ESRF	**Experiment title:** Deformation mechanisms and morphology of semi-crystallinge/Nanoparticles materials using Time-resolved WAXS/SAXS	**Experiment number**: SC-1959
Beamline:	**Date of experiment**: from: 12-may-2006 to: 15-may-2006	**Date of report**: 01-march-2007 *Received at ESRF:*
Shifts: 9	**Local contact(s)**: Dr. Peter Bösecke	

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Report:

Specimen program

As described in the proposal a wide range of materials was used. So we tested besides iPP and PA-6, pure and with different concentrations of nanofillers, for comparison also 2 grades of PE, PET as well as PC and PMMA as amorphous materials.

General experimental remarks

A custome-made micro-tensile rig was used with different grips, mainly for tension, but for some tests also shear load. The transfer of the mechanical data from the rig to the Controller, which added these informations to the ccd-files was very helpful for further evaluation.

Problems: In the case of shear load the condition of fibre symmetry was not fulfilled. So the general used evaluation scheme was not applicable. Generally here it is necessary to extend the experiments to scattering under different angles to reconstruct the whole information in reciprocal space. Whis will be prepared for the future.

Furthermore, the tensile rig was unfortunately mounted in that way, that the tensile direction was vertically like the direction of the segment of WAXS measurement. – So the more interesting equatorial direction WAXS-pattern of the fibre symmetric specimen were not observable.

Very strong changes in the scattering power during the experiments with semicrystalline as well as with the nanoreinforced materials were observed.. It was not always possible to adapt the exposure time, sometimes the use of a filter was necessary (including the danger of slight changes in the spectral composition of the beam). On the other hand the extreme reduction of exposure time to avoid overflow of the SAXS-detector produced some problems in the detection of WAXS-pattern. The latter were useful only in limited regions of the tensile experiment.

Unfortunately measurements were done only at room temperature. It is expected, that at elevated temperatures with a respective higher mobility in the amorphous phase the tendency of void formation will decrease drastically in support of the competition between defomation and relaxation of the amorphous phase and the rearrangement and recrystallisation/dissolution of the crystalline phase.

Inhomoegeneous stress distribution around the nanoparticles led mainly to interfacial failure at the interfaces perpendicular to tensile direction. This was nearly independent on the content of the nanoparticles.

Exemplary description of some results of iPP

Experimental

As an exemple results of iPP shall be described in detail. From an injection moulded isotactic polypropylene (iPP) plate of 80 * 80 mm^2 with a thickness of 1 mm test specimen were produced by CNC milling. For comparison also a quenched as well as an annealed plate were used.

To investigate local properties, small specimen were choosen. For local stress concentration at the beam position the specimen with total length of 30 mm were waisted in the middle. There they had a thickness of about 1 mm and a width of to 3 mm. Local strain was estimated by evaluating the deformation of an applied grid on the specimens surface. This allows to calculate also the local strain and the true stress. The processing induced differences in mechanical behaviour are shown in Fig. 1. With increasing distance from the inlet the stretching stress decreases and the strain at failure increases. The failure mechanism changes at the same time from crazing and nearly brittle to ductile and strain hardening behaviour. The most brittle material was compression moulded and slowly cooled. Over the whole deformation range stress relaxation is observed as soon as the tensile rig was stopped.

