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NANOMECHANICS OF ADVANCED POLYMER FIBRES

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ABSTRACT

The micro/nano-structural evolution before and after tensile/compressive loading, fatigue and ultimately, failure has been studied by Raman (and IR) microspectroscopy for PBO, PET, PA66, PP, silk and hair using three probes: the low wavenumber collective modes at $<150\text{cm}^{-1}$ as representatives of the crystalline/ordered and amorphous chains, the stretching and bending modes, as representative of the C-C/ C-N polymeric backbone, and the localized vibrations (OH, NH) to probe the inter-macromolecule segment distance. The wavenumber and bandwidth distribution across fibre diameters reveal different types of skin/core heterogeneity. The *in situ* analysis at different strain/pressure levels shows that amorphous chains in the fibre accommodate the stress differently. The *post mortem* analysis shows that amorphous domains can be highly stressed during the failure and the remnant stress can be measured.

- A. Fibres
- B. Fracture
- C. Deformation
- D. Raman spectroscopy
- D. IR spectroscopy

1. INTRODUCTION

The challenge for the nanotechnologies is to achieve a perfect control on nanoscale-related properties. This obviously requires correlating the parameters of the synthesis process with the resulting nanostructure and analysing the changes at the nanoscale, *in situ*, at work. The behaviour of fibres in compression and tension is not well known. It is not only the case for new systems like, for example, the PBO ZylonTM (paraphenylenebenzodinitrophenyl) but also for older materials like polyamide fibres or high performance natural fibres (*Bombyx mori* or spider silks, hairs). The fibre strength is a factor of primary importance in composite strength, because the resistance of single filament and multifilament tows are required for prediction of the ultimate failure of composites. The fatigue failure is also a key point in many applications. Actually even single filament has a complex micro/nanostructure and can be considered as composite materials. Complex processes of extrusion-extension or spinning from a liquid state crystal regulate the texture of high performance synthetic and natural fibres. The mechanisms correlating the texture and nano-/micro-properties remain to be clarified.

Not all conventional techniques are suited for the analysis of nanosized/nanostructured materials but IR/Raman spectroscopies have already proven to be one of them [1-4]. Two kinds of parameters will influence the vibrational signatures : i) those acting on vibration “mechanics” like atomic mass, bond strength or the system geometry will set the peak wavenumbers (the eigenfrequencies of matter vibration), ii) those acting on the “charge transfer” (ionocovalency, band structure,...) will set the peak intensities. Raman bandwidths are characteristic of the local order, more specifically the short range arrangement in the first (0.1-0.5nm) and second (~0.5-5 nm) atomic shells. Thus, Raman spectroscopy, and for some extent IR spectroscopy, analyse specifically the crystalline and amorphous components of the materials. Furthermore, on the basis of chemical bonds anharmonicity, any-stress induced interatomic distance alteration changes the atomic vibration wavenumbers and offers a tool to study the deformation and mechanics at the nanometric scale. We will try here to summarize the broad possibilities that Raman (and to some extent IR) microscopes offer in the study of the texture and the (nano)mechanical behaviour of the fibres by closely analyzing the vibrational spectra in the whole wavenumber range. Additionally, the techniques of deuteration developed for the study of compounds with hydrogen bonding [4] will be considered. We selected synthetic fibres exhibiting different properties, PBO, an elastic high modulus material, polyamide 66 (PA66) and poly(ethyleneterephthalate) (PET), two engineering thermoplastic polymers, isotactic polypropylene (i-PP) a viscoelastic material and natural fibres (silks and hair), both with a viscoelastic behaviour. The stress-strain curves are compared in Fig. 1. Note that the ultimate stress is

directly correlated to the density, i.e. to the number of chemical bond in the unit volume which depends on the fibre micro/nanostructure. However, this correlation should be treated with a caution; the ultimate strength depends not only on the density but also on many other parameters such as crystallinity, orientation, T_g and the short range order of the amorphous phase, etc. This review examines and compares the behaviour of the different types of fibres under tensile (and fatigue) loading until fracture and under hydrostatic pressure. Emphasis is given to the discussion between the fibre (nano)structure, structural heterogeneity and macromechanical properties.

