OBSERVATIONS OF PYROCARBON DEPOSITS ON FILMS BY SCANNING TUNNELING MICROSCOPY

E. Bouchard[+], J-C Roux[+], F. Langlais[°], P. Olry[Δ], P. Lespade[◇] and P. Delhaès[+]

[+] Centre de Recherche Paul Pascal CNRS – Université de Bordeaux 1 33600 Pessac (France)
[°] Laboratoire des composites thermostructuraux. Université de Bordeaux 1. 33600 Pessac (France)
[Δ] SNECMA division moteurs Le Haillan. 33165 St Médard en Jalles (France)
[◇] EADS-LV Aquitaine – 33165 St Médard en Jalles (France)

Introduction

The chemical vapor deposition of carbon materials is a very complex process mixing homogeneous and heterogeneous chemical reactions. Under defined conditions the nucleation and growth of pyrocarbons can be analized [1] thanks to scanning tunneling microscopy (STM). It has been recently demonstrated that a morphological change is observed when the deposit conditions are evoluting from smooth laminar (SL) to rough laminar (RL) type of microstructure. On an ideal pyrographite used as a substrate this controlled change is interpreted as a sort of wetting transition [2]. It appears that the extension of CVD process to useful carbon surfaces as found with fibers is a crucial step to control the interfacial properties and the pyrocarbon coating, then the formation of C/C composites. This work has been carried out on a series of selected ex-PAN fibers (see table 1).

Experimental

The CVD experiments have been realized under isothermal-isobaric conditions at fixed T=950°C and P=2kPa values with propane as precursor gas [3]. In this study the parameters are respectively the residence times (τ=0.3 see for SL microstructure and τ =4 see for RL one) and the deposition times, short for STM oberservations (with a Nanoscope III) (t_D=0.75 and 1.5 mm) or longer for microcomposite testing (t_D=2h45 mm) in order to obtain similar volumic fractions for the fiber and the matrix. All the STM observations are done at different scales (see figures 1 and 2) :

- in the micromic range, the morphology and the mean fiber radius
- in the submicromic range the roughness factor
- in the nanoscopic range the coherence length (La) for a graphene sheet.

Results and discussion

The comparison between pristine and coated fibers shows the relief and the asperities are progressively smeared out by CVD. Even in the case of supposed SL deposit or a graphitized fiber a complete wetting is observed as for a RL microstructure. This result at the opposite of the observation on a graphite surface demonstrates the influence of the surface roughness and the role played by the increased surface energy and the presence of active sites. We have also carried out traction measurements on microscomposites. A series of experiments (table 1) have allowed us to estimate the matrix tensile using the classical rule of mixtures. For the RL microstructure this value is around 100-200 GPa.

Conclusions

We have shown that the deposition mechanism is sensitive to the surface quality of the fibers including their surface treatments and the graphitization. Indeed the interfacial characteristics plays a crucial role on fracture type as evidenced by preliminary tensile tests on microcomposites.

References

1. E. Bouchard. Ph.D. Thesis
   University of Bordeaux I (1999)
2. E. Bouchard, J. Lavenac, J.C. Roux, F. Langlais and P. Delhaès. Advanced materials. CVD (to appear April 2001)
3. O. Ferron, F. Langlais, R. Naslain and J. Thebault Carbon (1999) 37, 1343-1353

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Table 1 : General presentation of fibers, pyrocarbon deposits and microcomposites.

Types and characteristics of ex PAN fibers				**STM observation** on bare fibers			after CVD of pyrocarbon +		
Name	HTT (°C)	d_{002} (nm)	traction modulus (Gpa)	roughness (nm)	La (nm)	surface observation	roughness (nm)	surface observation	microstructure &
TENAX HTA/HTS	1600 2200 2800	0.350 0.342 0.339	284 350	0.35 0.25 0.25	0.14 0.10 0.10	--- **Graphene steps**	- 0.36	- **-** **homogene**	**R L (*)** **R L (*)** **S L**
ZOLTEX Panex 33	1600 2200	0.246 0.342	275	0.45 0.37	0.13 0.08	irregular surfaces	0.62 0.40		R L (*) R L

