



In-situ study of the strain-induced structural changes of poly(vinylidene fluoride) and carbon nanotubes - poly(vinylidene fluoride) nanocomposites

Experiment number:
02-01-839

Beamline: BM02	Date of experiment: from: 13/11/2013 to: 16/11/2013	Date of report: 01/03/2014
Shifts: 9	Local contact(s): Cyrille Rochas	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

J. Defebvin*, S Barrau, G. Stoclet*, S. Ouchiar*, L. Leroy* , J. Pepin*, T. Pinalie*

Unité Matériaux Et Transformations (UMET) Equipe Ingénierie des Systèmes Polymères (ISP), Villeneuve d'Ascq, USTL (France)

Report:

In this study both WAXS et SAXS techniques were used upon uni-axial stretching at different temperatures in order to discuss the influence on the PVDF structural evolution and deformation mechanisms and to investigate the effect of carbon nanotubes. In this report we will describe a part of the obtained results.

Introduction :

Piezoelectric devices present a growing interest. The current tendency is to create devices able to combine flexibility and high electro-mechanical conversion. Poly(Vinylidene Fluoride) is a polymer known for its interesting piezoelectric properties. However such properties are highly dependant on the polymer crystal structure. Indeed, PVDF present at least two main crystalline forms :

-the α phase : the most common but non-polar phase.

- the β phase : the most polar phase classically obtained by stretchnig of the α phase.

Therefore to obtain the best piezoelectric properties PVDF must be in its β phase. It has been shown in many studies that the drawing temperature has a real effect on the rate of β phase obtained by stretching^{1,2}. The first objective of this study concerns the investigation of neat PVDF. The $\alpha \rightarrow \beta$ phase conversion and the deformation mechanisms were reported as a fonction of the drawing temperature

Moreover Carbon NanoTubes (CNT) were incorporated into the PVDF matrix to improve the electro-mechanical response of the piezoelectric polymers. The second objective of this study was the determination of the influence of these CNT on the PVDF structure but also on the PVDF deformation mechanisms.

1) Influence of the drawing temperature on PVDF

This part is focused on the $\alpha \rightarrow \beta$ conversion in neat PVDF films and on the deformation mechanisms. The objective is to verify the effect of the drawing temperature.

Samples (length 12 mm, width 4.5 mm and thickness between 0.2 and 0.35 mm) were stretched at a constant rate of $7.2 \text{ mm}\cdot\text{min}^{-1}$. Tests were made for 6 different temperatures between the glass transition temperature ($T_g \approx -40^\circ\text{C}$) and the melting temperature ($T_m \approx 165^\circ\text{C}$), as depicted in figure 1. On this range, an endothermic transition appears at 58°C and is present only at the first heating. This transition corresponds to the melting of secondary crystals and is noted $T_{m_{low}}$ (ref)

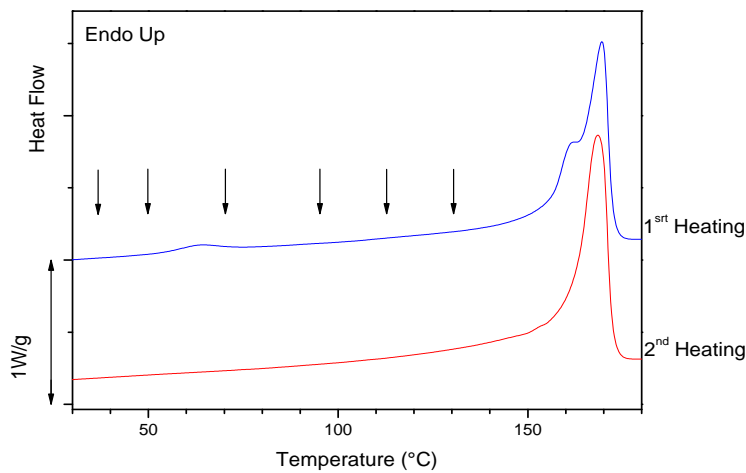
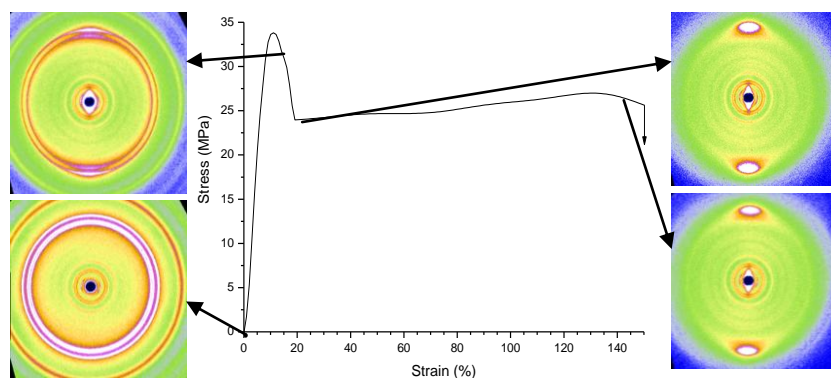


