavities by X-ray scattering). On the time scale $t_{break} \sim 10^5$ s, a volume fraction of about 1% of the material corresponds to cavities. This corresponds to a cavitation rate of $R \sim 10^{-2}/(d^3 t_{break}) \sim 10^{17} \text{ m}^{-3} \text{ s}^{-1}$. Assuming that $a_c \sim 1$ nm, the corresponding typical nucleation time, given by $\tau = 1/(Ra_c^3)$, is thus $\tau \sim 10^{10}$ s. The nucleation barrier is then

$$\zeta_c = k_B T \ln \frac{\tau}{\tau_0} \sim 50 k_B T \sim 2.10^{-19} \text{ J} \sim 1.2 \text{ eV} \quad (15)$$

Thus, the relevant values of free energy barriers can be deduced from the time scale of the experiment. Too small barriers would correspond to very short time scales, irrelevant in fatigue experiments: the applied stress is too large and the material breaks immediately. Too large energy barriers would correspond to very long time scales, inaccessible to experiments: at such stress or strain levels, the material suffers no damage and can be considered as unbreakable. These low stress levels are not of interest here. Note that the critical stress σ_c , deduced from eq. 13, depends only weakly on the time scale of interest:

$$\sigma_c = \frac{E}{\mu} \left(\frac{60\gamma^3}{K^2 \zeta_c} \right)^{1/4} \quad (16)$$

At 25°C, the surface tension of polyamide is $\gamma \approx 4 \times 10^{-2} \text{ J/m}^2$ [2]. The bulk modulus is $K \approx 5 \text{ GPa}$ and the Young's modulus of our samples is about $3 \times 10^9 \text{ Pa}$. By taking $\mu = 10$, the corresponding value for the critical stress is $\sigma_c \approx 60 \text{ MPa}$, which is comparable to the experimental values. The critical diameter is $a_c \approx 1 \text{ nm}$. Note that the strain amplification factor μ estimated here is much larger than that in the vicinity of spherical cavities as discussed above, which is only a factor of 3. Thus, the fact that damaging takes place in an accessible time scale at stress levels of order 60 MPa is an indication of the very broad distribution of strain amplification factor μ at

the micro-scale, which we estimate to be distributed between 1 and 10.

Note that the local stress may be as high as $\sigma_{max} \sim \sigma_c \mu \approx 600\text{MPa}$. This value would correspond to the so-called homogeneous nucleation, when nucleation takes place within the bulk of a pure material. In many instances, it is observed that nucleation takes place under less demanding conditions, whether this may be for crystal nucleation [59], or bubble nucleation when a gas is dissolved in a polymer (*e.g.* for making foams [60, 61]) as compared to what a homogeneous nucleation model would predict. The most common situation corresponds to the so-called heterogeneous nucleation and takes place in the presence of defects, or impurities. Indeed, the presence of heterogeneous particles can lower the free energy of nucleation by orders of magnitudes as compared to the homogeneous situation. For instance, it has been observed at a macroscopic scale that nucleation of cavities in polycarbonate takes place at a critical stress of order 90 MPa [62] whereas a model for homogeneous nucleation similar to the one described here would predict a critical stress of a few hundreds of MPa. Our interpretation of what is usually reported, is that the observed nucleation takes place on impurities which are always present in a polymer. In a semi-crystalline polymer, crystallites corresponding to large deformation amplification factor μ act like defects which facilitate nucleation. They may be the dominant factor for nucleation in a semi-crystalline polymer. Indeed, the number of crystallites per unit volume is very high, and may be much larger than the number of impurities due to synthesis or processing steps. In amorphous polymers, it is likely that the latter dominate the nucleation mechanism as it is the case for crystal or bubble nucleation [59–61].

