Spatially Resolved Orientation of Platelet-Shaped Nanoparticles in a Polyethylene Tensile Bar

D. Carmele¹, M. Servos¹, A. Elas², F. Puch², U. Vainio³, W. Michaeli² and U. Klemradt¹

¹II. Physikalisches Institut B, RWTH Aachen University, 52074 Aachen, Germany
²Institute of Plastics Processing (IKV), RWTH Aachen University, 52062 Aachen, Germany
³HASYLAB, DESY, Notkestraße, 22607 Hamburg, Germany

In plastic materials technology, considerable effort is spent on improving the mechanical properties of polymers by the incorporation of filler particles with at least one dimension on the order of a few nanometers [1, 2]. In investigations of this new class of materials called nanocomposites, the naturally available layered silicate montmorillonite is frequently used for industrial and scientific applications. The silicate layers have a thickness of approximately 1 nm and a typical lateral dimension in the range from a few hundred nanometers up to several microns [3], but they show a strong tendency to agglomerate in form of stacks built by a few single layers with nearly homogeneous basal spacing. The requested improvements depend not only on the dispersion on the nanometer scale, but also on the orientation of the anisotropic particles.

The influence of mechanical stretching on the orientation of the layered silicate in a polyethylene (PE) matrix is of particular interest for applications. The orientation of the particles was analysed with a spatial resolution of 0.3 nm by small angle x-ray scattering (SAXS) at beamline B1 at HASYLAB, DESY with two different sample-to-detector distances of 935 mm and 3635 mm, a photon energy of 11 keV, corresponding to a wavelength of 1.127 Å, and a beamsize of 0.3 x 0.3 mm². Injection moulded standard tensile bars (DIN EN ISO 527) consisting of a high-density polyethylene matrix, 3 wt.-% of layered silicate and 3 wt.-% of a compatibilisator were chosen as samples (Fig. 1). After a plastic deformation (deformation process DIN EN ISO 527-1), the centre positions were investigated. For comparison, an unstretched tensile bar as well as two tensile bars without filler particles (stretched and unstretched) were analysed in the same way.

Fig. 1: Geometry of the tensile bar and position of the cut out specimen.

Figure 2: Scattering patterns of the unstretched (a) and the stretched (b) tensile bars with (PEKompSS) and without layered silicate (PEKomp).
In Fig. 2, exemplarily two scattering patterns of the spatially resolved measurements of the border and the centre of the tensile bar are shown. For the unstretched as well as for the stretched specimens, the patterns exhibit clear differences between the samples with and without layered silicate. Due to the known orientation of the silicate layers parallel to the nearest surface [4], a section integration for every scattering pattern from ± 20° around the vertical axis of the scattering patterns were performed. The integrated scattering curves are shown in Fig. 3. Previous diffraction measurements showed that the incorporated layered silicate has basal spacing of 3.35 nm, corresponding to $q \approx 0.19$ Å$^{-1}$. While the scattering curves of the unstretched sample with layered silicate in the border region show a shoulder at a $q$-value of approximately 0.2 Å$^{-1}$ (Fig. 3a), for the sample without filler particles a monotonically decreasing intensity can be observed in this region of the scattering curve (Fig. 3b). For both samples, shoulders caused by the crystallinity of the polymer matrix exist for smaller $q$-values. Surprisingly, the scattering curves of the stretched sample with layered silicate also exhibit no distinct shoulder in the region of the layered silicate peaks as well as for smaller $q$-values (Fig. 3c). Only the stretched sample without layered silicate show a small shoulder in the region of 0.1 Å$^{-1}$, which can be assigned to the crystallinity of the matrix (Fig. 3d).

![Figure 3: Section-integrated scattering curves of the unstretched tensile bars with (a) and without layered silicate (b) and of the stretched tensile bars with (c) and without layered silicate (d).](image)

While the scattering curves of the unstretched sample with layered silicate show variations as a function of the measurement position, for the stretched one all scattering curves show the same decrease of the intensity. As expected, for both unfilled samples no influence of the measurement position can be observed which means that without filler particles the crystallinity of the polymer in this irradiation direction does not depend on the location.

Further evaluations of measurements in different direction relative to the stretch direction are in process.

References