Transcrystallization in In-situ Polymer Composites and Its Influence on the Mechanical Behaviour

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An important step in the production cycle of *in-situ* composites is the non-isothermal crystallization of the molten polymer matrix in the presence of crystalline reinforcing fibrils with diameters from several hundred nanometers to several micrometers. It is well known that under such thermal conditions heterogeneous nucleation can occur with sufficiently high density along the interface. This will result in the formation of layers of matrix material around the fiber, known as transcrystallinity (TC). There are indications that the TC layers can play an important role in load transfer and distribution thus changing the mechanical behavior of the composite materials.

The composites of this study comprise an isotropic matrix of high-density polyethylene (HDPE) (65-90 wt. %) reinforced by oriented and crystalline polyamide 6 (PA6) fibrils (10-35 wt. %), produced with or without compatibilizing agent (0 – 10 wt. %)[1]. In some of the samples the fibrils contained up to 7.5 wt. % of exfoliated organically treated commercial montmorillonite (MMT). SAXS patterns under simultaneously applied static or cyclic load were obtained with a MAR CCD two dimensional detector at the A2 beamline of HASYLAB. The data processing and evaluation employed are described in [2]. Some typical SAXS images and output curves are presented in Figure 1.

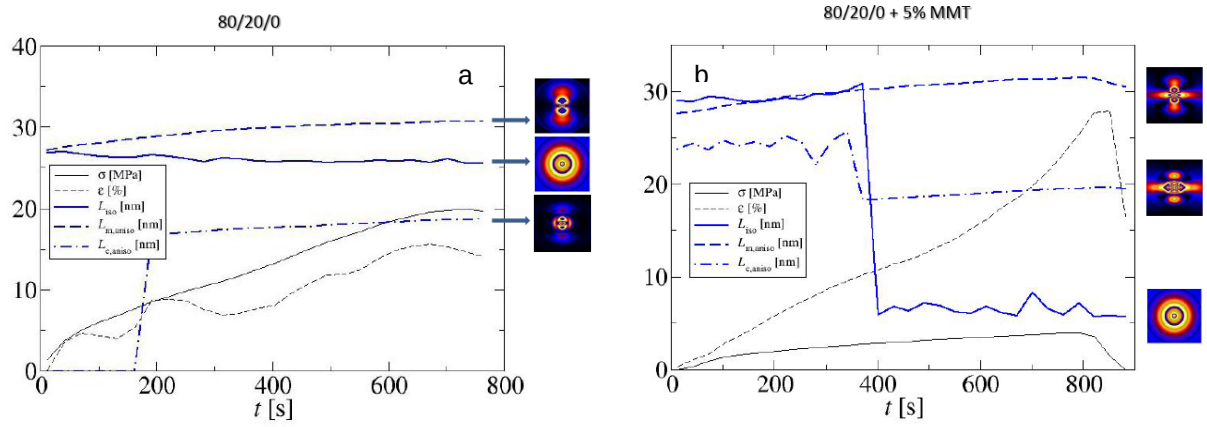

Figure 1: Output of the simultaneous SAXS/stretching experiments of *in-situ* composites comprising an HDPE matrix (80 wt. %) reinforced by PA6 fibrils (20 wt. %); (**a**) – without and (**b**) with 5% MMT in the PA6 phase. The black curves show the time dependence of the real stress and the real strain. The blue curves indicate the evolution of the long spacings derived from the isotropic HDPE matrix (solid line) and from the equatorial and meridional reflexes of the oriented transcrystalline HDPE fraction.

For each SAXS data frame separation of the isotropic from the oriented scattering was made thus visualizing the contribution of the HDPE of the matrix and of the TC layer respectively and calculating of the respective long spacing (L) as a function of the elongation time. Figure 1 shows that the introduction of nanoclay results in lower tensile stress values accompanied by an abrupt decrease of the isotropic L values. All nanoclay-containing samples were characterized by a meridional streak. In the samples without MMT after a certain time (*i.e.*, elongation), there appears a meridional long spacing not present before straining. These two phenomena vary as a function of the MMT concentration and type. They also seem to depend on the presence of compatibilizing agent (maleic anhydride modified HDPE).

The WAXS patterns were obtained with the same detector in the temperature range of 30-300ºC without application of external force. The separation of the isotropic from oriented scattering was performed as described previously [1]. Combining this structural information with the scanning electron microscopy data and supposing that the fibril has a cylindrical geometry and co-axial structure, the following equation was deduced:

$$2R_1 = 2R_2 \cdot \sqrt{\frac{f}{k+f}}$$

wherein $2R_2$ and $2R_1$ are the average diameters of the reinforcing fibrils with and without the HDPE TC layer; k accounts for the different electron density of HDPE and PA6 and f is the relation of the scattering intensities of PA6 and HDPE, respectively. Then, the average thickness of the TC layer will be given by $R_2 - R_1$. Thus, TCL was found to vary between 75-100 nm for HDPE/PA6 composites without MMT and between 160 and 250 nnm for MMT containing systems. In a subsequent study, the TCL thickness obtained by WAXS and the changes in its structure during straining determined by SAXS will be correlated with the composition and the mechanical performance of the respective *in-situ* composites.

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References

[1] N. Dencheva, M. Oliveira, O. Carneiro, A. Pouzada, Z. Denchev, J. Appl. Polym. Sci. **115**, 2918 (2010).

[2] Z. Denchev, N. Dencheva, S. S. Funari, M. Motovilin, T. Schubert, N. Stribeck, J. Polym. Sci B **48**, 237 (2010)