Since we are particularly interested in stress levels close to σ_c , the energy barrier can be calculated as a function of σ by a linear approximation around σ_c , $\zeta(\sigma) = \zeta(\sigma_c) + (\sigma - \sigma_c) \frac{d\zeta}{d\sigma}(\sigma_c)$, that is

$$\zeta(\sigma) = U_0 - \frac{K\nu\mu\sigma}{E} \quad (17)$$

with

$$U_0 \approx \frac{300\gamma^3}{K^2 \left(\frac{\mu\sigma_c}{E}\right)^4} \sim 3 \times 10^{-19} J \quad (18)$$

and

$$\nu \approx \frac{240\gamma^3}{K^3 \left(\frac{\mu\sigma_c}{E}\right)^4} \left(\frac{K^2\zeta_c}{60\gamma^3}\right)^{1/4} \sim 1.3 \times 10^{-27} m^3 \quad (19)$$

At room temperature, we find that the activation volume is of order $\nu \approx 1 \text{ nm}^3$. Note that activation volumes for plastic deformation of amorphous or semi-crystalline polymers are typically

found between 1 nm^3 and 10 nm^3 in the literature [17, 63–66]. In the limit where the local deformation is not influenced by the drop of modulus, $\epsilon_{v,loc} = \mu\sigma/E(0)$, we get

$$\tau = \tau_0 \exp \left(\frac{U_0 - \frac{\mu\sigma K\nu}{E(0)}}{k_B T} \right) \quad (20)$$

which is the classical nucleation time given by the Eyring model [67, 68]. Note that a cavitation model has been discussed for polyethylene by Humbert et al [69].

B. Accumulation of defects versus crack propagation

Once a cavity nucleates, it grows. If the growth was unimpeded, the material would break by crack propagation. Both mechanical and USAXS experiments show that this is not the case. We do observe indeed that the life-times of our samples are very large under the considered applied stress. USAXS experiments show the appearance of cavities between 10 and 100 nm in diameter. This indicates that the propagation of elementary cracks stops at this size. We assume that this is the consequence of the disordered nature of the material at the scale of a few tens of nanometers. Indeed, Wide Angle X-ray Scattering (WAXS) spectra obtained in our samples (not shown) show relatively broad Bragg peaks associated to the crystalline structure. Using the Scherrer formula [70], the lateral extension of crystallites deduced from the peak width is estimated to be typically a few tens of nanometers: crystallites do not extend perfectly regularly over larger distances. These defects of the crystallites may stop crack propagations at typical sizes of a few tens of nanometers (see Figure 14.b).

Stress concentration (stress amplified by a factor 3 typically for a spherical cavity) may favor nucleation ahead of an already formed cavity, giving rise to a catastrophic propagation process. Then, once a cavity has stopped to propagate, what may prevent nucleation of a new cavity just ahead of it? As discussed above, the width of the distribution of stress amplification factors, or equivalently of free energy barriers, extends up to typically 10, due to the disordered nature of the material. We suggest that this is the reason why this catastrophic process does not take place. If the barriers are broadly distributed through the material, nucleation may occur randomly in the material. The dominant damage mechanism then results from the competition between the two following mechanisms: either 1) independent cavity nucleation processes throughout the sample, until the density of cavities reaches a critical value above which the material crumbles, or 2) the growth of a single cavity which results in the appearance of a crack. Indeed, once a microscopic damage has nucleated, the broken region can no longer sustain stress and the latter is redistributed

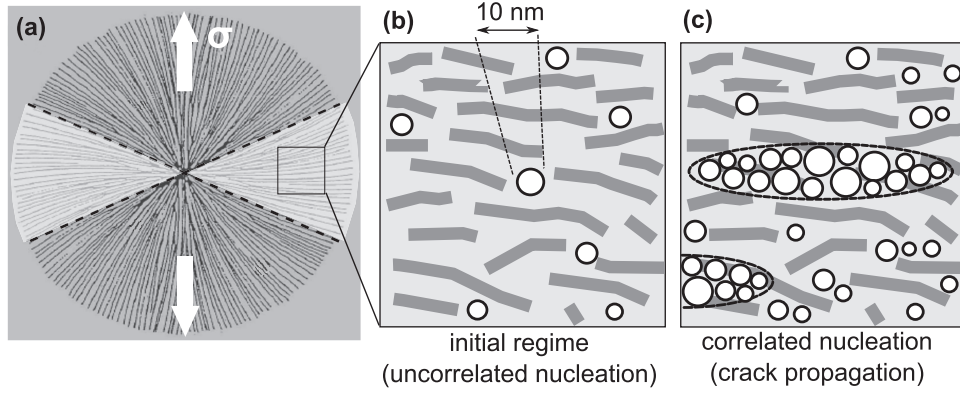


FIG. 14: Schematics of cavity nucleation in the equator of spherulites (a): (b) initial, logarithmic regime (nucleation of uncorrelated cavities); (c) final, crack propagation regime. In the initial regime, growth of cavities is limited to about 10-20 nm due to semi-crystalline disorder. Dark grey line fragments schematize crystallites.

