In-situ observation of particle orientation in layered-silicate nanocomposites during a tensile test

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Considerable effort is spent on improving the material properties of polymers by incorporating filler particles. Especially particles in the nanometer range are of great interest for the enhancement of the mechanical properties of these composite materials [1,2]. Naturally available layered silicates, which consist of single layers with a thickness of approximately 1 nm and lateral dimensions in the range of a few hundred nanometers, represent one of the most interesting nanoparticles for the preparation of so-called nanocomposites [1]. However, the single layers show a strong tendency to agglomerate in form of stacks (tactoids) in the micrometer range consisting of a few layers with a nearly homogeneous basal spacing [1,2]. For a homogeneous dispersion of the silicate layers in a polymer matrix, the tactoids have to be disaggregated during the incorporation process. To obtain a better dispersion, in a first step the layered silicate becomes chemically modified [1,2], which enhances the basal spacing up to approximately 3.35 nm [3 4] and additionally, a compatibilisator is used [1]. However, a complete dispersion of the silicate layers could not be achieved so far. The regular arrangement of the layers in the tactoids still exists with the result that Bragg reflection could still be measured in the SAXS range [2-4]. Owing to their anisotropic shape, the orientation of the disc-like particles also plays an important role for the mechanical properties [1]. Previous measurements showed that the layers have a strong tendency to be oriented parallel to the nearest surface [3-5], with their orientation changing when subjected to mechanical stress [3,4].

In this work, the change of the particle orientation during a tensile test is investigated. The measurements took place at beamline BW 4 with a photon energy of 8.98 keV, corresponding to a wavelength of 1.381 Å, and a sample-to-detector-distance of 402 mm. Thus, the Bragg peaks of the layered silicate could be registered at the 2D detector. Tensile bars (DIN EN ISO 527) consisting of a high-density polyethylene (PE-HD) with 3 wt.-% of a matched compatibilisator and 3 wt.-% of a chemically modified layered silicate were tensile-tested with different stretching velocities between 0.2 and 1 mm per minute. During the tensile test, the SAXS experiment were performed in-situ.

On the left in Fig. 1, the stress-strain-diagram of tensile test performed with a stretching velocity of 0.5 mm per minute is shown. Exposure times for SAXS patterns were 120 s. Due to the finite measurement interval, the change of the particle orientation within one pattern was averaged over 1 mm during continuous straining.

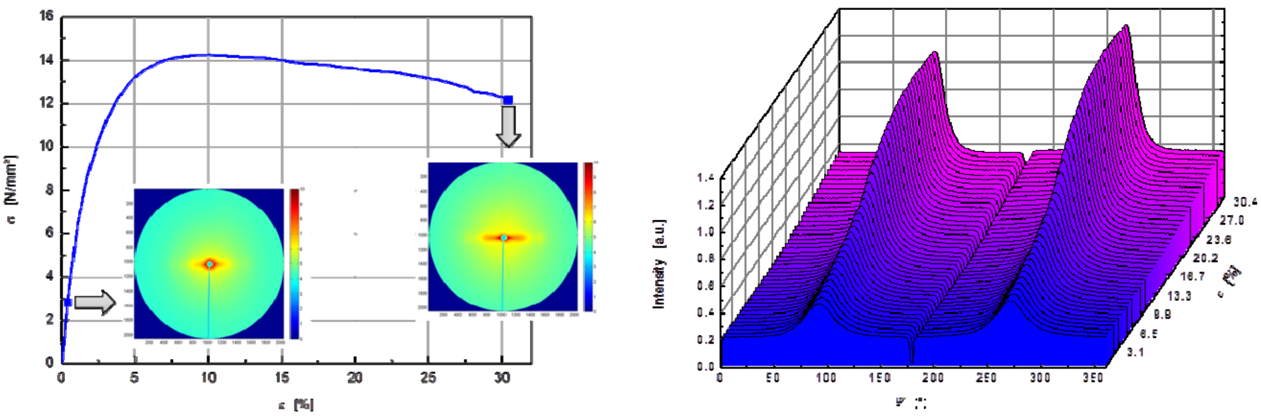

Figure 1: Stress-strain-diagram of the nanocomposite tensile bar including the first and the last scattering pattern (left) and an azimuthal integration of the intensity for a q-value of (0.20 ± 0.03) $Å^{-1}$ (right).

