EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

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.

ESRF	**Experiment title:** **The influence of zirconia nanoparticles on flow induced crystallization of HDPE having broad molecular weight distribution (MWD)**	**Experiment number**: **SC-2432**
Beamline: **ID11**	**Date of experiment**: from: **16 July 2008 to: 20 July 2008**	**Date of report**:
Shifts:	**Local contact(s)**: **Dr. Aleksei BYTCHKOV**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The influence of zirconia nanoparticles while shearing at two different temperatures on oriented structure formation is investigated by using high resolution time resolved wide angle X-ray scattering (WAXS) for high density polyethylene having broad molecular weight distribution (MWD). In the previous beamtime (26-02-398: 03 December 2007 to: 07 December 2007), our results indicated that it could be possible to generate initial structures at high temperature ***(142^{0}C)*** just above equilibrium melting point ***(T_m= 141.2^{0}C)*** for linear polyethylene using time resolved small angle x-ray scattering (SAXS). However, the result also suggested decrease in the intensity of the equatorial streak with the increasing amount of zirconia – i.e. the presence of zirconia inhibits chain orientation prior to crystallization. The pulse of shear (100/s for 1s) is applied to HDPE of broad molar mass distribution having four different concentration (0.25%, 0.5%, 1.0% and 2.0%) of zirconia nanoparticles at two different temperatures: 136^{0}C and 142^{0}C, followed by cooling to crystallization temperature (T_{Cryst} =125^{0}C), where the sheared sample was kept at isothermal condition for 600s to monitor the structure development, subsequently followed by cooling to room temperature. The azimuthal offset between the maxima of 110 and 200 reflection suggest the overgrowth of twisted kebabs. It is noticeable that the highly oriented arc-like patterns are obtained at T_{cryst} = 125^{0}C which tends to become intense as a function of zirconia concentration while shearing at 136^{0}C, thus favouring orientation, whereas, the arc like patterns becomes less intense as a function of zirconia concentration while shearing at 142^{0}C, thus inhibiting the orientation. The striking observation of the experiments obtained at T_{cryst} = 125^{0}C, when sheared at 136^{0}C is that 110 and 200 reflections in samples containing 2.0% zirconia, lies at equatorial regions as compared to those of neat HDPE and HDPE containing other concentrations of zirconia [0.25%, 0.5% and 1.0%], where 110 reflection appears at equatorial region while 200 reflection appears at meridional region. Thus increasing concentration of zirconia nanoparticles when sheared at 142^{0}C, perturbs the chain orientation in the polymer.

The 2D-WAXS patterns at two different temperatures and azimuthal distributions of the intensities after shear at two different temperatures for HDPE in presence of zirconia nanoparticles are shown in the figures below.