with a local intensification in front of the nucleated defect. A number of theoretical studies have shown that, depending on the amplitude of the disorder and stress level, different regimes may appear, such as abrupt rupture, rupture with localized damage or rupture with diffuse damage [40–42, 71–77]. A model which allows for studying the competition between these two mechanisms has been proposed in [44]. The authors modeled the system with a distribution of rupture thresholds. Note that, in terms of activation energy distribution, this is equivalent to a distribution of local stress intensification due to heterogeneities of the material. A phase diagram for the damage evolution in a 2D representation (applied stress, level of disorder) has been proposed (Figure 15b). At high stress or low disorder, exponential decay of the modulus is observed. At lower stress or higher disorder, a logarithmic decay, analogous to the fatigue regime studied here, is observed. This slow evolution of the modulus is accompanied by a growing number of nucleated defects (cavities). Final rupture takes place when a large number of cavities have nucleated.

The transition from mechanism 1) to mechanism 2) may be obtained by reducing the width of the energy barrier distribution, so that the increase of stress ahead of a small defect may be sufficient to induce the nucleation of another cavity just ahead of this defect on a short time scale, resulting in a catastrophic fracture process.

It was found that mechanisms 1) and 2) correspond to very different rupture patterns: narrow disorder results in fast/exponential decay of modulus and rupture by localized crack growth, whereas broad disorder results in slow/logarithmic damaging and in rupture by accumulation of random nucleation of defects (cavities,...) throughout the sample. The corresponding simulations

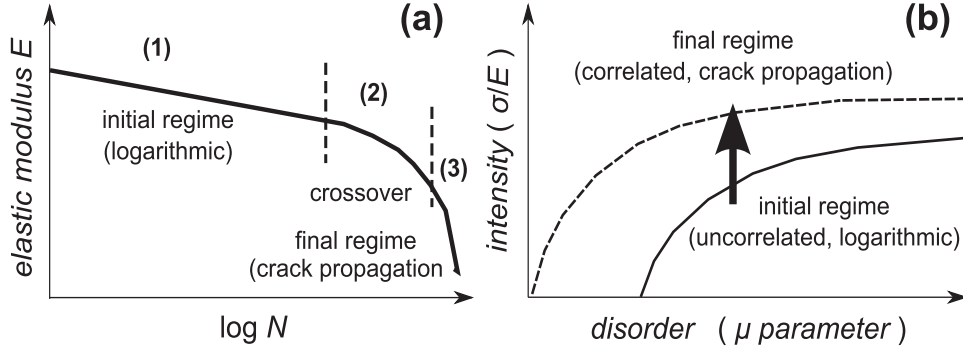


FIG. 15: (a): Schematics of the modulus evolution during fatigue tests. Regime 1 is associated to random and uncorrelated nucleation of cavities a few tens of nanometers. These cavities do not grow, only their number increases. Regime 2 is characterized by correlated nucleation of cavities in the vicinity of already present cavities. As a consequence, cavities grow in size and their number decreases. Regime 3 corresponds to crack propagation and the final breaking of the material; (b): Phase diagram for the fatigue behavior of the material, as a function of the macroscopic stress level (in ordinate) and the microscopic disorder (in abscissa). The dashed curve is the boundary of the regime of fast/exponential damaging (high stress/small disorder). The continuous curve is the boundary of the regime of slow/logarithmic damaging (low stress/large disorder). Along fatigue experiments, the system may evolve from the logarithmic regime (regime 1 in (a)) to a faster decay regime (regime 2 then 3 in (a)). Indeed, due to the decrease of the modulus E along the test, the system goes progressively from the initial logarithmic (nucleation of uncorrelated cavities) regime (1) to a crack propagation regime (3), as indicated by the vertical black arrow (inspired from ref [44]).