Figure 1 : Thermograms of PVDF. An arrow indicates the position of the stretching temperature used ($T = 35^\circ\text{C}$, 50°C , 70°C , 90°C , 110°C and 130°C).

Structural evolution of PVDF upon stretching was followed by WAXS. Patterns show that for each drawing temperature the α to β phase conversion occurs at the start of the necking. The content of β phase increase along the necking as described in figure 2.



(Drawing axis horizontal)

Figure 2 : Structural evolution during stretching at $T = 35^\circ\text{C}$. From the diffractograms the residual α phase present in the neat polymer just before the break can be estimated.

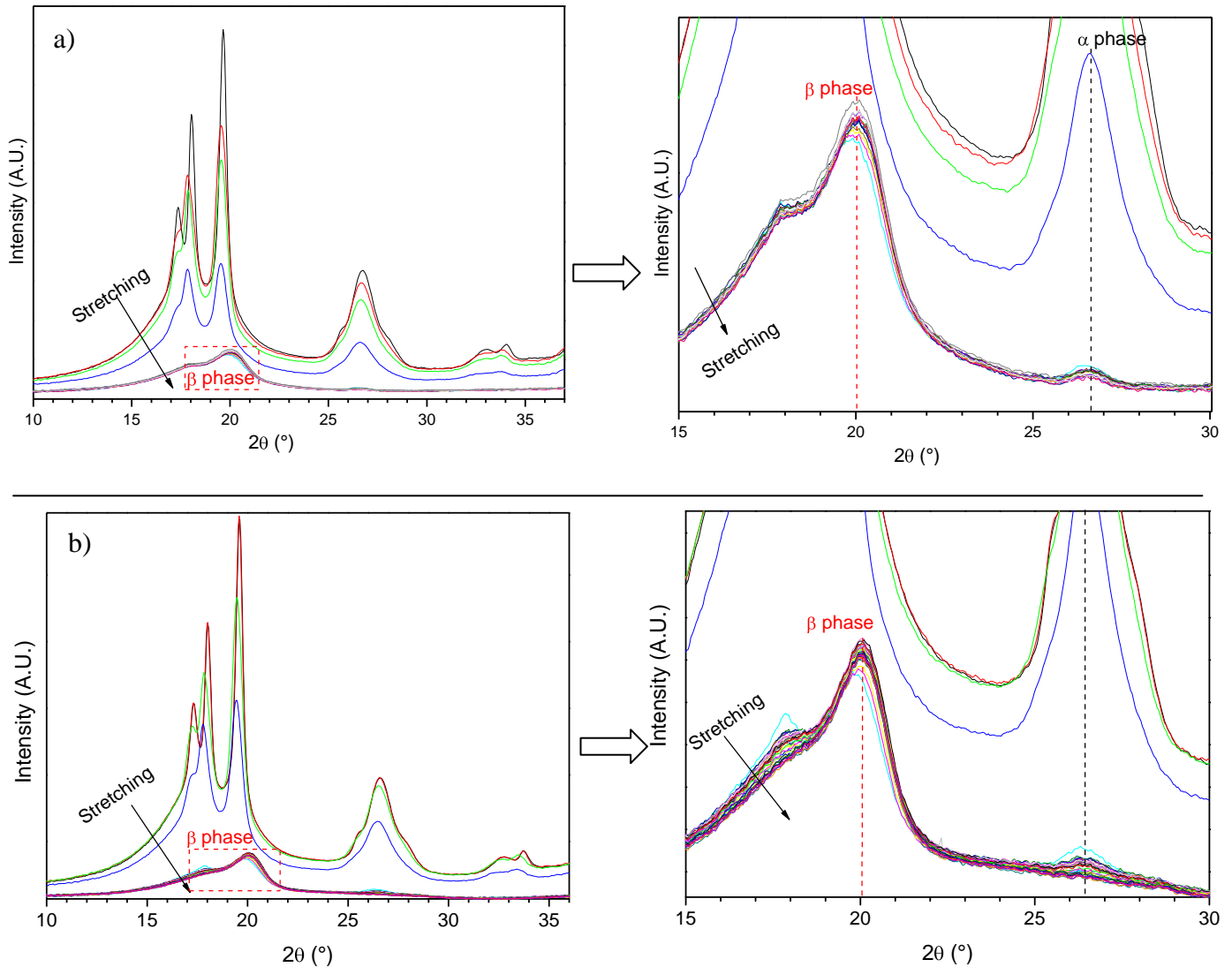


Figure 3: Evolution of PVDF structure upon stretching at a) 35°C and b) 40°C.

Regarding the diffractogram, the α initial phase with four peaks at $2\theta_{Cu} = 17.6^\circ$ (100), 18.3° (020), 19.9° (110) and 26.5° (120) is in agreement with literature^{3,4} Upon stretching, the α phase converts into β phase with the apparition of one peak at 20.6° . The shoulder at 18° is attributed to the amorphous phase. The proximity of the three first peaks of α phase and those of the amorphous phase makes the quantification difficult, then to determine the presence of α , we focus on the peak at 26.5° .

The α phase disappears completely after stretching at $T_d = 50^\circ\text{C}$, 90°C , 100°C while a residual α phase persists for drawing temperatures of 35°C and 70°C . More precise characterizations are still in progress.

SAXS results indicates that drawing temperature has a significant effect on deformation mechanisms. Indeed, for the temperatures below $T_{m_{low}}$, a of cavitation appears (figure 4a, pattern 2). The cavities increases until the fracture and formation of fibrils (figure 4a, pattern 4).

For the temperatures above $T_{m_{low}}$ none cavitation appears. A reorientation of crystalline lamellae at 45° is shown in figure 4b pattern 2). Finally a new long period shorter than initially is obtained oriented along the drawing axis as described figure 5).