2. EXPERIMENTAL

Raman and IR vibrational analysis were performed on single fibres extracted from the yarn as described in refs [1-3]. Single fibres were mounted in the grips and were loaded in a Universal Fibre Tester [1] as shown in Fig. 2, and the fibres were submitted to different strain levels up to their fracture. Simultaneously Raman spectra were recorded *in situ*. In addition, some fibres, which had been broken during fatigue tests, have been analysed at points ahead of the fatigue crack tip [3].

A single fibre small fragment (length $< 150 \mu\text{m}$) was cut and placed in the diamond-anvil cell. A ruby ball was added for the pressure measurement (Fig. 2). The diamonds used were selected for their low fluorescence, allowing "good" transparency, both for IR and Raman measurements.

A "XY" spectrograph (Dilor, Lille, France) equipped with a double monochromator filter and a back-illuminated, liquid nitrogen-cooled, CCD detector was used to record the Raman spectra between 10 and 2000 cm^{-1} , using 514.5 and 647.1 nm exciting lines (Ar^+ - Kr^+ laser). The power of illumination was between 0.5 mW and 10 mW. The backscattering illumination and collection of the scattered light were made through an Olympus confocal microscope (long working distance Olympus x50, x80 or x100 objectives, total magnification x500, x800 or x1000).

The infra-red microscope/ATR is an Equinox 55 Fourier Transform Michelson interferometer (Bruker, France) with a ATR "golden gate" input designed to examine the surface (a few microns) of a material brought into "perfect" contact with the ATR crystal. A "Irscope II" microscope with Cassegrain objectives makes it also possible to work in transmission with the same diamond anvil cell used for Raman measurements. The spot diameter $\sim 200 \mu\text{m}$ is reduced to $\sim 20 \mu\text{m}$ with a diaphragm, to separately analyse the core and skin of a fibre.

3. CRYSTALLINE/AMORPHOUS CONFORMATIONS

Not only the position (wavenumber) but also the form (Lorentzian or Gaussian), the width, and the polarized modes of the Raman and IR components give valuable information on the composition (elongation modes), the structure (polarizations and collective low energy modes) and the texture (polarization mappings) of the fibres. The comparison of the polarized signatures for // (H) and \perp (V) configurations obtained by changing the orientation of the fibre with respect to the spectrometer slit entrance (Fig. 3), is a good mean of measuring the axial character of the fibre and to compare the crystallinity and texture of different fibres, including their precursors [2]. The Raman cross section of the O-H vibrators being very weak, a discussion on the water content has to rely on the IR spectra obtained with the Irscope (Fig. 4), in particular using the band at $\sim 3450\text{ cm}^{-1}$ that strongly weakens after drying. In the case of the X-H vibrators, the intrinsic mode width (resulting from the structural disorder alone) is obtained only in the case of an isotopic dilution $[H]/[D] < 10\%$. Very light vibrators normally couple in a complex way (mechanical, electric, and quantum) with the other phonons and only isotopic dilution, by removing the essence of these couplings it becomes possible to obtain a spectrum giving details on the vibrators environment [4].

Recently, the high resolution instruments make it possible to analyse the low wavenumber region, where modes have a collective character. This is obvious from the comparison of polarized spectra (Figs 3-4): the modes at about $80\text{-}150\text{ cm}^{-1}$ assigned to modes involving the movement of the chains of the unit-cell exhibit the stronger degree of polarization. Roughly speaking, these modes can be described as a translation (T') of the macromolecule with respect to the adjacent ones. These modes involve the modifications of the electron-richer bonds and hence give rise to very strong peaks. The greater number of atoms involved in the motion, the lower wavenumber will be. On the other hand, the inter-chain coupling will shift the peak toward higher wavenumbers. These low wavenumber collective modes may be preferred for the study of the relationship between the chain structure and the macroscopic mechanical behaviour. The differentiation between crystalline/ordered macromolecules (with a polarised Lorentzian Raman signature) and amorphous/disordered (down-shifted Gaussian un-polarised homologue) informs on the fibre nanostructure.

