Nanostructure and Mechanical Properties of Microfibrillar Reinforced HDPE/PA Blends

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Experimental Setup. Time-resolved 2D SAXS measurements are performed at HASYLAB beamline A2 during mechanical testing of polymer fibers with a cycle time of 30 s and a cross-bar speed of 0.4 mm/min of the HASYLAB tensile tester. A marccd 165 detector is used in 1024 $\times$ 1024 pixel mode. A manuscript that reports the results has been submitted [1].

Summary of Scientific Results. We study oriented polymer blends based on high-density polyethylene (HDPE) and strain them until failure. SAXS patterns monitor the nanostructure evolution. Data evaluation methods for high-precision determination of macroscopic mechanical and nanoscopic structure parameters are developed. The hardest materials exhibit a very inhomogeneous nanodomain structure. During straining their domains appear to be wedged together. This inhibits transverse contraction on the nanometer scale.

Further components are polyamides (PA6, PA12) (20–30%) and as compatibilizer Yparex® 8102 (YP) (0–10%). Some HDPE/PA6 blends are additionally loaded with nanoclays (Nanomer® or Cloisite®). Blending of HDPE with PA12 causes no synergistic effect. In the absence of nanoclay, PA6 and HDPE form a heterogeneous nanostructure with high Young's modulus. After addition of YP a more homogeneous scaffold structure is observed in which some of the PA6 microfibrils and HDPE crystallites appear to be rigidly connected, but the modulus has decreased. Both kinds of nanoclay induce a transition from a structure without transverse correlation among the microfibrils into a macrolattice with 3D correlations among HDPE domains from neighboring microfibrils. For extensions between 0.7% and 3.5% the scattering entities with 3D correlation exhibit transverse elongation instead of transverse contraction. The process is interpreted as overcoming a correlation barrier executed by the crystallites in an evasion-upon-approaching mechanism. During continued straining the 3D correlation is reduced or removed.

Methods for High-Precision Determination of Elongation. Whenever materials are studied that break at elongations in the order of 10%, monitoring requires high-precision determination of macroscopical and nanoscopical deformation of the sample. Corresponding methods have been developed [1]. Figure 1 demonstrates the method for the determination of the macroscopical elongation. Photos (Fig. 1a) are recorded with twice the cycle-time of the SAXS detector. Marks have been applied on the sample by means of a rubber stamp [2]. The user defines a rectangular region of interest (ROI) in the photo that contains the grid marks. The SAXS autocorrelation function of this part of the photo is computed and the "long period peak" is fitted by a polynomial of 2nd degree. The accuracy of the correlation method is demonstrated in a load-cycling experiment (Fig. 2). In a similar manner subtle variations of the microfibrillar nanostructure of the samples are determined. For this purpose the SAXS patterns are transformed into the real-space representation of the CDF [3]. Here the caps of the observed narrow domain peaks are fitted by bivariate polynomials of 2nd degree [4]. The influence of peak overlap is minimized by feeding the regression algorithm with a cap that contains only the top 5% of the peaks. From the coefficient matrix position and shape of the peaks is computed with high accuracy.

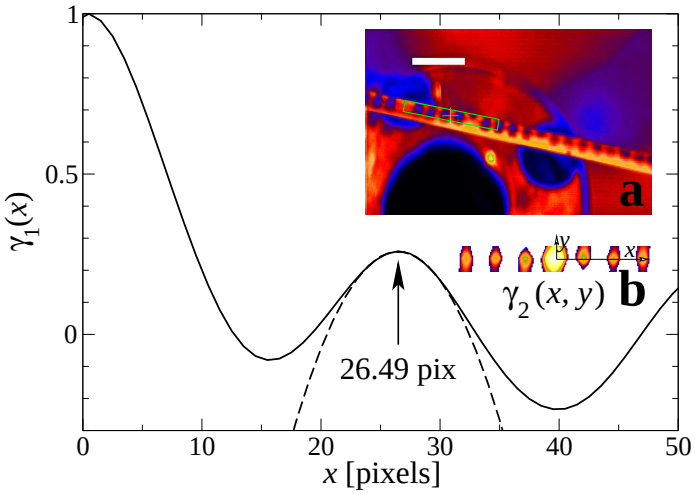

Figure 1: Elongation from recorded video frames. Inset **a**: In the first video frame a region of interest (ROI) with fiducial marks is defined. Inset **b**: From the ROI the 2D correlation function $\gamma_2(x,y)$ is computed. Main drawing: The center of the long-period peak in $\gamma_1(x) = \gamma_2(x,0)$ is fitted by a parabola (dashed line) to compute the distance between the fiducial marks

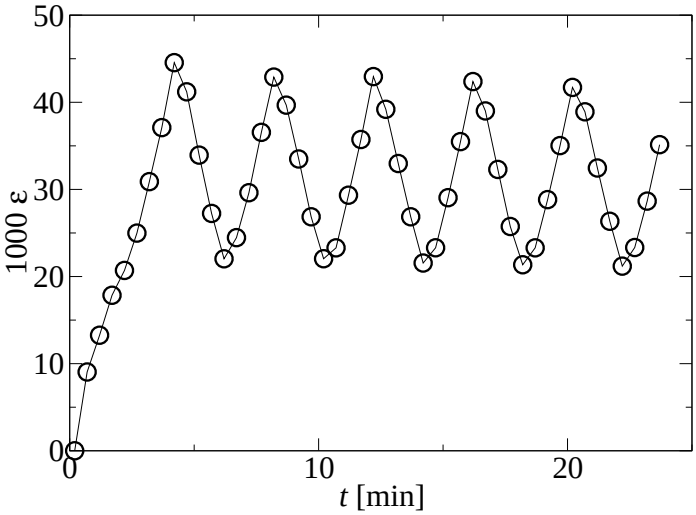

Figure 2: Accuracy of the correlation method is demonstrated by the smooth variation of the macroscopic elongation $\varepsilon(t)$ determined in a load-cycling experiment of one of the fibers

Conclusion. The new methods permit to automatically evaluate extended series of fiber patterns that are recorded mechanical studies of soft matter. We expect that it will become very useful for the management of extensive data series that will be recorded with high time resolution at PETRA III beamlines.

References

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