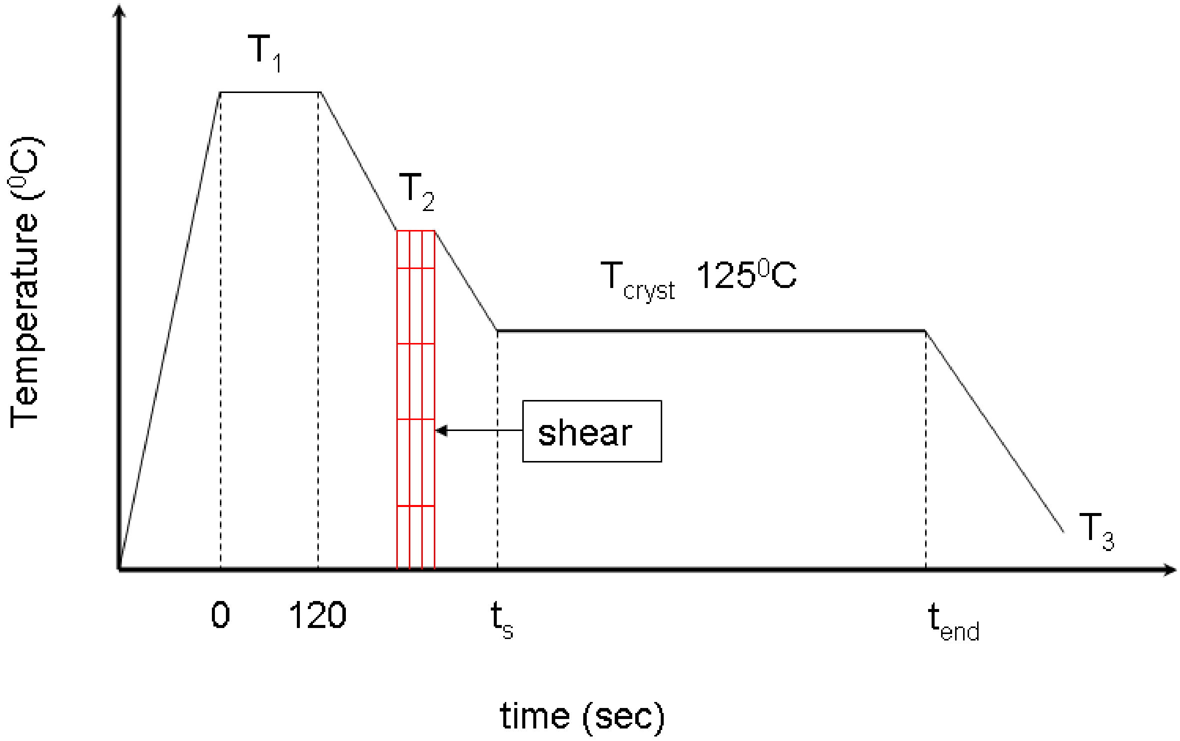

Figure 1: The figure shows the schematic drawing of the thermal history applied to study the structure development under shear. T_1 corresponds to the high temperature above melting point at which sample was kept for 2 minutes to remove the melt history, T_2 corresponds to the temperature at which shear was applied while T_3 corresponds to the room temperature.

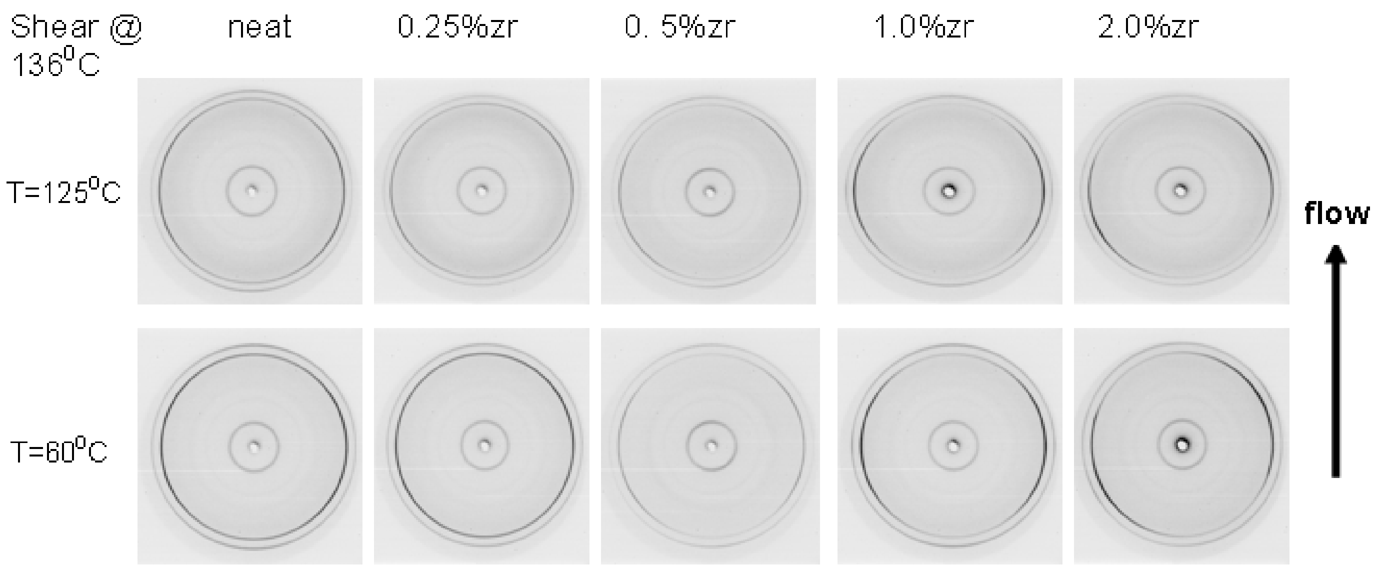

Figure 2: The figure shows the 2D-WAXS patterns for the given HDPE of broad molar mass distribution with four different concentration (0.25%, 0.5%, 1.0% and 2.0%) of zirconia nanoparticles at two different temperatures (125^{0}C and 60^{0}C). The shear was applied at 136^{0}C, while the sheared samples were kept at isothermal condition at T_{Cryst} =125^{0}C for 600s to follow the formation of oriented structures. Note that highly

