

 ESRF	Experiment title: Internal Structure of Spherulites in Compatible Blends of Two Crystallizable Components	Experiment number: SC 135
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Report:

Polymer alloys exhibit a rather complicated crystallization behaviour since it is determined by a superposition of equilibrium thermodynamic and kinetic boundary conditions. This results in a large variety of crystalline and supermolecular structures. During crystallization of a homogeneous binary melt, composition inhomogeneities can arise since far reaching diffusion is induced which competes with the growth rate of the spherulites. As a result, distinct composition profiles develop around the spherulites. These in their turn can cause a spatial variation of the internal degree of crystallinity of the spherulites which can change from the center to the surface because of the changes in composition at the crystal growth front with time, and the habit of the spherulites can change between purely globular and extremely dendritic. Whereas the aforementioned composition profiles have been detected and evaluated with respect to the diffusion coefficient (1), there is so far no knowledge about the associated spatial variation of the internal structure of the spherulites. The experiments at ESRF about which we report here should shed light on these issues.

The used polymers were poly (vinylidene fluoride), PVDF, poly (ethyl acrylate), PEA, and poly (methyl methacrylate), PMMA. From them, several blends were prepared (Table) from which samples with thicknesses of 50µm were got by isothermal crystallization between capton films of 12.5mm thickness. Samples I and III were earlier proven to exhibit isolatedly

grown spherulites surrounded by distinct composition profiles (1) and sample II exhibits a distinct dendritic habit (2).

Table: sample materials and preparation

Sample	blend	composition/wt-%	crystallization temperature/°C	crystallization time
I	PVDF/PEA	30/70	155	until com-
II	PVDF/PEA	5/95	quenched to RT	pletion of
III	PVDF/PMMA	60/40	142	crystallization

The samples were stabilized by a sticker-on washer, and a wolfram wire was also stuck on them whose tip and direction served as origin and orientation of an orthogonal frame. The intended positions of illumination with the primary X-ray beam within a chosen spherulite were read in a polarization microscope. The sample was then mounted on a goniometer head which in its turn was set on a x-y stage movable through the X-ray primary beam of the microfocus X-ray camera at IDI 3. Unfortunately, this mounting technique lead to additional shadow scattering from the boundary of the (steel) washer which disturbs the sample scattering remarkably. The WAXS patterns were recorded with a CCD camera and scanned into files ready for further evaluation with the program FIT2D (3). The monitored scattering patterns disappeared after about 10 seconds since the very intense X-ray beam caused rapid degradation of the PVDF, The degradation area within the sample could later be imagined by optical microscopy and served as check for the position of the pertaining irradiation spot.

From a preliminary interpretation of the WAXS patterns during registration it could be concluded that within the resolution limit of the experiment no change in the degree of crystallinity occurred from the middle of a spherulite to its surface. A detailed analysis of the X-ray patterns with respect to the spatial distribution of the PVDF crystallinity and degree and direction of chain orientation is however still under progress.

References

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