are much in line with the experiments described here, in which a logarithmic decay of the elastic modulus is observed. Indeed, in our experiments, breaking takes place when a large fraction of the material (up to 1 vol%) has been damaged. Note that if a single crack would propagate, this fraction would be zero outside of the crack itself, or, conversely, if the damage zone was about 20 nm around the crack, the corresponding volume fraction of damaged material would be orders of magnitude smaller than what is observed by USAXS experiments (for which the probed zone is about $100\mu m \times 100\mu m$ in size). Our experiments indicate that damaging during fatigue takes place in a first step by a large accumulation of nucleated cavities. No crack propagation takes place during this regime (Figure 14b). Crack propagation finally appears when the modulus has decreased sufficiently so that the ratio between the applied stress and the elastic modulus is large enough and that faster damaging may start. At intermediate levels of stress relevant to the fatigue regime, this effect appears after a very large number of cycles. This transition is schematized in Figure 15.

The transition between rapid/exponential and slow/logarithmic damaging regimes as a function

of the stress or disorder levels has been described in reference [44] by numerical simulations. The model proposed in [44] takes elasticity into account (though in a simplified way), which allows for describing quantitatively the competition between nucleation of cavities or crack propagation. The logarithmic decay of the modulus may be described as well by simpler arguments within the framework of a mean field picture, as described in Appendix.

C. Cross-over between logarithmic regime and final rupture

As we have seen, we interpret the logarithmic decrease of the elastic modulus as a function of the number of cycles as the consequence of a slowing down of the damaging rate of the material. USAXS results (see Table I and Table II) show that the size of the cavities remain constant and that their total volume fraction increases for test durations up to 10^4 cycles. We interpret this behavior as the consequence of random uncorrelated cavity nucleations, as discussed above. Then, at 3×10^5 cycles, the volume fraction of the cavities has increased further, from 0.64% up to 1.29%, while the total number of cavities has decreased by a factor of order 10. Note also that the form factor evolves from 1 (sphere) to 5 (ellipsoids). We interpret this result as the consequence of the fact that nucleations tend to be correlated in this regime. Nucleations take place preferentially in the vicinity of existing defects. As a consequence, defects tend to grow in size by coalescence between large defects and new cavities which nucleate in their vicinity. Hence the increase of the form factor from 1 (spherical cavities) to 5 (ellipsoidal cavities), the increase of cavity radii, and the decrease of the number of cavities observed at cycle 3×10^5 as compared to cycle 10^4 in Tables I and II. This process of correlated nucleations and coalescence is schematized in Figure 14(c). This process is probably accompanied by a progressive acceleration of the damaging rate, even though it is not identified clearly in our mechanical measurements. This acceleration is schematized in Figure 15(a). This process may thus be seen as a cross-over between the regime of logarithmic/uncorrelated cavity nucleation and the final growth of macroscopic crack. This cross-over regime extends over a long period of time: the damaging rate remains slow and is still slowing down in this regime. The main feature is that cavity nucleation has evolved from an uncorrelated towards a correlated process. The transition between the regimes of uncorrelated towards correlated nucleation is triggered by the decrease of the macroscopic modulus, which can no longer be neglected at some point of the fatigue test.

D. Summary

The distribution of cavity radii R has been determined by USAXS experiments as a power law with exponent $\alpha \approx 2.5$ between $R_{min} \approx 10$ nm and a maximum value R_{max} which depends on the cycle number and is of order a few hundreds of nanometers at the late stage of fatigue experiments. At this stage, these cavities represent a volume fraction of order 1% and are elongated in the direction normal to the applied stress with a form factor of about 5, which explains the modulus drop of about 8%. Assuming that these cavities are full of polymer at 90% corresponds quantitatively to both USAXS experiments and the decrease of the density of the sample.