oriented arc-like patterns obtained at $T_{cryst} = 125^0C$ becomes intense with the increasing concentration of zirconia nanoparticle thus favouring orientation.

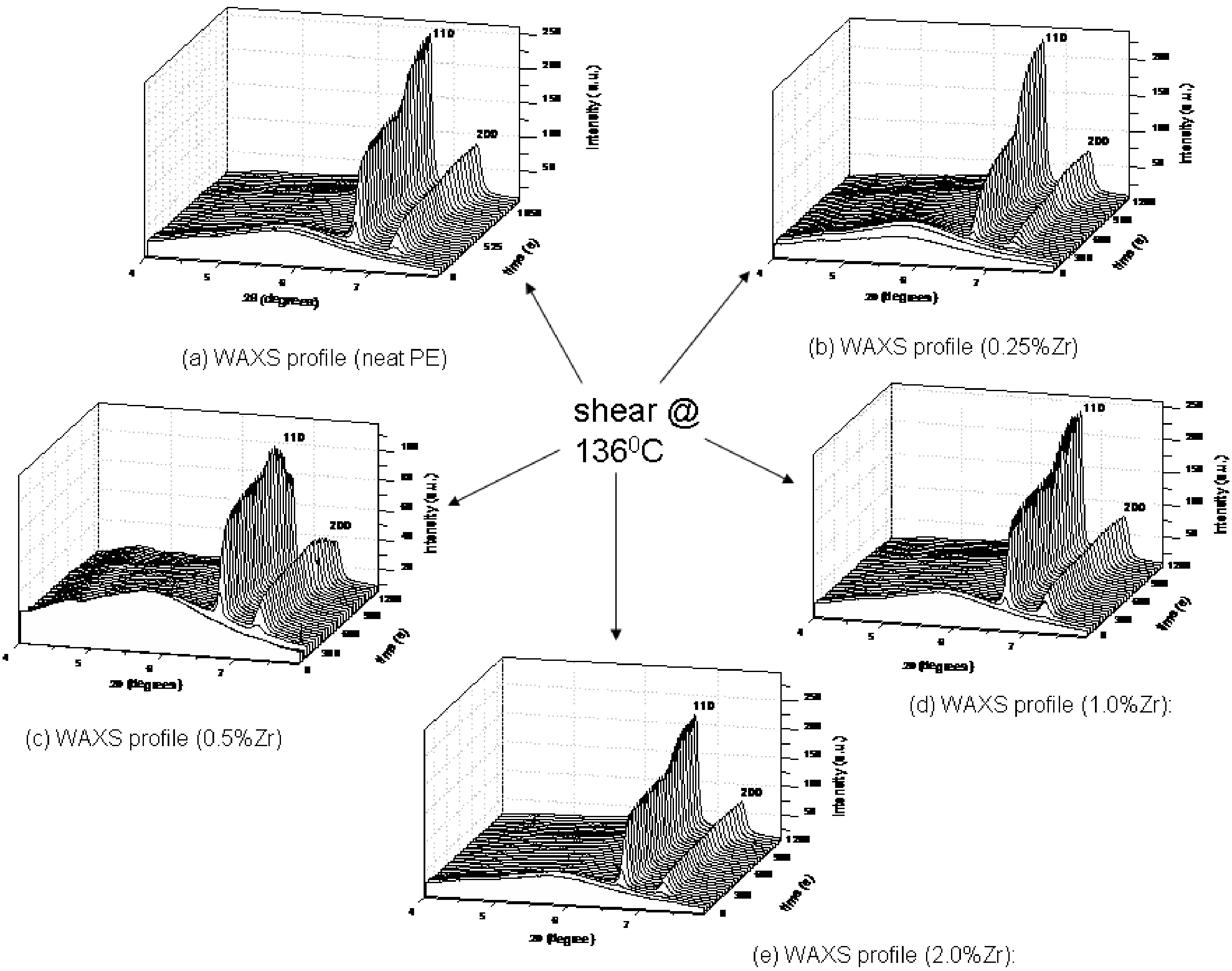

Figure 3: The figure shows the time resolved 3D plots of intensity (a.u) vs. 2θ (degrees) for full profiles after sample were sheared (100/s for 1s) at 136^0C. It is expected that the onset of crystallization shifts to higher side of temperature with the increasing concentration of zirconia nanoparticles.