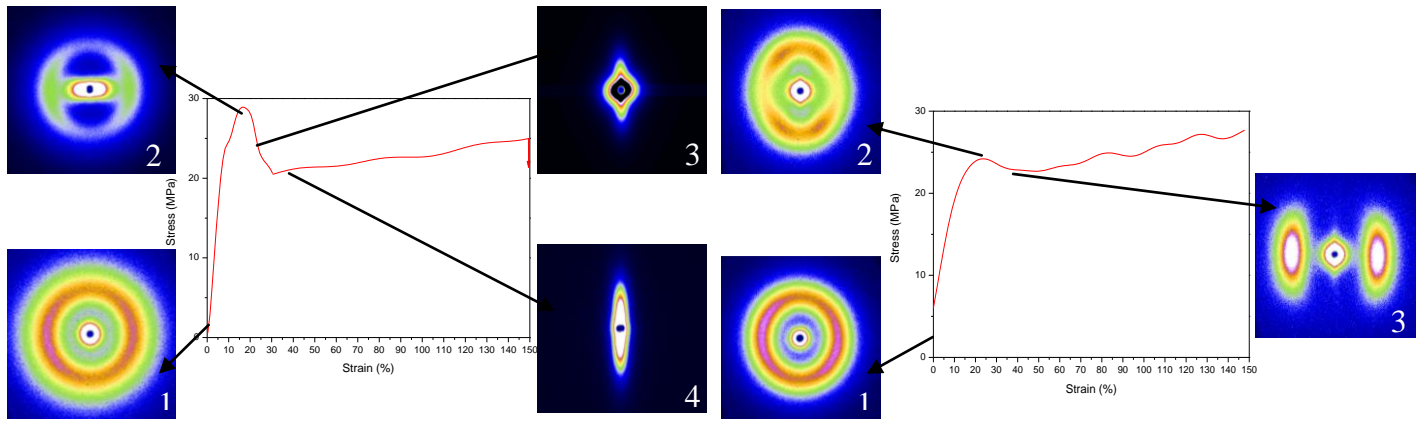


Figure 4 : Stress – strain curves and selected SAXS patterns registered upon uniaxial stretching at a) $T_d = 40^\circ\text{C}$ and b) $T_d = 80^\circ\text{C}$.

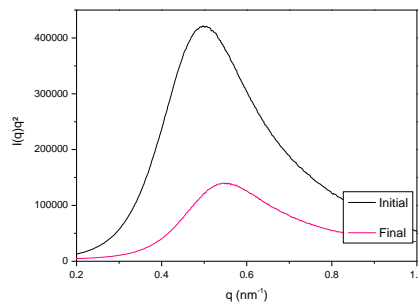


Figure 5 : Long period evolution at $T_d = 80^\circ\text{C}$

The deformation mechanisms in PVDF are then very dependant of the drawing temperature. For the experiments performed at $T > T_{m_{low}}$ the macromolecular mobilities are expected high enough to delay the cavitation onset.

2) Influence of carbon nanotubes :

The second part of this study was devoted to the understanding of the influence of carbon nanotubes (CNT) on the α to β phase conversion and on the deformation mechanisms. An important point was the determination of the electric percolation threshold (insulating to conducting transition). This percolation threshold was determined at 0.7wt% of CNT. Three composites were made : pristine PVDF which is the reference, a composite below the percolation threshold (0.1wt% of CNT) and one above the percolation threshold (1wt% of CNT).

The first result appears without stretching. As depicted figure 6, the insertion of CNT has an influence on the PVDF phase.