Fatigue damaging of semi-crystalline PA 6,6 has been interpreted as due to random nucleation of cavities, which are essentially not correlated in an early stage (up to a few 10^4 cycles in the experiments reported here). The critical nucleation radius is about 1 nm. Cavities grow within the amorphous phase between crystallites up to sizes of about 10-100 nm on a short time scale. Further growth requires new nucleation of cavities. Larger cavities of a few 100 nm-up to 1 μ m, as observed in USAXS experiments, appear at a later stage when the decrease of the modulus may induce a feed-back between cavity nucleation and faster nucleation in the vicinity of the already present cavities: nucleation starts to be correlated. This process may thus appear as the cross-over between early stages, during which nucleations are totally uncorrelated, and final breaking of the sample when cracks end up by propagating throughout the sample.

V. CONCLUSION

We have studied fatigue mechanisms in PA 6,6 by a combination of mechanical experiments, X-ray scattering (SAXS and USAXS), electron microscopy and density measurements. The dynamic modulus decreases linearly with the logarithm of the number of fatigue cycles. At break, the drop of dynamic modulus is about 8%, whereas the density drop is only 0.1%. X-ray experiments indicate that the damage is initiated between crystalline lamellae perpendicular to the direction of the fatigue stress. In a first stage, damaging corresponds to uncorrelated nucleations of essentially spherical cavities with sizes distributed between 10 and 100 nm. The number of these cavities increases progressively. At the end of this stage, the volume fraction of the damaged regions in the samples is of order 1%. At a later stage, the number of cavities decreases, whereas the size and anisotropy of the cavities increase. Defects become ellipsoidal cavities, elongated in the direction normal to the applied stress, which we attributed to nucleations which take place

preferentially in the vicinity of exiting defects and to a coalescence process. At the very late stages of fatigue, these low density domains grow to form crazes observed in SEM. The rupture of the material is the consequence of an accumulation of damage, and is not due to the propagation of a single crack. More precisely the latter takes place in a later stage, after a large amount of damage has been accumulated, so that the modulus has significantly decreased. This behavior is the consequence of the strongly disordered nature of these materials, as it has been proposed in reference [44] by simulating slow damaging mechanisms in disordered materials.

Note that we considered only a single value for the R parameter ($R = 0.1$) and a single frequency. However, our point of view is that the nature of the microscopic mechanisms do not depend on these parameters, though their kinetics do. **In the case when the dominant failure mechanism is crack initiation and growth, increasing of frequency or increasing of the stress amplitude, (*i.e.* reducing the R parameter at fixed maximal stress) result in a decrease of the life-time [78].** The simulations performed in reference [44] considered only static stress (and therefore $R = 1$). One may question then what would be the prediction of this model as regard to the effect of frequency and stress amplitude R . Though further studies will be required, a clue can be given by the effect of fluctuations which have been included in this model. In addition to the local value of the stress, a fluctuating term is added, which accounts for either the effect of temperature, or the effect of other kind of fluctuations. We do observe a reduction of the life-time when increasing these fluctuations. Regarding experiments in cyclic conditions, we expect that the stress field at the microscopic level is different at time t and $t + T$ where T is the period, as a consequence of the disordered nature of the materials. Thus, our point of view is that the reduction of life-time in cyclic conditions (as compared to static one) or when decreasing R at fixed maximal stress may be explained by the increase of the fluctuations of the stress at the local level. **Validating this picture will require further experimental studies and theoretical ones however.** We hope that our work will stimulate further experimental studies, in particular for exploring the effects of various relevant parameters on fatigue kinetics, and theoretical work for elaborating a more complete description of these damaging mechanisms and kinetics.

VI. APPENDIX

A. Mean field model for damaging in disordered material: Exponential versus logarithmic decay of the modulus

Polyamide is a semi-crystalline material, and is thus heterogeneous in nature. Strain is thus heterogeneous at a microscopic scale and the local strain may be much larger than the macroscopic one. There is thus a distribution of nucleation times, related to the distribution of local strain (or stress) amplification factors. Let us assume that cavities nucleate in a uncorrelated way. The nucleation of a fraction of cavities (or failure of a fraction of defect sites) does not influence the rupture times of remaining sites. This hypothesis amounts to assume: 1) that the drop of the modulus is negligible, so that the local strain at one (yet unbroken) site is not affected by the fraction of defects already broken. 2) that the disorder is large enough so that the nucleation of one cavity does not lead to fracture propagation because the neighboring sites are much stronger. The local stress amplification due to the appearance of a cavity is not large enough to induce nucleation of the neighboring cavity on the same time scale. Let us denote by μ^+ the largest amplification factor. The shortest breaking time in the material, given by Equation (20), is

$$\tau = \tau_0 \exp \left(\frac{U_0 - \frac{\mu^+ \sigma K \nu}{E(0)}}{k_B T} \right) \quad (21)$$