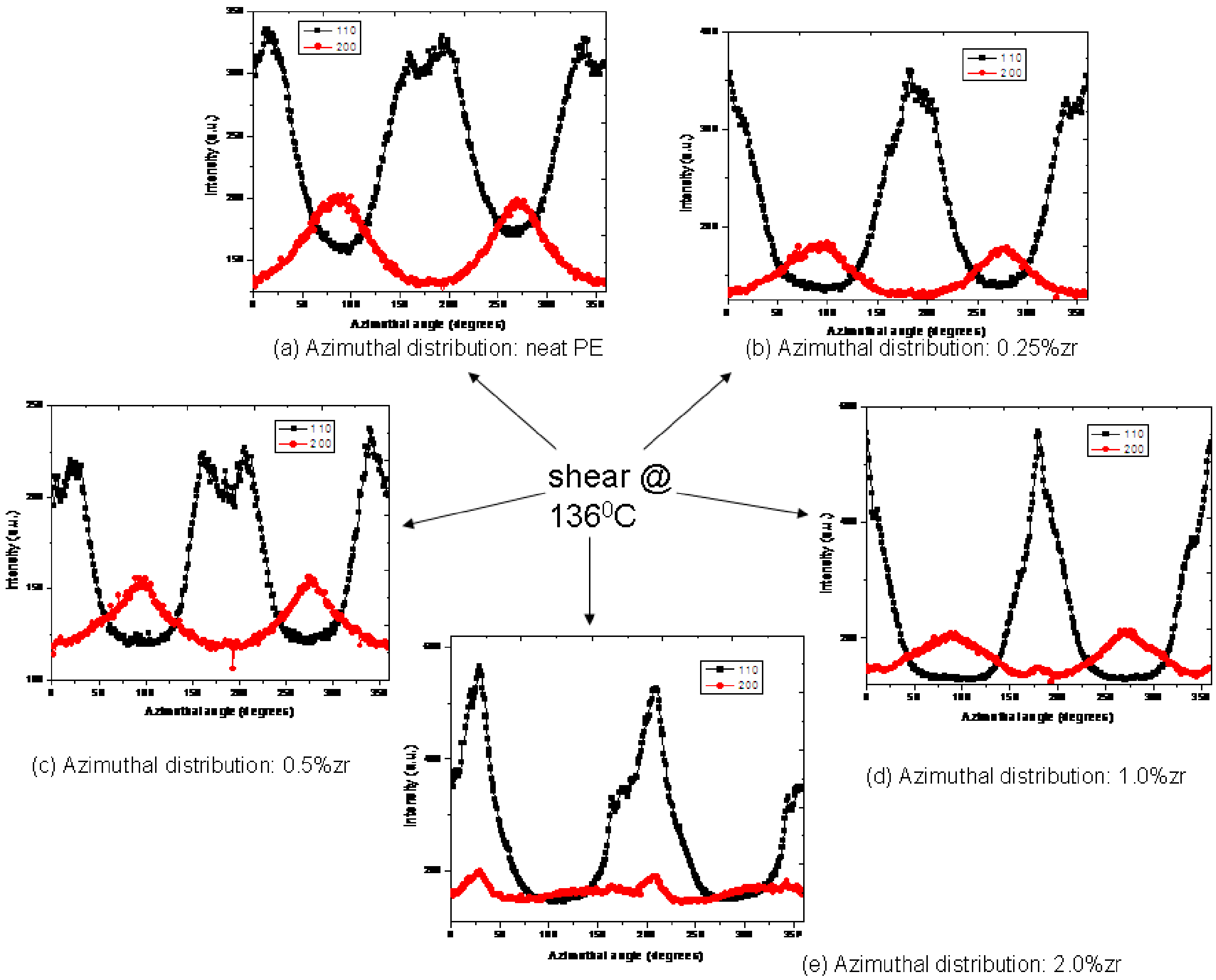

Figure 4: The figure shows azimuthal distribution of intensities at 60^0C after the application of shear at 136^0C. Note that 110 and 200 reflections in (e) i.e. for samples containing 2.0% zirconia, are striking at equatorial regions as compared to those of neat HDPE and HDPE containing other concentrations of zirconia [(a), (b), (c) and (d)], where 110 reflection appears at equatorial region while 200 reflection appears at meridional region. The azimuthal offset between the maxima of 110 and 200 reflection suggest the overgrowth of twisted kebabs.