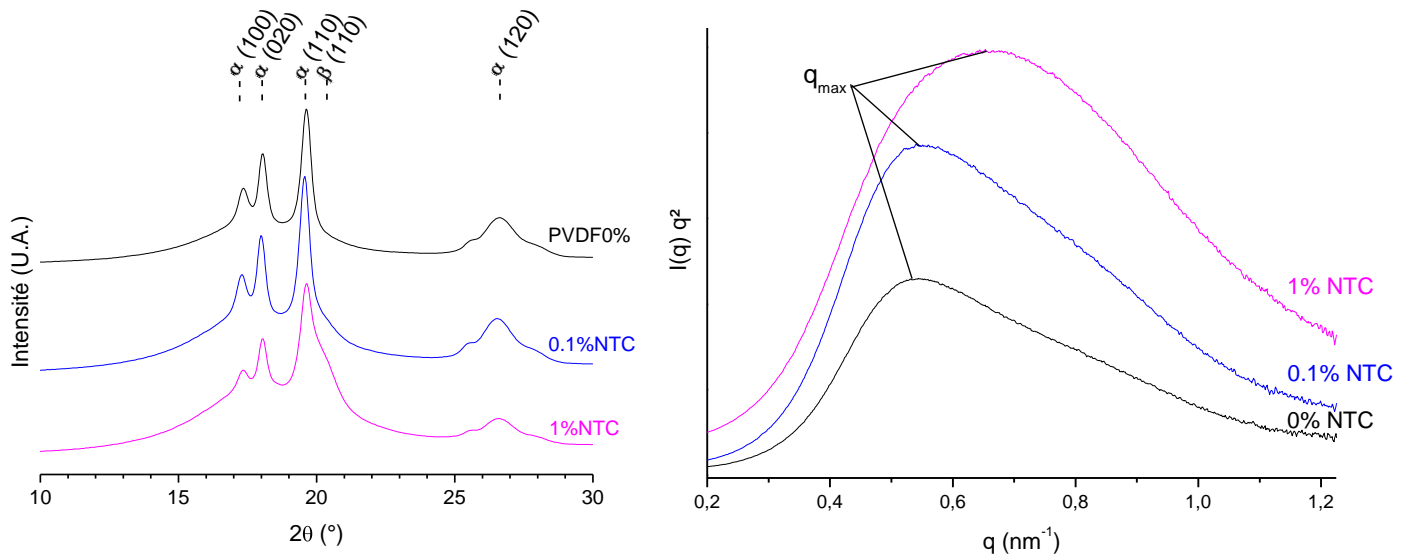


Figure 6: WAXS and SAXS diffractograms of the composites at 0%, 0.1% and 1 % of CNT.

The WAXS diffractogram points out a shoulder at around $2\theta = 20.5^\circ$ for the composite at 1wt% of CNT. This corresponds to the peak attributed to the β phase. Deconvolution of the integrated profiles gives a content of 10% of β phase.

SAXS diffractogram with the Lorentz correction enables to determinate the value of the long period (L_p). L_p decreases with the addition of CNT. CNT modify the morphology of PVDF.

In this part, the strain induced structural change of the composites was investigated.