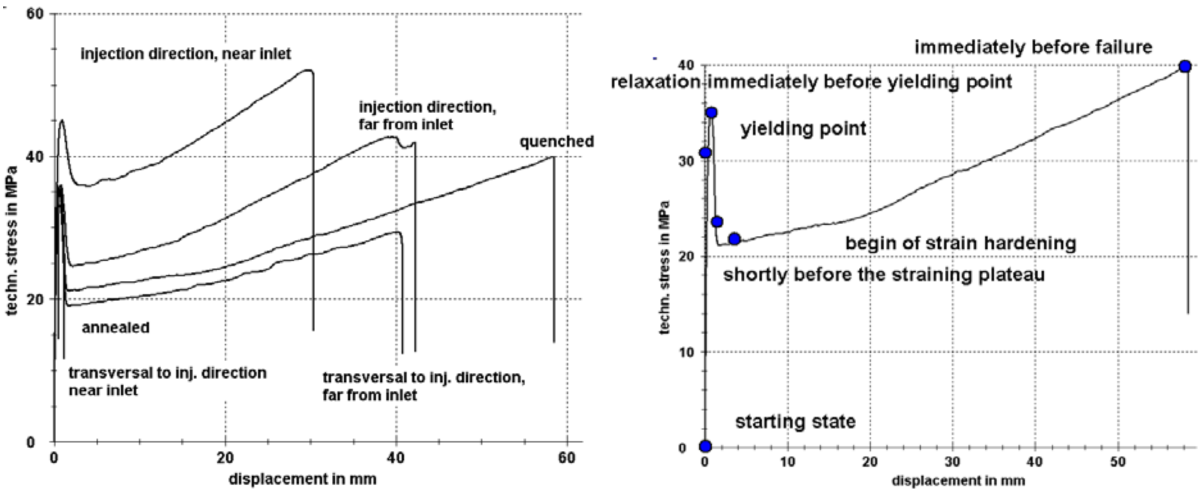

Figure 1: Stress-displacement-curves of waisted specimen from injection moulded iPP compared with a quenched as well as an annealed specimen. Right: Positions of the stress-displacement-curve, where the structure is discussed in detail below

For structural characterisation during the mechanical experiment USAXS was measured mounting a miniaturised tensile rig in the Synchrotron beam. The equipment is described in detail by Davies et al.[1] In the case of simultaneous SAXS and WAXS the changes in the crystallites can be followed in much more detail. While the overall crystallinity determined by DSC was comparable for samples taken at opposite positions of the plate, wide angle x-ray scattering (WAXS) shows evident differences.

Results and Discussion

The characteristic pattern at the different regions of deformation of the quenched specimen are shown in Figure 2. The 2-d pattern with fibre symmetry were evaluated according to the procedures developed by N. Stribeck[2] to get Cord Distribution Functions (CDF's), which reflect the correlation lengths in the different directions. Positive values specify dimensions of homogeneous phases, negative values characterise distances between similar entities. Special attention was paid on the reliability and reproducability of data treatment as well as the advancement of the used procedures. The CDF's in positive as well as negative directions for characteristic points of the stress strain curve are shown in Fig. 2.

[1] R. J. Davies, N. E. Zafeiropoulos, K. Schneider, M. Burghammer, C. Riekel, J. C. Kotek, M. Stamm, *Colloid. Polym. Sci*, **2004**, 282, 854

[2] N. Stribeck, *"X-Ray Scattering of Soft Matter"*, Springer, Heidelberg (2007)

