SAXS study on the confined crystallization of PET and PP within nanolayered PET/PP films.

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The basic understanding of polymer crystallization in physically confined environments is a topic of increasing interest for the application of polymers in nanoscience and nanotechnology [1]. In preceding small- and wide-angle x-ray scattering (SAXS and WAXS) studies, we have reported the influence of confinement below the micrometer scale on the lamellar structure of polyethylene terephthalate (PET) in PET/PC [2] and polypropylene (PP) in PP/PA6 multilayered systems [3], prepared by continuous layer-multiplying coextrusion.

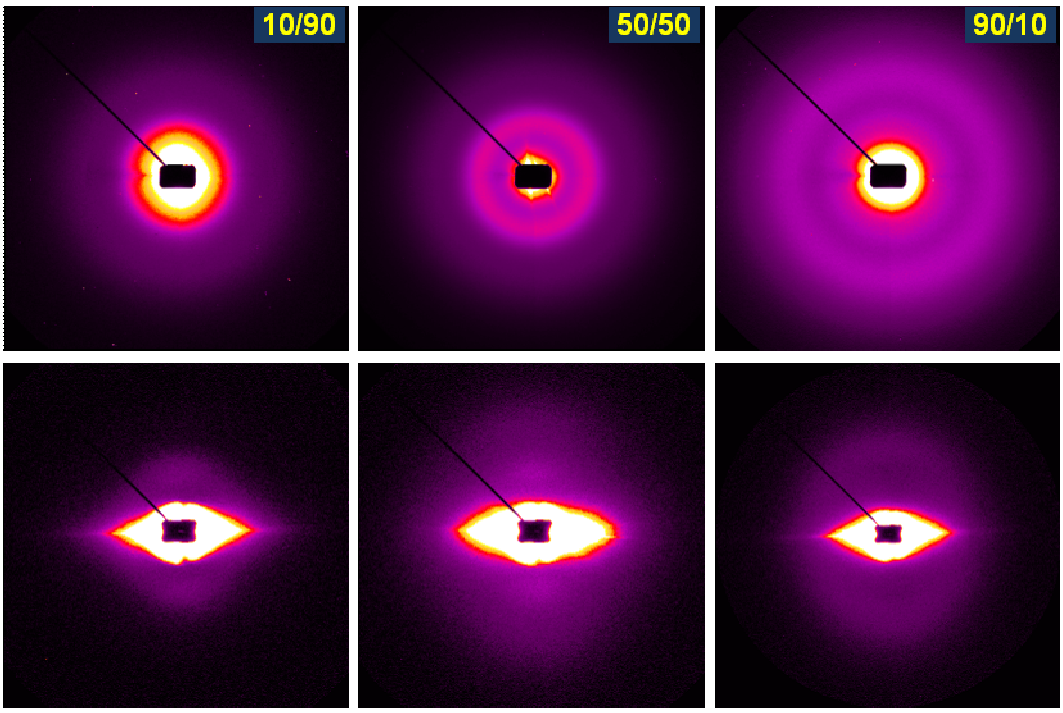

Figure 1: Room temperature SAXS patterns after isothermal melt crystallization of PP for PET/PP nanolayered films with layer thicknesses, from left to right, of 40/360, 200/200, and 360/40 nm. Upper row: films perpendicular to x-ray beam. Lower row: films parallel to the beam.

The present work is concerned with the influence of layer thickness on the lamellar structure and possible orientation arising within the alternating nanolayers of amorphous-crystallisable/semicrystalline films. For this purpose, selected PET/PP films with different volume ratios (90/10, 70/30, 50/50, 30/70 and 10/90) consisting of 128 alternating layers have been investigated. The corresponding PET and PP layer thicknesses were 360, 280, 200, 120 and 40 nm. SAXS measurements were performed in the Soft Condensed Matter Beam Line A2 at HASYLAB (DESY, Hamburg) using a two-dimensional MAR CCD detector. Two types of in-situ crystallization experiments were carried out: a) cold crystallization of PET from the glassy state at T_c=130ºC and b) crystallization of PP from the melt (T_m=200ºC for 10 min and then T_c=130ºC).

Polymer films were placed with their surfaces parallel and perpendicular to the x-ray beam. In the latter case, the small thickness of the samples required to stack several films in order to increase the scattering volume.

Preliminary results show that all samples with their surfaces perpendicular to the x-ray beam, irrespective of heat treatment, yield room temperature (RT) isotropic SAXS rings for both PET and PP (see for example: figure 1, upper row). In the parallel direction, the cold crystallized samples are also found to be isotropic at RT. However, most interesting is the fact that those films heated up to 200ºC present uniaxially oriented SAXS patterns in the meridian (figure 1, lower row), which reveal edge-on oriented lamellae. At least in the 50/50 composition, the edge-on orientation seems to occur simultaneously for both PET and PP layers, while for other volume ratios, the meridional scattering only corresponds to the dominant polymer component.

Figure 2 depicts the azimuthally averaged curves calculated from the SAXS patterns of figure 1, upper row. It is observed that after isothermal crystallization of PP from the melt, two distinct peaks at q-values in the range 0.25-0.3 nm^{-1} for PP and around 0.55 nm^{-1} for PET are present for all volume ratios. While PP long spacing values do not show a clear trend, those for PET increase with increasing confinement. The latter behaviour coincides with previous results found for PET crystallized within a PET/PC system [2]. It was shown that crystallite size is practically constant for PET and the small long spacing increase, associated to finite size effects, must be due to a thicker amorphous phase between crystalline lamellae.

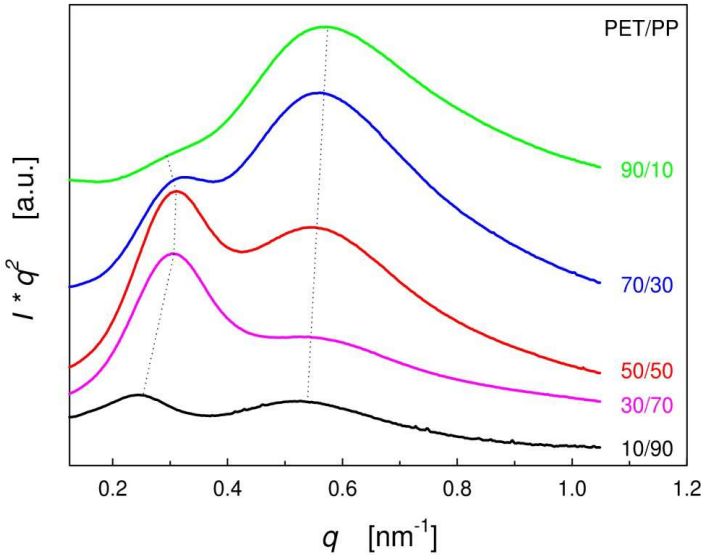

Figure 2: Azimuthally averaged SAXS curves of PET/PP nanolayered films with different volume ratios after isothermal crystallization of PP from the melt. Films perpendicular to x-ray beam (figure 1, upper row). Curves are shifted upwards for clarity.

Acknowledgements

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