+ : experimental parameters : gas = propane, T_D = 950°C, τ = 0.3s /SL or 4s/RL

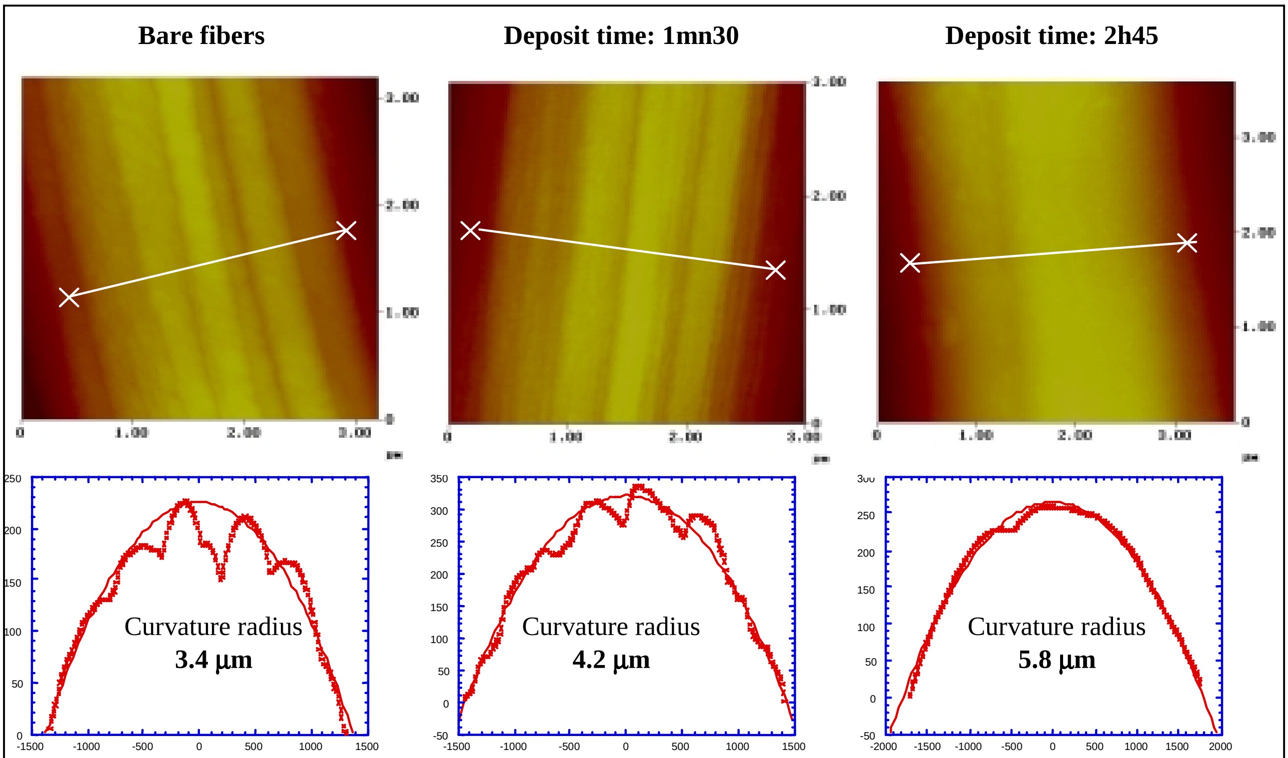

Figure 1 : STM observation on TENAX HTS fibers (HTT = 2200°C) in micronic scale

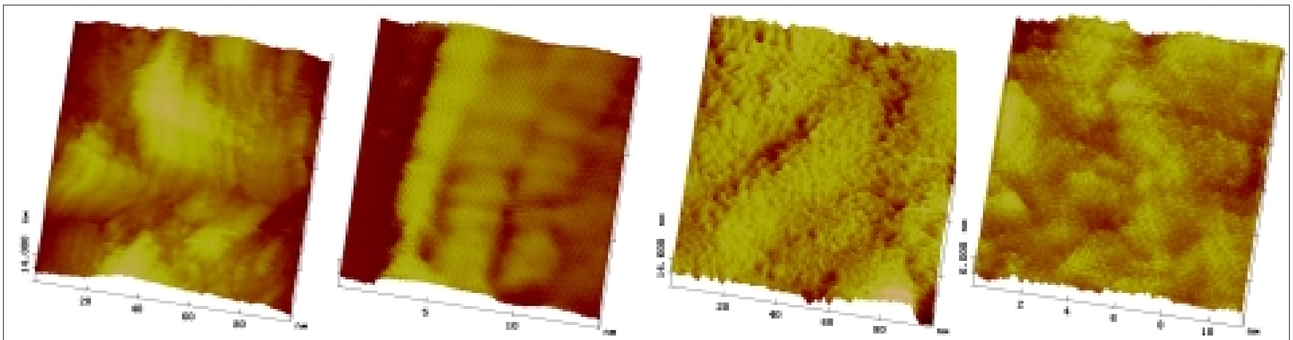

Figure 2 : STM observation of Tenax HTS fibers heat-treated at 2200°C (a,b)
then coated with RL pyrocarbon for 1mn30 (c,d) in a nanometric scale