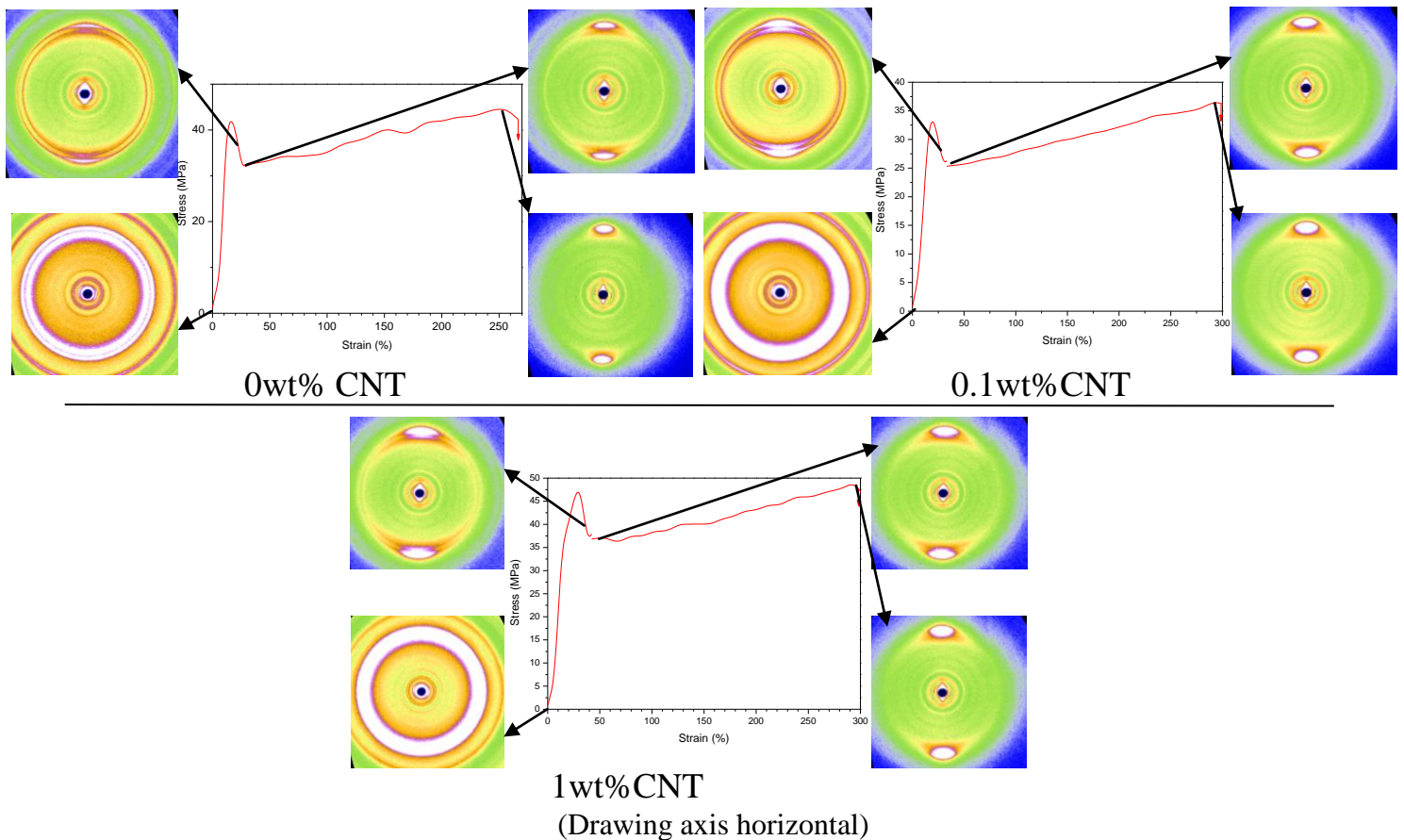


Figure 7 : Structural evolution upon drawing at 40°C for the composites

WAXS patterns indicates the same behavior for pritisne PVDF, 0.1 wt % of CNT and 1wt% of CNT that means CNT don't disturb the α to β phase conversion of the PVDF matrix, even for the composite at 1 wt % CNT film which already contains a part of β phase.

Moreover, for the three composites a total conversion of α to β is observed when the strain is over 300%.

SAXS study of these composites was made on the same drawing conditions than WAXS then performed.

The results are similar to those of PVDF. Two mechanisms of deformation appears, the first one at lower temperatures in which cavitation are created, the second one at higher temperature without cavitation but by a reorganization of lamellae and appearance of new long period, shorter than initially. No influence of CNT on these mechanisms was seen, but analysis of these results are still in progress.

Finally these WAXS experiments allow to characterize properly the structure of both PVDF and CNT - PVDF composites at different drawing temperatures. It has been shown that the α to β phase conversion starts at the beginning of the necking, and the β phase propagate during the necking. Another important result is the presence of β phase initially in composites.