4. CORE/SKIN TEXTURES

The recording of series of spectra across the fibre diameter (e.g. Fig. 5) makes possible to analyse the texture anisotropy of the various fibres [1-3]. A core-skin effect is obvious from the wavenumber shift across the fibre

diameter. For instance in the PA 66 fibre, the variations indicate a weak tension of the crystalline chains and a strong compression of the amorphous bonds in the fibre core. The strong width reduction of the "amorphous" macromolecular chain component in the fibre core undoubtedly indicates a much better organization, at the local scale, of the amorphous "phase". This characteristic, related to the slower cooling of the fibre core, disappears after annealing above T_g . The PBO fibre diameter line scan shows rather similar behaviour: the bandwidth of the amorphous chain signature strongly increases in the fibre centre. On the contrary, the crystallinity of the studied PET fibres does not vary across the fibre diameter and a wavenumber shift down is observed from the periphery to the fibre centre indicating the tension of the macromolecules.

5. THE RELATIONSHIP BETWEEN NANOMECHANICS AND MACROMECHANICS

The vibrational spectroscopy through the chemical bond nano-scale probe allows distinguishing the changes in conformations (nanostructure), chain orientation, and the increase of intra and inter-macromolecule distances and the strain/stress of the chemical bonds. Very different behaviours are observed for the crystalline and amorphous signatures. As for the macro stress/strain curve recorded using the Universal Testing Tester two or more important stages in the mechanisms of deformation can be seen in Figs 6-7 for the two examples considered: PET and keratin fibres. Additional information on the PA 66, PP and PBO fibres are given in refs [1-3]. The initial plateau behaviour, observed for both crystalline and amorphous chains signature (Fig. 4), is consistent with an initial alignment of the chains without energy dissipation up to a threshold which differs as a function of the molecular chain (PET ~300 MPa (4%), PP ~50 MPa (5% of strain), PA 66 ~300-550 MPa (10-12%)) and also as a function of the fibre grade and producer. Above this threshold two opposite behaviours are observed for the signature of crystalline chains : i) a very small increase in wavenumber for PP and PET followed by a plateau regime indicating that the fibre stretch leads to a slight compression of the crystalline chains; ii) a small down-shift for PA 66 and keratin fibres. These two opposite behaviours provide information about the structural arrangement. Note the perfect plateau due to α/β transition in the keratin fibre takes place after an elastic regime. The analysis of the PA 66 fibres broken in fatigue highlighted a state of compressive stress of the amorphous phase close to the point of initiation of the rupture and its progressive decrease over 200 to 300 μm beyond this point, all occurring as if the rupture in fatigue resulted from the loss of viscoelasticity, at certain points, of the amorphous phase.

The comparison of the macroscopic (stress/strain plot) and nanometric (wavenumber shift versus applied strain) shows that the stage threshold observed at the (macromolecule) nano and macroscopic scale almost coincides.

Rather similar conclusion can be made from data obtained using the diamond anvil cell. Under hydrostatic pressure the coming together of the chains (reduction in ν_{N-H}) can be clearly seen and the existence of a threshold from which the geometry of the PA 66 fibres is modified. On the other hand, the compression of the PBO macromolecule starts immediately, according to the very high Young modulus resulting from the very rigid aromatic cycles.

6. CONCLUSION

The possibility of separately analysing "crystalline" and "amorphous" macromolecule conformation/structure allows a better comprehension of the processes of (nano)rupture and fatigue of any fibre built with covalent-bonded molecular entities giving a good vibrational signature.