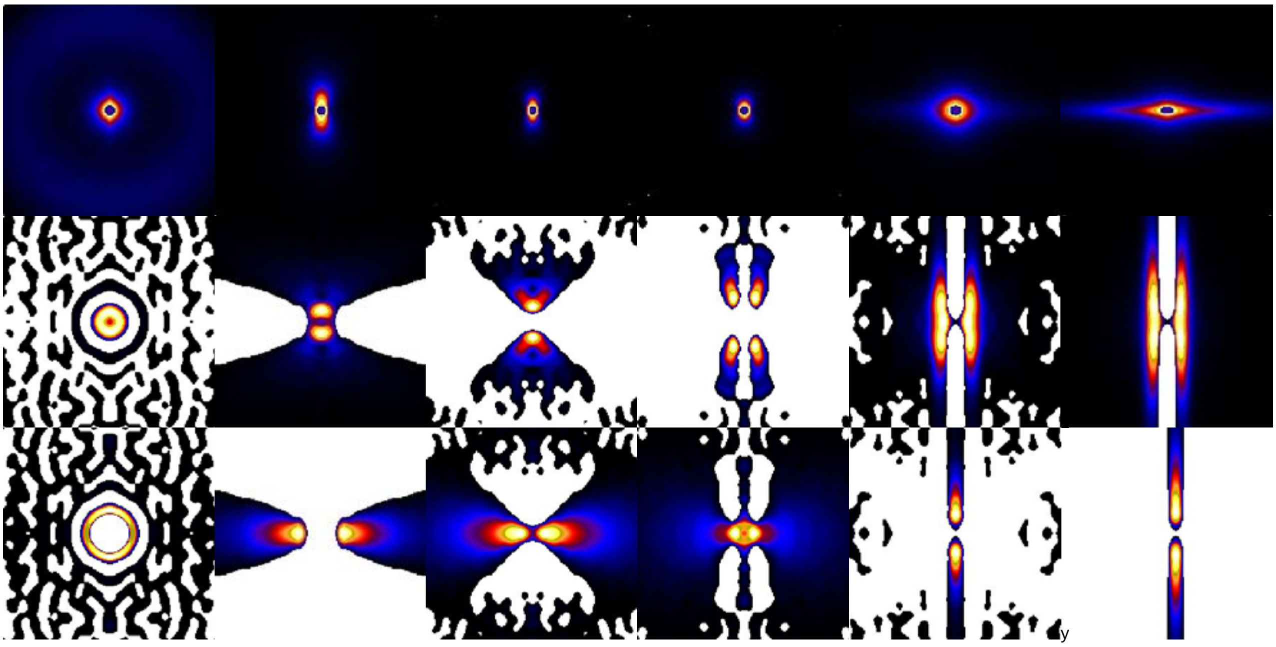

Figure 2: SAXS-pattern, log-scale (top) and CDF's in positive (middle) as well as negative direction (bottom), alwaxs scaled with respect to the maximal intensity; characteristic points of the whole deformation scenario (from left): (1) Starting state, (2) relaxation immediately before the yielding point, (3) yielding point, (4) shortly before the straining plateau, (5) begin of strain hardening, (6) immediately before failure. Each pattern over ± 0.06 nm^{-1}, CDF over ± 95 nm

Initial situation: Isotropic distribution of lamellae with characteristic thickness (left inner ring) and next neighbours distance. There is no remarkable change during deformation resp. relaxation in the visco-elastic range The ring in negative direction characterises the long period. Due to processing the radial symmetry is slightly disturbed.

Yielding: Yet approaching the yield point the crystallites were rotated and aligned in stress resp. strain direction. The correlation to the next neighbours in equatorial direction vanishes. A strongly increasing scattering due to micro crack formation soon dominates the pattern. The positive signal reflects cracks, opening range here below 10 nm. During further yielding the crack opening goes on and the cavities rotate to meridional direction creating transiently a four-peak correlation (oblique) via local shearing. Finally the voids enlarge, merge and arrange in meridional direction. Due to the high difference in electron density of the voids compared with crystallites, mainly the voids dominate the scattering. The correlations reflected by negative CDF's seem to be mainly due to repetitions of crystallites arrangement.

Strain hardening: Fibrils and mainly elongated voids, characteristic dimension and distance in equatorial direction are in the order of 10 nm dominate the specimen. In longitudinal direction there are repetitions in the range of 45 nm . Only small changes/stretching during the whole hardening process are observed.

Conclusions

The presented experiments enable to follow the continuously changing mechanisms of plastic deformation and energy dissipation (transformation of amorphous and crystalline phases and void formation). The major changes appear between the yielding point and the stretching.

Publication of results

Many pattern of high quality, partially evaluated and reported up to now, perliminary results reported/accepted on different conferences (P2006 Halle, 27.-29.9.06; COST-P12-workshop Mittelwihr, 8.-11.10.06; COST-P12-workshop Diamond Light Source, 23.-25.10.06; Usermeeting Hasylab/BW4 25./26.1.2007 (Poster); DPG-Frühjahrstagung Regensburg, 27.-30.3.0; ICPP Peking, 18.-20.5.2007). An extended presentation of the results in a journal is planned.