

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Is it possible to use carbon nanotubes to template polymer crystallization?	Experiment number: SC 1809
Beamline:	Date of experiment: from: 26/8/2005 to: 29/8/2005	Date of report: 19/1/2007
Shifts:	Local contact(s): Dr. Pierre Panine	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Tiberio EZQUERRA* Dr Aurora NOGALES* Mr. Jaime HERNANDEZ* Dr Daniel R. RUEDA Dr. Mari Cruz GARCIA-GUTIERREZ		

Report:

1.Introduction

A nanocomposite can be defined as a nanofilled system in which the total interfacial phase becomes the critical parameter rather than the volume fraction of the filler¹. Single-wall carbon nanotubes (SWCNTs) are shown to be promising reinforcing elements, with Young's Moduli in the TeraPascal (TPa) range, for a new generation of nanocomposite materials¹. A typical SWCNT sample consists on micron-size aggregates, frequently referred to as bundles or ropes, in which single nanotubes self-assemble in a two-dimensional hexagonal close packed lattice¹. Upon mixing with a polymeric matrix a homogenization of the nanoparticles down to the nanometer level can be achieved by different procedures including compounding, sonication and shear among others¹⁻⁴. In general, typical polymer and polymer-nanocomposite processing (such as injection molding, extrusion, spinning, etc.) involves solidification, either by crystallization or by vitrification, from the molten state which is distorted by a combination of shear and elongational flow fields. The effect of flow fields, mimicking those used in industrial processing, both on the structure of SWCNT within a nanocomposite and on the structure of the polymer matrix itself remains untreated until now. The effect of processing induced flow fields on the nanostructure of polymer nanocomposites is crucial because of the profound impact on the physical properties¹⁻⁵. In this report of experiment SC1809 we attempt to show under which shear conditions SWCNT templates an anisotropic crystallization of Poly (butylene terephthalate) (PBT) in PBT-SWCNT nanocomposites prepared as described elsewhere²⁻⁴.

2.Experimental

Rheo-SAXS experiments were performed on PBT-SWCNT nanocomposites with SWCNT weight concentrations of 0, 0.01, 0.05, 0.1 and 0.2 %. Two types of crystallization approaches were followed:

- Step Shear in the Melt (SSM). Isothermal crystallization at a crystallization temperature $T_c < T_m$, being T_m the melting temperature of PBT ($T = 230^\circ\text{C}$), after application of a step shear and subsequent fast cooling to T_c . Different shear rates and strains were applied during different times.

- b) Step Shear at the Crystallization temperature (SSC). Isothermal crystallization at a crystallization temperature T_c after application of a step shear at T_c .

3. Results and Discussion

3.1. Isothermal crystallization of the polymer matrix

Fig. 1 shows that the polymer matrix of the nanocomposite, PBT, do not exhibit significant orientation at the end of the crystallization process under the shear conditions investigated.