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Figures Captions

Figure 1 : Stress-strain plots for studied fibres (note the PBO stress reaches ~ 3 GPa) and the correlation between ultimate strength and density.

Figure 2 : Detail of the experimental setting for Raman examination of the single filament fibre under controlled load; the PET fibre in the diamond-anvil cell (cell diameter $\sim 200\mu\text{m}$).

Figure 3 : Examples of polarised Raman spectra showing the (PET) crystallisation and texturation of a amorphous precursor filament under tension into a high crystalline oriented fibre; comparison between polarised spectra of high crystalline polyamide and low crystalline keratin fibres.

Figure 4 : Collective low wavenumber Raman modes in // polarisation for PET and PA 66 single fibres. Comparison between IR signatures of pristine and deuterated (H isotopically diluted) PA 66 single fibre. Broad and narrow components respectively show the amorphous (α ,am) and crystalline (C,Cr) conformations.

Figure 5 : Plot of the crystalline and amorphous low wavenumber component across the diameter ($\sim 30\mu\text{m}$) of a PA 66 single fibre, before and after heating above the T_g temperature.

Figure 6 : Comparison between the nano- and macromechanic behaviour for PET (low wavenumber probe) and (dry) keratine (νNH and amide I probes) fibres; measurements have been made under controlled load (PET, hair $<4\%$) or strain (hair $>4\%$).

Figure 7 : Example of Raman and IR wavenumber shift as a function of hydrostatic pressure for the PA 66 and PBO single fibre for different probes. Note the PA 66 macromolecule accommodates the pressure below 4 GPa.

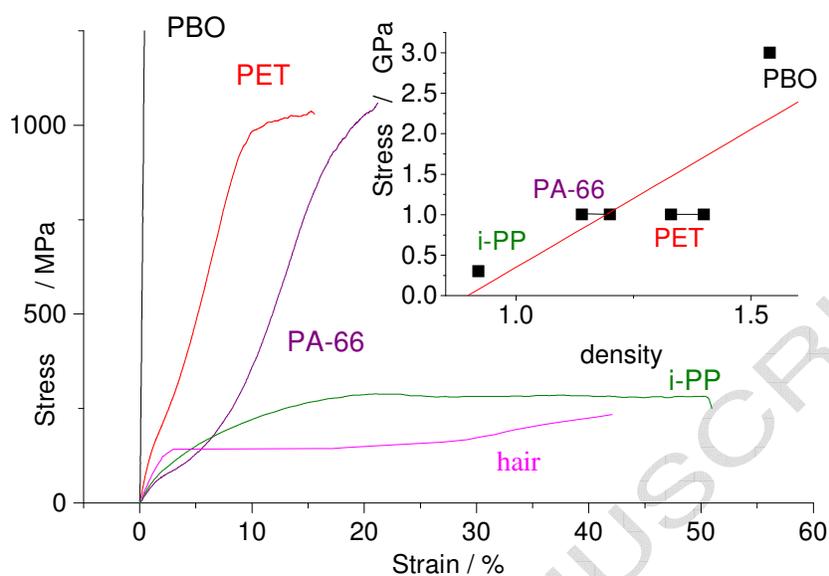


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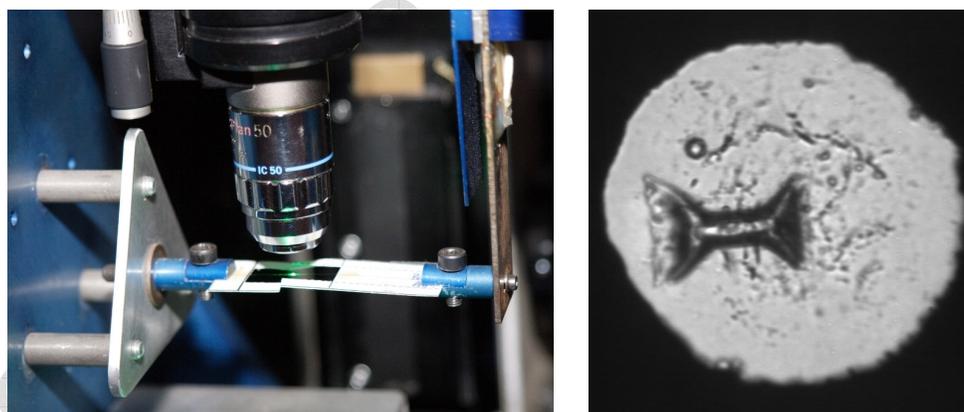