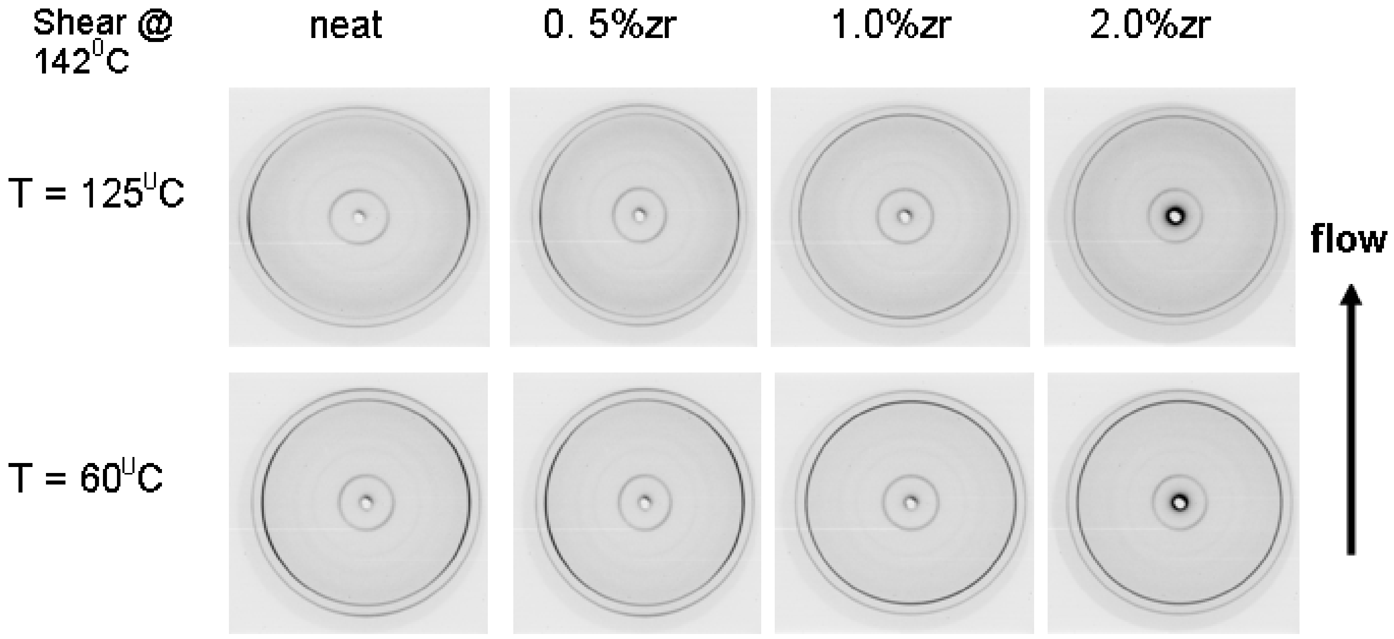

Figure 5: The figure shows the 2D-WAXS patterns for the given HDPE of broad molar mass distribution with three different concentration (0.5%, 1.0% and 2.0%) of zirconia nanoparticles at two different temperatures (125^0C and 60^0C). The shear was applied at 142^0C, while the sheared samples were kept at isothermal condition at T_{Cryst} =125^0C for 600s to follow the formation of oriented structures. Note that highly oriented arc-like patterns obtained at T_{cryst} = 125^0C becomes less intense with the increasing concentration of zirconia nanoparticle thus inhibiting orientation.

