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Investigation of changes in crystalline and amorphous structure during deformation of nano-reinforced semi-crystalline polymers by space-resolved synchrotron SAXS and WAXS

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Abstract

Complex structural changes occur in semi-crystalline polymers during deformation. In (nano-)filled systems the situation becomes even more complicated, since not only phase changes may take place, but also local (interfacial) failure between phases may occur.

To help identify specific processes taking place within these systems, simultaneous small- and wide-angle X-ray scattering (SAXS/WAXS) measurements were performed using synchrotron radiation during in situ deformation. Using a highly focused beam, spatially resolved local information can be extracted by scanning the beam across the deformed/damaged region within the sample. The characteristic changes in the different phases are presented and discussed. While the study of WAXS patterns gives insight into the orientation and dimensions of the crystallites, SAXS provides information about the mutual arrangement of phases and the interfacial failure phenomena.

Based on the analysis of the results obtained in our experiments it will be shown that the first changes in the crystalline phase appear long before macroscopic yielding of the sample is reached, i.e. the onset of irreversible deformation takes place. In the post-yield regime radical changes are observed in both the long- and short-range structures.

It is concluded that the presence of nano-fillers exerts a strong influence on the establishment of microcrystalline structure, and hence also on the deformation behaviour at the microscopic scale.

Keywords: Synchrotron SAXS / WAXS; structure characterisation; deformation, PA-6 / ZnO

1. Introduction

The stress-strain behaviour of semi-crystalline materials is affected by the differentiated interaction of the different phases. Three characteristic deformation regimes are observed. In the initial apparently elastic region of low stresses up to the yield point stress relaxation can be observed due to the rearrangements in the amorphous

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phase. The extent and rate of relaxation depends on the difference between the test temperature and the polymer's glass transition temperature. Upon loading beyond the yield point, a local neck is formed with high local but small overall strain. During subsequent deformation, the neck propagates over the entire specimen. In the third stage during further elongation strain hardening occurs, ultimately leading to failure. The model of Strobl et al.[1,2] separates the deformation of semi-crystalline polymers into different mechanisms of stress transfer (due to the amorphous and crystalline units) and makes it possible to describe this behaviour.

In practice, the behaviour becomes much more complex in the case of nano-filled materials due to the presence of the additional phase and interfaces as the potential positions of local failure. In addition, the well-known processes of cavitation in polymers under deformation should be considered.

In recent studies Schneider et.al.[3] showed a continuous generation of the voids in the plastic phase starting close to the yield point, which led to a conspicuous increase in the small angle scattering power. Furthermore, a change in the SAXS scattering profile indicates a monotonic modification in the size and shape of the voids.

As an example, in this study the properties of neat PA-6 and PA-6 filled with nano-sized ZnO particles were investigated by tensile loading. Simultaneously, the structural changes were characterised by synchrotron WAXS and SAXS. The observations are discussed in connection with the mechanical properties and deformation behaviour.

2. Experimental

PA and PA-ZnO-nanocompounds were investigated. Polyamide 6 (PA-6) was purchased from BASF, grade Ultramid B3 with the molecular weight of Mw=66200 g/mol, Mn=27700 g/mol, Mw/Mn=2.39. The NanoTeK® Zinc Oxide nanoparticles were obtained from Nanophase, with the crystal phase being Zincite (hexagonal). The averaged primary size of ZnO nanoparticles was 60 nm with an elongated morphology. The compounds were manufactured by a twin screw extruder, the PA-6 polymer pellets and ZnO nanofiller were separately added by gravimetric dosing. The pure (neat) PA-6 specimens and PA-6/ZnO nanocomposites were prepared by injection moulding in the form of plates of 80×80 mm^2 area and the thickness of 1 mm, from which tensile samples were produced by CNC-milling.