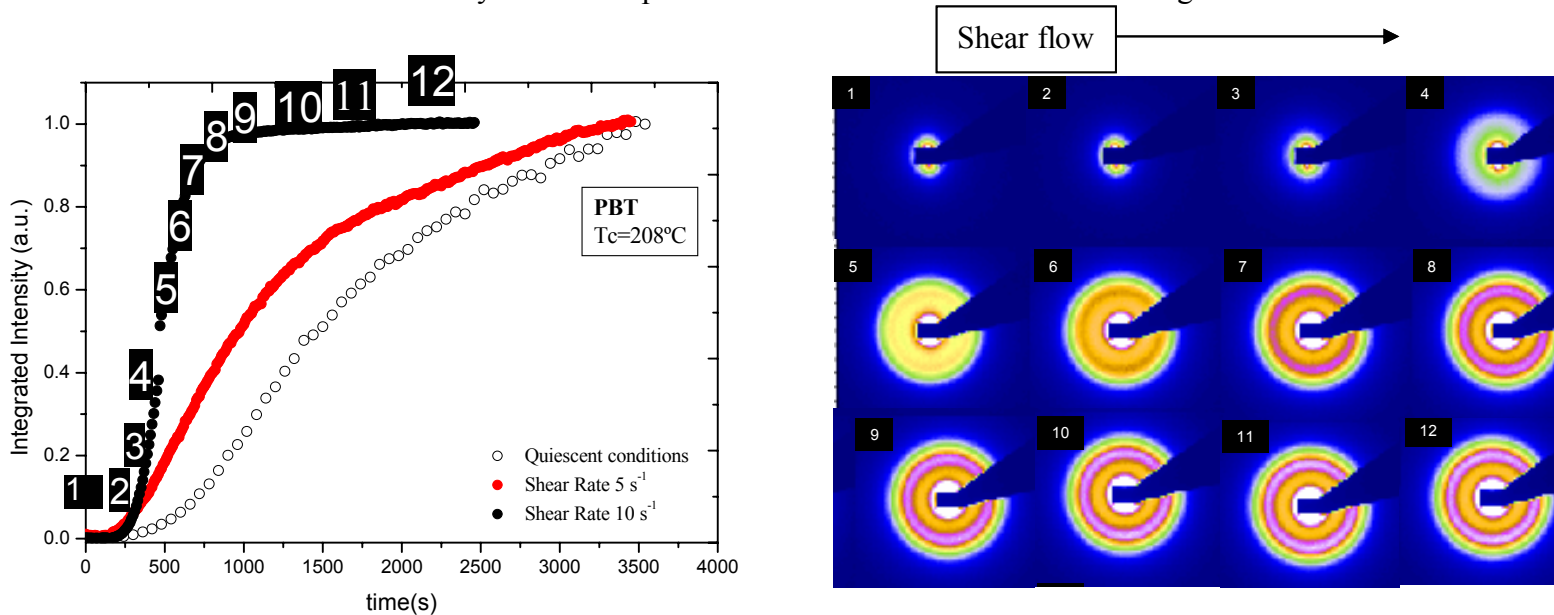


Fig.1. (Left panel) Integrated intensity versus time at $T_c=208^\circ\text{C}$ for a SSM experiment at different shear rates and a constant strain of 20. (Right panel) SAXS patterns of PBT at a shear rate of 10 s^{-1} . Arrow indicate shear direction

3.2. Isothermal crystallization of the nanocomposites

Fig.2 shows an example of two interesting aspects:

1. **Nucleation effect** of SWCNTs: the crystallization of the nanocomposites accelerates as compared with of the PBT matrix
2. **Templating effect** of SWCNT: The SAXS patterns for the nanocomposites exhibit a clear orientation while those of the PBT matrix do not (see fig.1).

Surprisingly the templating effect have been observed at all shear rates investigated including shear rate of 0 s^{-1} (quiescent conditions).

3.3. Oriented fraction during isothermal crystallization of the nanocomposites

In order to evaluate the evolution of the oriented crystalline fraction during isothermal experiments a special deconvolution procedure to separate the oriented from the unoriented fractions was implemented in a MATLAB subroutine⁵. Fig. 3 shows an example of the evolution of the oriented fraction with crystallization time for a SSM experiment. In the early stages there is an increase of the oriented fraction which can be associated to the crystallization of crystalline blocks perpendicular to the nanotube surface on a shish-kebab fashion. In the last stages orientation decreases probably due to the unoriented crystallization of a polymer fraction which is not in contact with the nanotube surfaces.

3.4 Conclusions and perspectives

A paper discussing in detail all the above commented facts is in preparation⁵. Extension of these experiments to nanocomposites with Multi Wall Carbon Nanotubes (MWCNT) will be very useful specially if rheo-WAXS measurements were performed.