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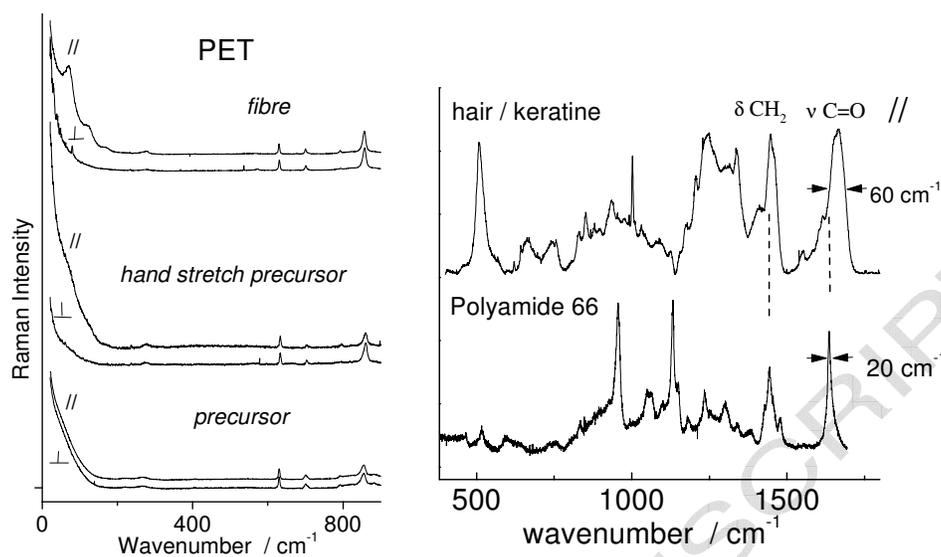


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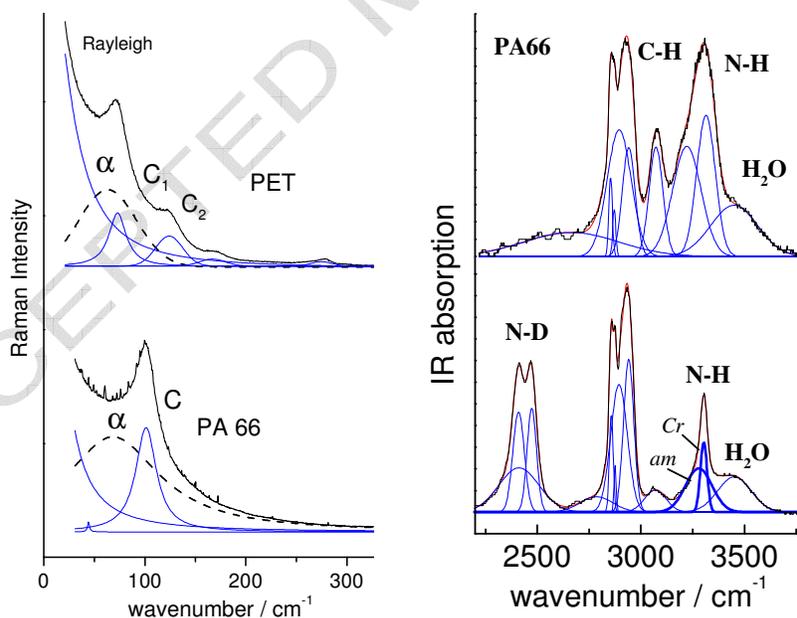