WAXS and SAXS measurements were performed at ESRF/ID13 in Grenoble with a micro-beam (wavelength 0.997Å, beam diameter about 20 µm) using a 2-dimensional MarCCD-detector. A sample-detector-distance of 181 mm enabled the simultaneous collection of SAXS and WAXS patterns. Due to the much higher scattering intensity at small angles, the SAXS-region of the detector was shielded by an additional absorbing glass sheet in front of the detector. The SAXS results reported were complemented with some previous measurements.

In order to carry out structural modification during the X-ray scattering experiments, we collected patterns from samples mounted in a miniaturised tensile rig placed in the synchrotron X-ray beam. General description of the equipment was given in detail by Davies et al.[4]. The rig is illustrated in Figure 1. By applying simultaneous displacements to both end grips, the middle of the specimen loaded in tension remained in stationary with respect to the beam position.

In order to help maintain the beam at the same position in the gauge section of the sample throughout the measurement, a waisted specimen shape was used, so that the stress state was maintained uniform within the middle segment of the sample. The strain was determined optically by observing the deformation of a grid pattern applied to the specimen surface.

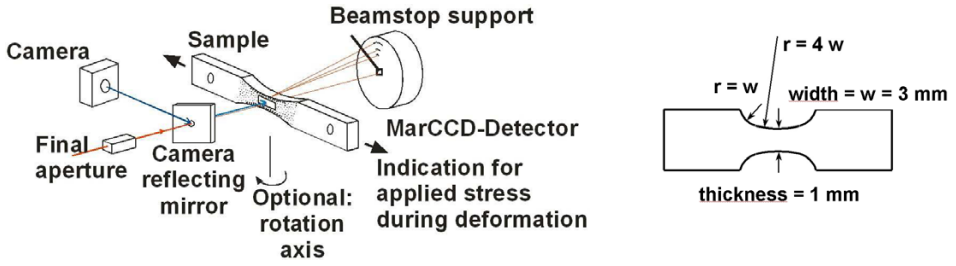

Fig. 1. Arrangement of the miniature tensile test rig with the specimen within the synchrotron X-ray beam and specimen geometry.

3. Results and Discussion

3.1. Mechanical behaviour

Tensile experiments were performed with tensile elongation rate of about 0.8 mm/min. A pattern was collected approximately every 15 s (10 s exposure) for neat PA-6 or 10 s (5 s exposure) for PA-6 with 10 % ZnO. The collection time was shorter for the composite due to the higher scattering strength of the filled sample.

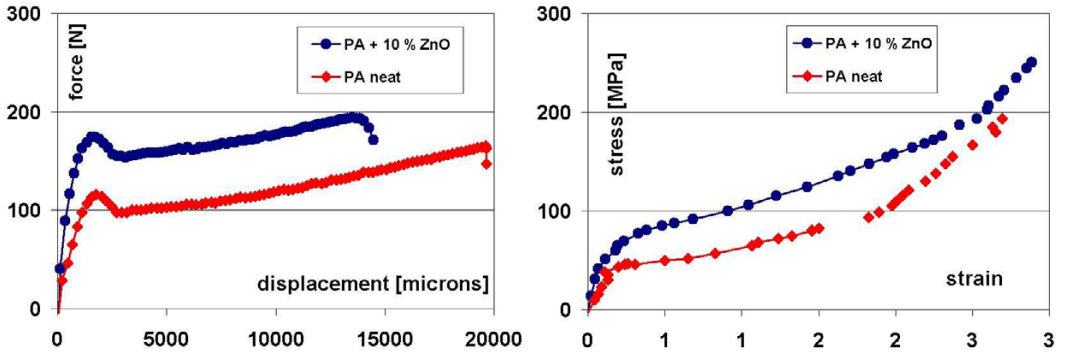

Fig. 2. Force-displacement and stress-strain curves of the neat and the ZnO-filled PA-6 samples, measured using waisted specimens.