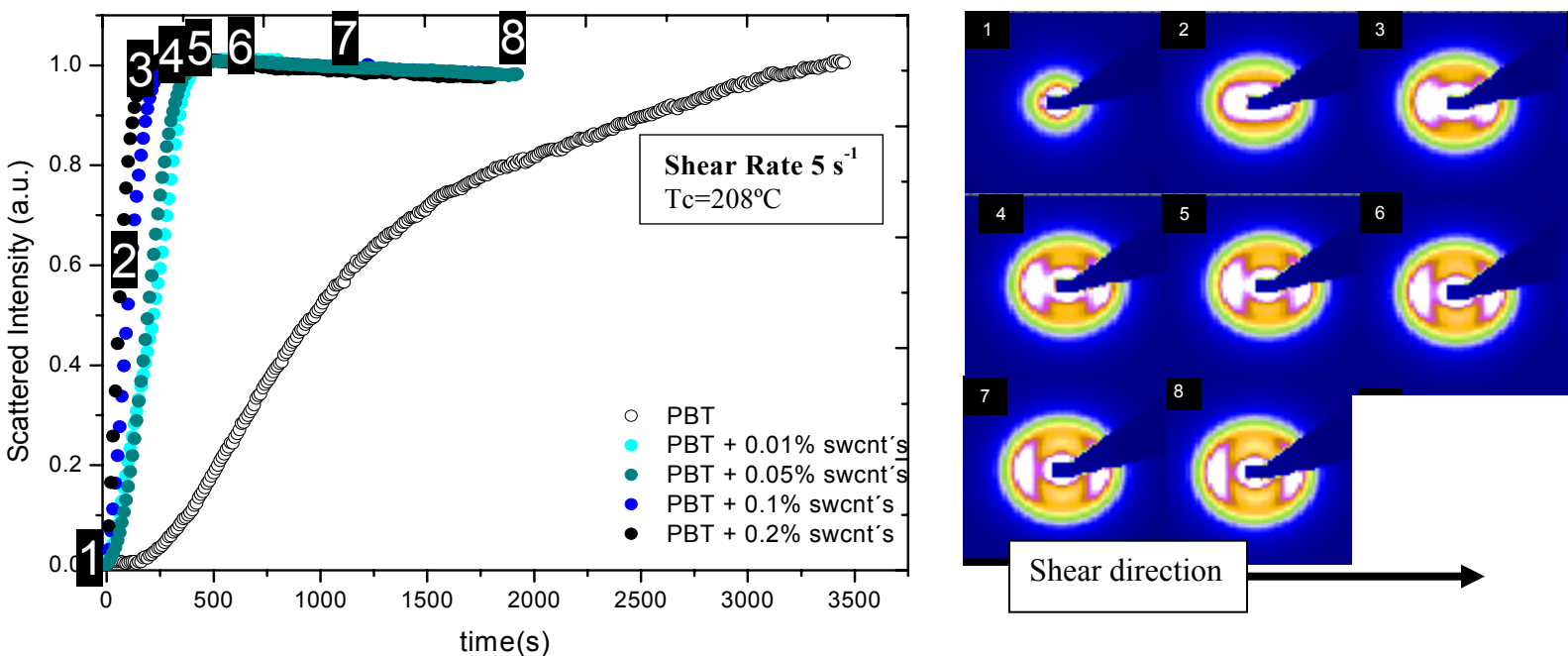


Fig.2. (Left panel) Integrated intensity versus time at $T_c=208^\circ\text{C}$ and a shear rate of 5 s^{-1} for a SSM experiment with different SWCNT weight concentrations. (Right panel) SAXS patterns of a nanocomposite with 0.2% of SWCNT. Similar oriented patterns are obtained for all concentrations.