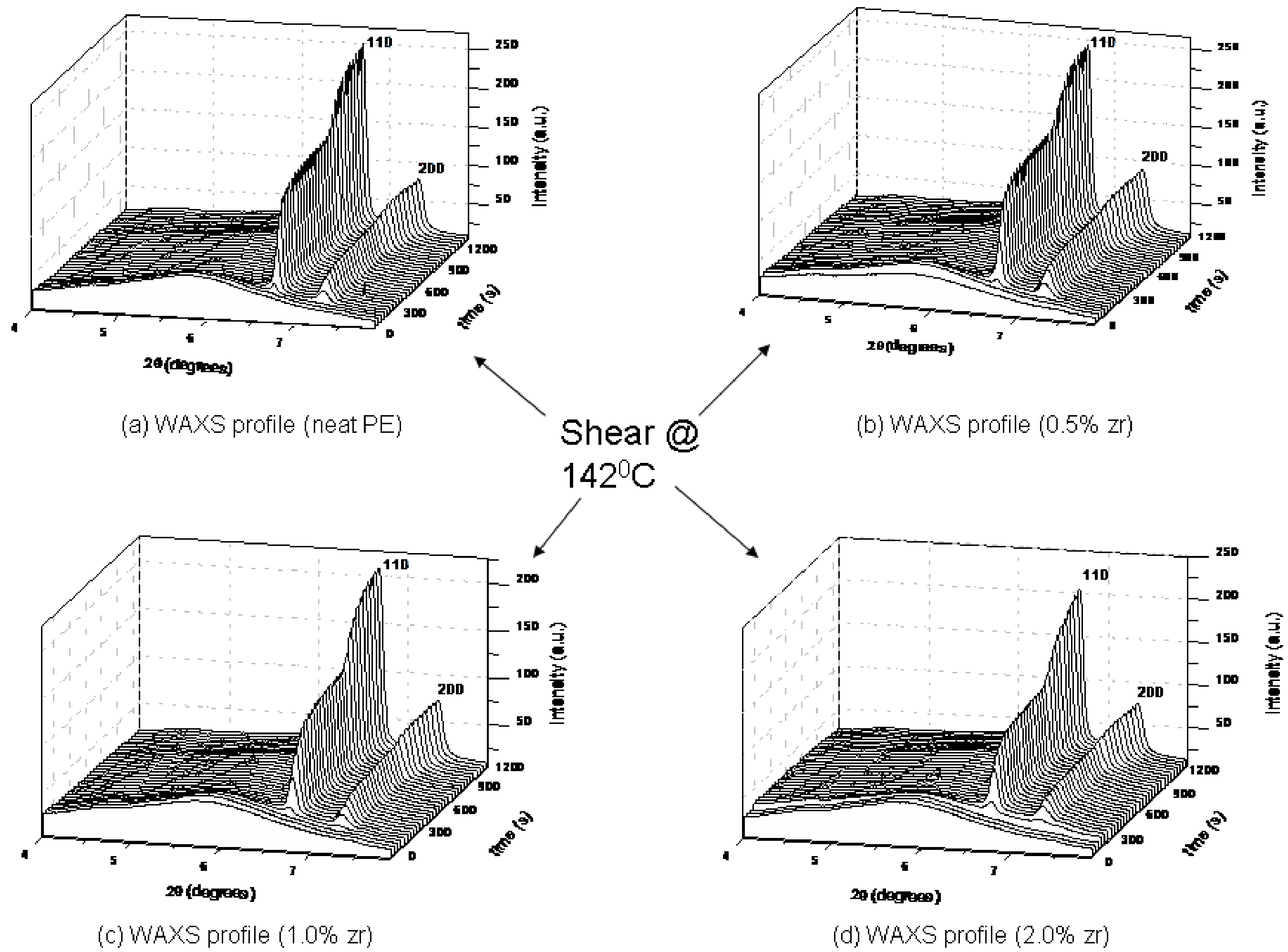

Figure 6: The figure shows the time resolved 3D plots of intensity (a.u) vs. 2θ (degrees) for full profiles after sample were sheared (100/s for 1s) at 142^0C.