Currently the main result of this study is obtained by SAXS experiments, showing two different mechanisms of deformation. These results directly correlated to the $T_{m_{low}}$ transition have never been demonstrated and could be published in an international journal. Moreover, analysis of data are still in progress mainly on the influence of CNT on kinetics of transformation in the deformation mechanisms.

Communication of the obtained results :

- Results will be presented through an oral communication at the DEPOS25 Presqu'île de Giens, France, Mars 2014.
- A publication is in preparation.

Publications :

- ¹ Vijayakumar, R. P., Khakhar, D. V, & Misra, A. (2010). Studies on α to β Phase Transformations in Mechanically Deformed PVDF Films. *Journal of Applied Polymer Science*, 117, 3491–3497.
- ² Du, C., Zhu, B., & Xu, Y. (2006). Effects of Stretching on Crystalline Phase Structure and Morphology of Hard Elastic PVDF Fibers. *Journal of Applied Polymer Science*, 104, 2254–2259.
- ³ Esterly, D. M., & Love, B. J. (2004). Phase Transformation to β -Poly (vinylidene fluoride) by Milling. *Journal of Applied Polymer Science*, 42, 91–97.
- ⁴ Gregorio, R. (2006). Determination of the α , β , and γ crystalline phases of poly(vinylidene fluoride) films prepared at different conditions. *Journal of Applied Polymer Science*, 100(4), 3272–3279.