3.2. WAXS – Information about the crystalline phase

Direct comparison of the patterns for PA-6 and PA-6/ZnO (Figure 3) shows, in addition to the presence of the 3 diffraction rings of ZnO [(10.0), (00.2) and (10.1)], a slight modification of the WAXS pattern for PA-6. Figure 4 shows the details in sections in different directions. ZnO-reflexes show a grainy structure due to the use of small beam cross-section. With deformation, a strong alignment of the crystallites is observed, which reflects in the change of the relative intensity of the peaks (see Figure 4 b). There is a small asymmetry found in the PA-6 pattern associate with the processing history and the smaller net peak intensity of the undeformed filled specimen. This correlates well with the lower crystallinity found by DSC, and corroborates the influence of the nano-filler on the crystallization behaviour. The two principal PA-6 reflexes in the angular range 10-20° correspond to (200) and (002) planes[5]. The presence of the filler also increases the background.

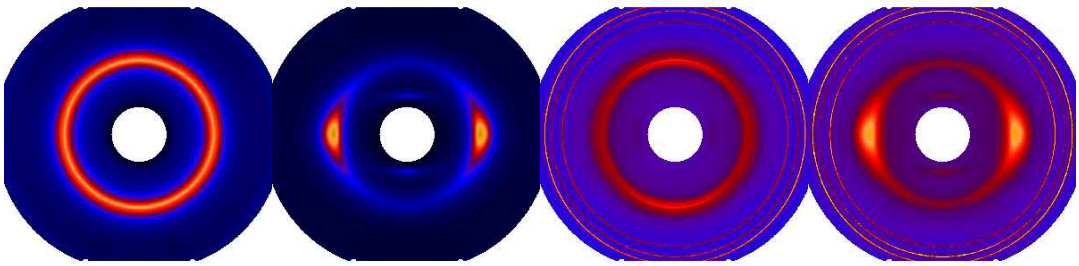

Fig. 3. Harmonized WAXS scattering pattern of the neat PA-6 (a, b) and ZnO-filled PA-6 specimens (c, d), always from start of deformation (a, c) and at strain 1.7 (b) and 2.3 resp. (d)

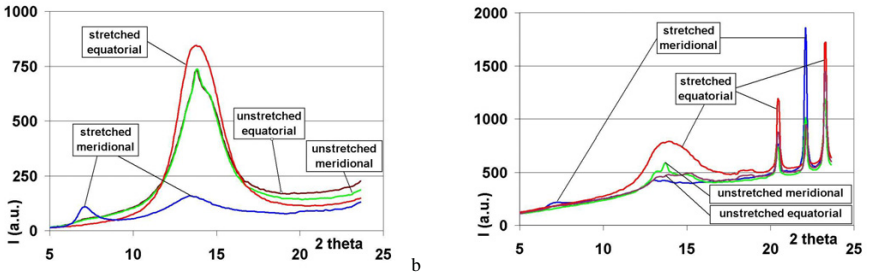

Fig. 4. Scattering intensity in the equatorial and meridional directions of the neat (a) and ZnO-filled (b) PA-6 (exposures 10 s and 5 s respectively).

3.3. SAXS – Information about the morphology and voids

The 2D SAXS-patterns were evaluated according the standard techniques described by Stribeck[6] in order to extract three-dimensional chord distribution functions in the case of cylindrical symmetry of the specimen.

In the present case a strong increase in the scattering power with increasing ZnO content was observed. Offline measurements of the SAXS region show a change in the scattering intensity by a factor of about 1000 for 10 % ZnO. Hence, it was not possible to separate directly the small effects of primary structural changes and damage of the PA-6 from the ZnO signals that were superior in strength. A parallel investigation by electron microscopy is likely to help in separating these effects.

4. Conclusions

The experiments presented here enable the monitoring of the continuously changing mechanisms of elastic and plastic deformation and energy dissipation (the transformation of amorphous and crystalline phases, and void formation). Due to the high number of parallel processes, the use of structure characterisation by X-ray scattering techniques should be complemented by further independent investigations, e.g. by electron microscopy. This combination of methods is likely to provide a well-founded basis for material development and optimisation.

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