Thermally induced variation of the amorphous/amorphous multilayered structure in PMMA/PS films

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In a recent paper [1], comparison of ultra-small-angle X-ray scattering (USAXS) and atomic force microscopy (AFM) results offered new aspects about the nanolayered structure in polyethylene terephthalate/polycarbonate (PET/PC) films prepared by the layer-multiplying co-extrusion technique [2]. Annealing of these multilayered films at different increasing temperatures above the glass transition temperature of PET (75^{o}C), induced the crystallization of the PET layers and, as a consequence, the scattering power increased due to a larger electron density difference between the alternating layers of PET and PC [1]. On the other hand, for all annealing temperatures up to 150^{o}C, the angular position of the observed USAXS peaks only showed minor changes. This means that, on heating, the nanolayered architecture of the films was well preserved even at temperatures which were slightly higher than the glass transition temperature of both constituent polymers. Forced assemblies of two immiscible glassy polymers with up to thousands of layers and layer thickness reaching a lower limit of around 10 nm have also been obtained by the co-extrusion method [3]. As shown in a preceding study [4], the experimental long spacings derived from the scattering maxima of a series of amorphous/amorphous polymethyl methacrylate/polystyrene (PMMA/PS) films offered a linear relationship with their nominal values. However, a more detailed look revealed that the thinner long spacings tended to be larger than their corresponding nominal values, while the opposite behaviour was observed for the thickest layers. A result that accounted for a possible tendency of thinner layers to merge and yield an average long spacing value larger than expected.
The aim of the present report is to discuss the changes observed in the USAXS patterns obtained after thermal treatment of two different multilayered films of the mentioned PMMA/PS (50/50) series. Samples were annealed, under a slight pressure, for 30 min at different temperatures up to 150^{o}C. USAXS experiments were performed at room temperature at the BW4 beam-line of the DORIS III storage ring at HASYLAB/DESY (Hamburg). The X-ray wavelength was fixed to 0.138 nm and the sample to detector distance, determined using a mouse-tail standard, was 13.4 m. The scattered intensities were recorded using a two-dimensional CCD camera in 2048 x 2048 pixel arrays. Polymer films, 100–150 μm thick and 1.5 mm wide, were placed with their surfaces forming an angle of about α_i = 5^o, with the incident X-ray beam [4].
Fig.1 illustrates the USAXS profiles scanned along the meridian for the nanolayered samples with a nominal long spacing of a) 200 nm and b) 280 nm as a function of different annealing temperatures T_a. It can be observed that the as-received samples show a well-defined USAXS scattering peak. This maximum becomes much weaker after a heat treatment at around 100^{o}C, a temperature which is close to the glass transition of both polymer components. The scattering peaks remain poorly defined until 130–140^{o}C where, unexpectedly a much stronger USAXS maximum is clearly present. Finally, annealing at still higher temperatures (150^{o}C) provokes the total disappearance of all scattering peaks.
Provided that AFM images show that the nanolayered architecture is still preserved after heating at 130–140^{o}C, a tentative explanation for the initial reduction of the scattering peaks could be the decrease in the scattering contrast between the two polymers related to changes of their respective electron densities with the temperature treatment. An increased roughening of the interfaces between alternating layers due to polymer melting could also increase the diffuse scattering blurring,

as a result, the presence of any weak scattering maxima. For T_a around 130^{o}C the nanolayers become increasingly unstable and an interfacially driven breakup of the layers is probably initiated. First, and in certain domains, layers might break and merge but still keeping a stacked multilayered architecture that yields a different long spacing than the initial one. After annealing at temperatures above 140^{o}C, AFM results reveal the presence of a distorted globular nanostructure which is not capable of giving rise to any discrete scattering. A previous paper [5] shows that, on heating into the molten state, a forced assembly of alternating high density polyethylene (HDPE) nanolayers and thicker layers of PS also broke up into a dispersion of HDPE nanoparticles in a PS matrix.

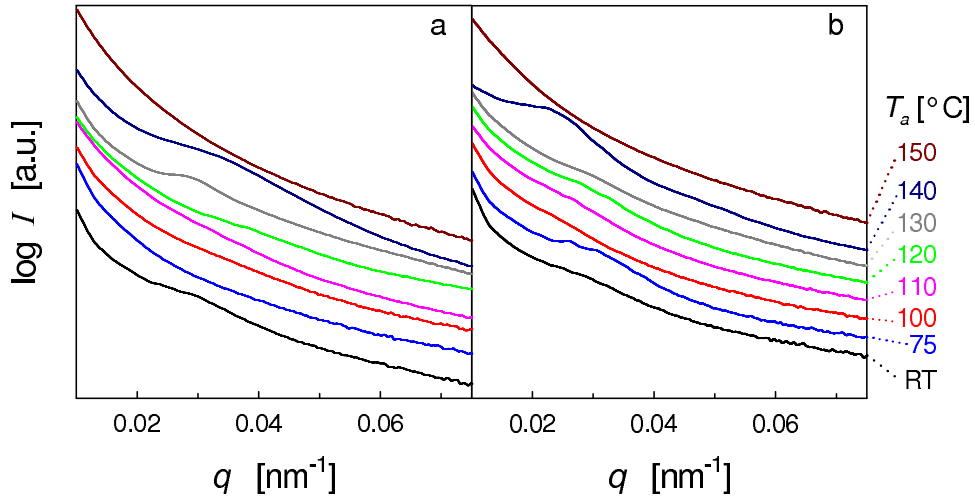

Figure 1: USAXS profiles scanned along the meridian for the PMMA/PS nanolayered samples with a nominal long spacing of a) 200 nm and b) 280 nm as a function of different annealing temperatures T_a.

Acknowledgements

Grateful acknowledgement is due to MEC, Spain (grant FIS2007–60534), DESY project II–20070031 and the European Community contract RII3–CT–2004–506008 (IA–SFS) for the support of this work.

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