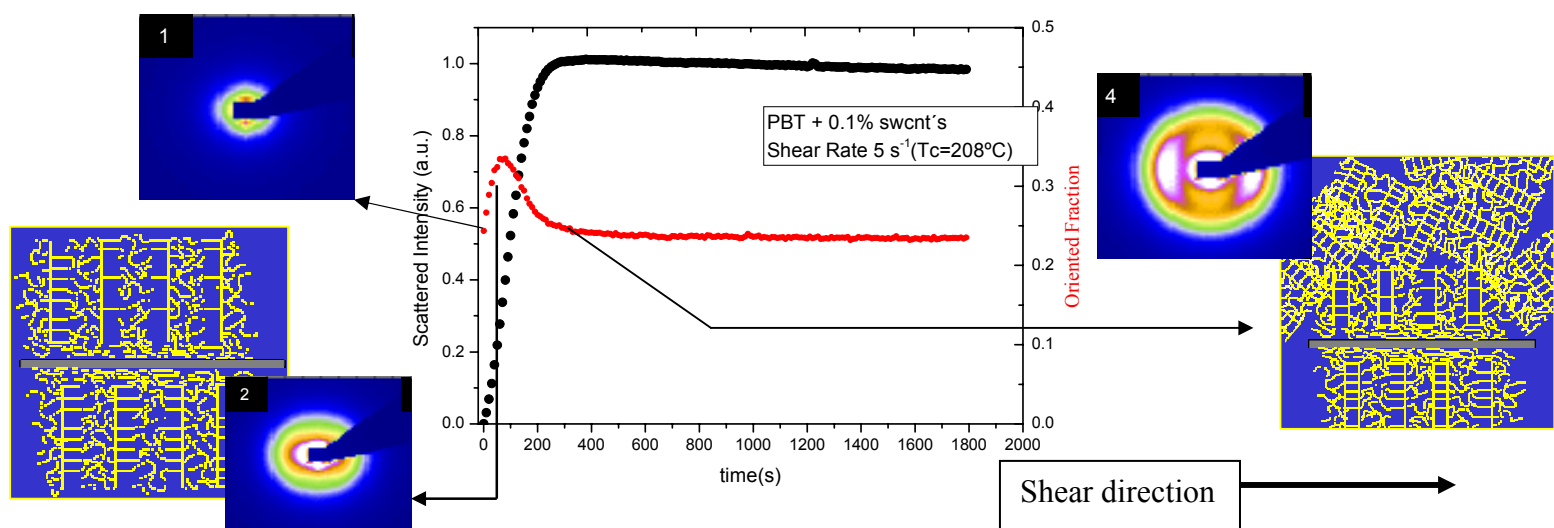


Fig.3. (Left y-axis) Integrated intensity versus time at $T_c=208^\circ\text{C}$, shear rate of 5 s^{-1} for a SSM experiment for a 0.1% SWCNT nanocomposite. (Right y-axis) Calculated oriented fraction. SAXS patterns at different times indicated by the arrows. Structural models of oriented crystallization templated by SWCNTs.

References

- [1] R.A. Vaia, and H.D. Wagner, *Materials Today*, November, 32 (2004).
- [2] A. Nogales G. Broza, Z. Roslaniec, K. Schulte, I. Šics, B. S. Hsiao, A. Sanz, M.C. García-Gutiérrez, D.R. Rueda, C. Domingo, T. A. Ezquerro., *Macromolecules* 37, 7669 (2004).
- [2] M.C. García-Gutiérrez, A. Nogales, D.R. Rueda, C. Domingo, J.V. García-Ramos, G. Broza, Z. Roslaniec, K. Schulte, R. Davies, T. A. Ezquerro. *Polymer* 47 (2006) 341.
- [4] M.C. García-Gutiérrez, A. Nogales, D.R. Rueda, C. Domingo, J.V. García-Ramos, G. Broza, Z. Roslaniec, K. Schulte, R. Davies, T. A. Ezquerro. *Composites Science and Technology* 67 (2007) 798.
- [5] J. Hernández, M.C. García-Gutiérrez, A. Nogales, D.R. Rueda, P. Panine, T. A. Ezquerro. (paper in preparation)