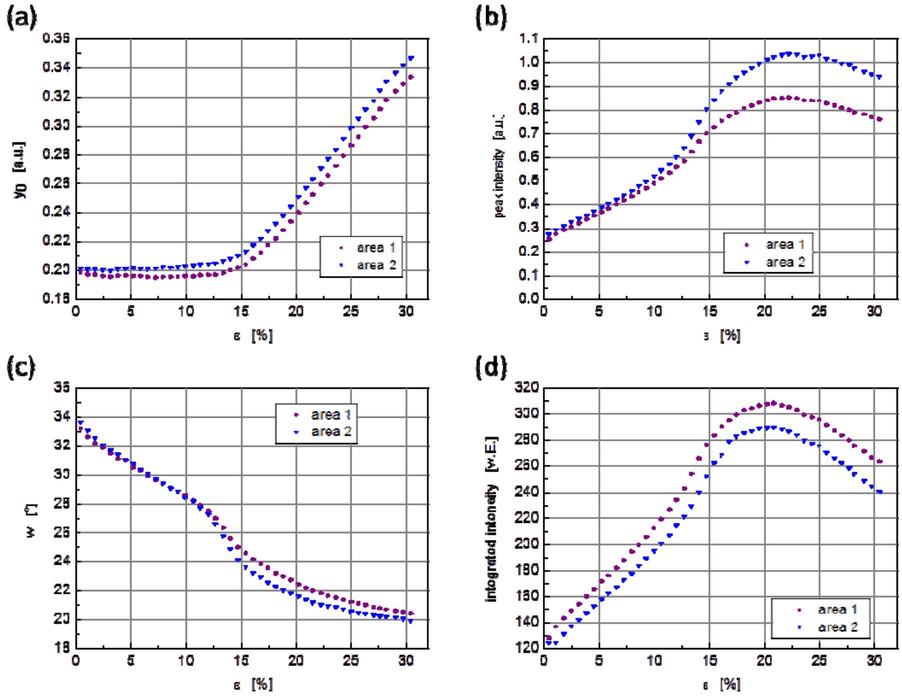

Figure 2: Azimuthal integration of the intensity for a *q*-value of (0.20 ± 0.03) $Å^{-1}$.

Compared to scattering pattern at the beginning, the pattern at the end of the tensile test shows an increased anisotropy. Based on the known basal spacing of the layered silicate, the related Bragg peak is expected at a *q*-value of 0.20 $Å^{-1}$. Hence, for this *q*-value the strain-dependent intensity is integrated over the azimuthal angle Ψ using a ring of ± 0.03$Å^{-1}$ width, as can be seen in Fig. 1 (right). The anisotropy of the scattering patterns is reflected in form of two peaks in the curves at approximately 90° and 270°. The peak intensity as well as the intensity of the background increase during the stretching process. For a better evaluation, Pseudo-Voigt functions are fitted to the peaks in both areas. The relevant results of the fits are shown in Fig. 2, where absorption effects cause the difference between the curves of the two areas. The increase of the background (Fig. 2(a)) starts approximately at a strain of 15 %, while the peak intensity (corrected for background) increases from the beginning up to approximately 20 % strain (Fig. 2(b)). For higher strains, the peak intensity is first constant and then starts to decrease at a strain of 25 %. The peak width decrease with a drop in the curve at a strain of 12.5 % (Fig. 2(c)). The integrated intensities of the peaks (corrected for background) (Fig. 2(d)) increase up to maximum at a strain of approximately 20 % and afterwards decrease.

These results show that the microscopic silicate layers, present in the form of tactoids in the tensile bar, are aligned during the stretching process in accordance with Ref. [3,4], but obviously without any effect on the macroscopic stress-strain-diagram. The reduced peak width can be interpreted as an enhancement of the degree of particle orientation, while the increased maximum peak intensity and the increased integrated intensity indicate an enlargement of the number of oriented tactoids.

References

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