If the distribution of amplification factor is strongly peaked *i.e.* $P(\mu) = \delta(\mu - \mu^+)$ where $\delta(x)$ is the Dirac function, the number of non-broken sites decay exponentially $N(t) = N_0 \exp(-t/\tau)$ where τ is given by Equation (21). Then, the modulus decreases exponentially. In addition, when the distribution of amplification factor is narrow, depending on the applied stress either no-damage are observe on the experimental time scale, or the material breaks almost immediately: the range of stress of which progressive damage can be observed is very narrow as it has been shown in reference [44]. To observe a logarithmic behavior, one needs a broad distribution of amplification factor. Let us consider such a broad distribution of local amplification factors μ . The regions where strain amplification is the largest break first, then other regions will undergo nucleating events on longer time scales. To make things as simple as possible, we assume that the local stress amplification factor μ is evenly distributed between two extreme values μ^- and μ^+ . The normalized distribution $p(\mu)$ is thus assumed to be a constant over the interval $[\mu^-, \mu^+]$ (equal to $p(\mu) = 1/(\mu^+ - \mu^-)$). Let us calculate the fraction of nucleated sites at time t . The Eyring relation can be inverted to obtain the strain amplification $\mu_P(t)$ which corresponds to sites that nucleate

on time scale t . The amplification factor $\mu_P(t)$ that corresponds to a nucleating time t is given by

$$\mu_P(t) = \frac{E(0)}{\sigma K \nu} (U_0 - k_B T \ln(t/\tau_0)) \quad (22)$$

At a time t , we assume that all sites with lifetimes shorter than t (μ larger than μ_P) have broken while all sites with lifetimes longer than t (μ smaller than μ_P) are still intact. Note that this point of view is meaningful only when the distribution of strain amplification is broad, leading to a very broad distribution of nucleation times. In a mean field picture, the value of the modulus at time t is proportional to the remaining non-broken sites fraction and is thus given by:

$$E(t) = E(0) \left(1 - \int_{\mu^-}^{\mu^+} \exp(-t/\tau(\mu)) p(\mu) d\mu \right) \quad (23)$$

With the approximation $\exp(-t/\tau) \approx 0$ for $t > \tau$ and $\exp(-t/\tau) \approx 1$ for $t < \tau$, we get:

$$E(t) = E(0) \left(1 - \int_{\mu_P}^{\mu^+} p(\mu) d\mu \right) \quad (24)$$

The modulus as a function of time is then given by

$$E(t) = E(0) \left(1 - \frac{\mu^+ - \mu_P}{\mu^+ - \mu^-} \right) \quad (25)$$

Combined with equation 21, this finally gives the logarithmic evolution:

$$E(t) = E(0) \left(\frac{\frac{E(0)(U_0 - k_B T \ln(t/\tau_0))}{\sigma K \nu} - \mu^-}{\mu^+ - \mu^-} \right) \quad (26)$$

Thus, the slow, logarithmic drop of modulus may be simply explained by uncorrelated rupture events, with rupture times distributed over a broad interval. We interpret this broad distribution of local rupture times as due to a broad distribution of local strain amplification factors, giving rise to a broad distribution of local breaking times.

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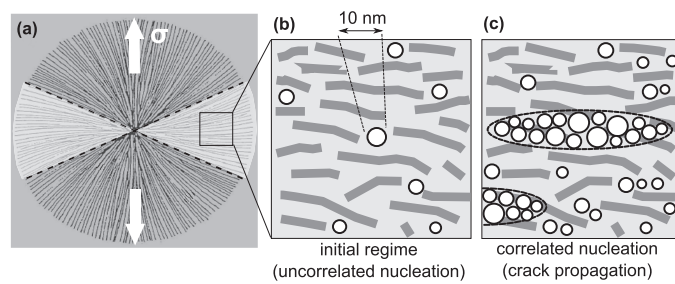
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