ESRF	**Experiment title:** **Internal structure of lamellar bundles and of spherulites from melt compatible crystallizable binary polymer blends**	**Experiment number:** **SC 286**
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Report:

The crystallization of one component in a homogeneously mixed melt of a polymer blend causes far reaching diffusional displacements of the involved macromolecules. At an intermediate rate ratio between crystallization and diffusional displacement rates, respectively, a composition profile can arise at the surface of the growing crystalline entities (which usually are spherulites) with enrichment of the amorphous component at the crystal growth front. The composition changes at that location should, in principle, cause corresponding spatial changes of the morphology of the spherulites and their internal composition. Infrared (IR) microscopic investigations with a spatial resolution of about 10μm on poly (vinylidene fluoride)/poly (methyl methacrylate) blends (PVDF/PMMA) with PVDF as crystallizable component revealed however, that, surprisingly, the composition is constant across the spherulites in the limits of error of this technique. It has been one aim of the wide angle X-ray scattering (WAXS) experiments with the microfocus X-ray camera at ESRF/ID13/BLl to investigate the crystalline structure within the spherulites with respect to the described effects with the same spatial resolution.

The crystallization behaviour is much more complicated if both components can crystallize and form a homogeneous melt. Then, for steric (i.e., basically, thermodynamic) reasons, mixed crystallization of the involved polymers is a seldom exception. Moreover, the blend can crystallize eutectically, if at all, only in rare cases since the melting point depression of polymeric alloys is very small, and the respective phase lines do not intersect at an intermediate composition unless the equilibrium melting temperatures are almost equal. It should, nevertheless, almost always be possible to enforce simultaneous crystallization kinetically by suitable undercooling ("kinetically eutectic" crystallization). Another aim of the present investigations has therefore been to detect such common crystallization and to unvail the resulting supermolecular morphology.

Sample materials and preparation

blend material	composition / wt-%	crystallization temperature / °C	crystallization time / h	film thickness / μm	diameter of investigated spherulite/um
PVDF/PMMA	60/40	158	12	50	100
PVDF/PMMA	70/30	158	12	50	110
PVDF/PHB	60/40	156	2.5	30	(PHB) 130
PVDF/PHB	70/30	156	2.5	30	(PHB) 200

PHB: (crystallizable) poly (hydroxy butyrate)

The table collects the investigated blend systems and their compositions. The blend PVDF/PMMA allows comparison with the IR microscopic results with respect to the internal crystallinity and composition distributions, respectively. In contrast, the system PVDF/PHB may behave kinetic-eutectically and the experimental results may consequently give information on common crystallization and its spatial variation. The PVDF/PMMA blend samples were crystallized until the individual PVDF spherulites of a-modification filled the whole space as revealed by light microscopy. The PVDF/PHB blend samples were crystallized until the crystallization had stopped. They exhibited large spherulites with a habit which is typical for those of the PHB component. They were however not space filling. The spherulites to be investigated were scanned in 5μm steps, this also defining the spatial resolution of the experiment. At any position, the 2-dim-WAXS pattern was recorded. Additionally, the scattering of the empty sample holder in order to separate the air scattering, and the scattering pattern of $Al(OH)_3$ in order to calibrate the sample-counter distance, have been measured. The registrated patterns were recalculated by the program FlT2D to yield averaged over the scattering azimut $I(2\theta)$ scans. Their evaluation is difficult since the natural change of texture within a spherulite due to lamellar twisting must be considered in an appropriate manner. They give nevertheless good insight into the crystalline morphology and its spatial variation inside a spherulite.

The (preliminary) results confirm for both investigated blend systems the IR microscopic investigations in the limits of the experimental resolution and accuracy. The internal structure of the spherulites with respect to crystallinity does consequently not vary from the middle to the surface although they developed distinct composition profiles of the described manner as detected by independent other means. This is most probably due to the fact that the mentioned composition profile developes already in an early stage of the crystallization process and then stays constant in the remaining time. The PHB/PVDF samples revealed additionally the surprising result that within a particular large spherulite, the overall morphology of which is dominated by the PHB component, both blend partners have crystallized in their own lattices to a remarkable and essentially position independent extent. This is also true for the surroundings of these spherulites where the space is obviously filled by precursors of PVDF and PHB spherulites, respectively, which can not be resolved by light microscopy because of their small size.

The questions arise whether (in those large spherulites) both components have crystallized simultaneously or subsequently, whether mixed lamellar stacks have developed (as suggested by R.S. Stein et al. who made comparable observations with a polycarbonate/poly-ε-caprolactone blend), and how the internal structure of those lamellar stacks may look like. A similarly likely explanation for the experimental observations is however that the dominant PHB spherulites have engulfed and included those PVDF spherulite precursors. In any case, the actual structure and its spatial distribution will depend on the individual nucleation and growth behaviour of the blend components which in their turn are determined by the crystallization temperature and the blend composition. All these questions shall be answered by suitable forthcoming experiments for which a proposal is presently submitted to ESRF.