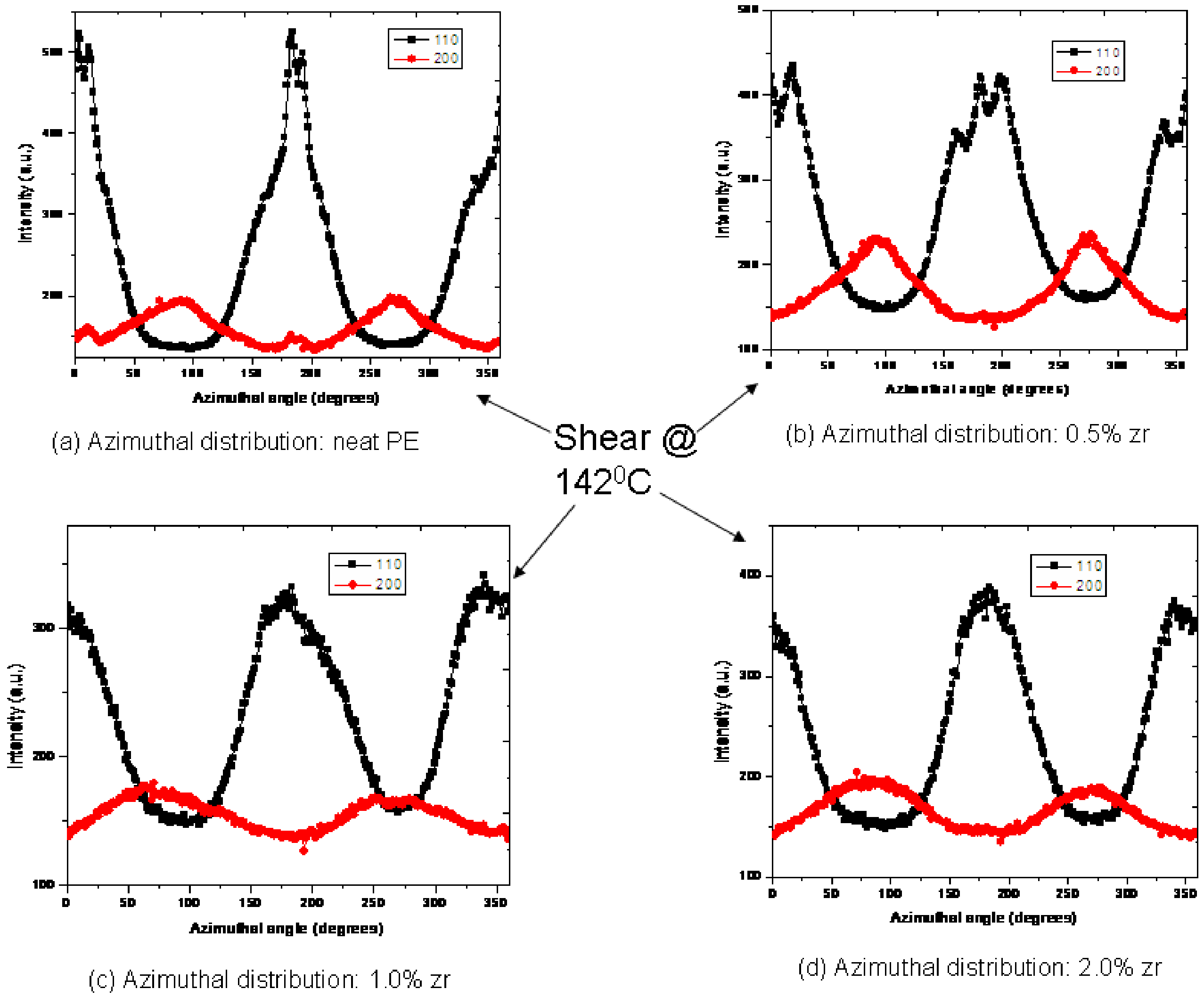

Figure 7: The figure shows azimuthal distribution of intensities at 60^{0}C after the application of shear at 142^{0}C. Note that 110 reflection appears at equatorial region while 200 reflection appears at meridional region in all the concentrations (0.5%, 1.0% and 2.0%) of zirconia nanoparticle. The azimuthal offset between the maxima of 110 and 200 reflection suggest the overgrowth of twisted kebabs.