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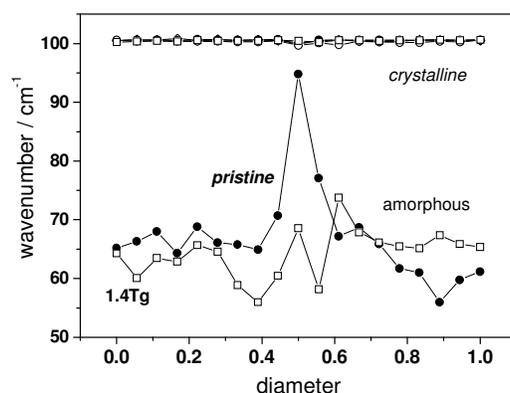


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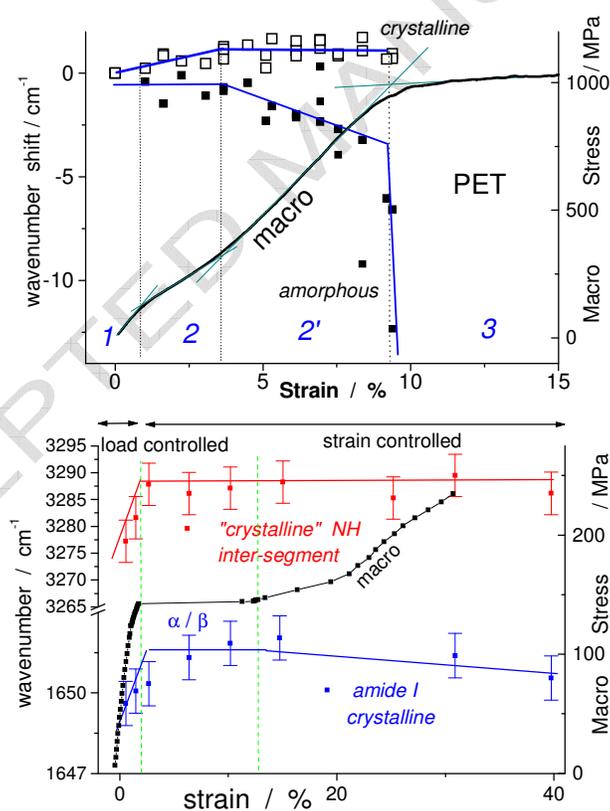


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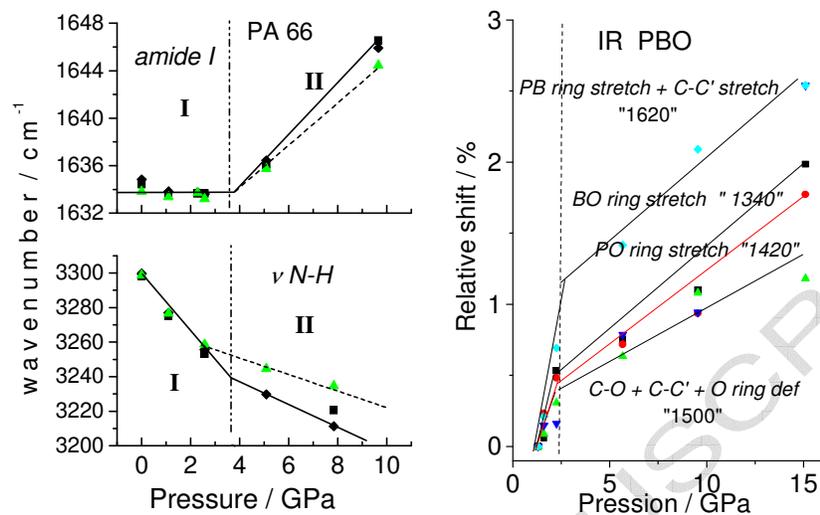


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